

## Chapter 2

# Elementary Kinetic Theory of Gases

In this chapter emphasis is placed on the mathematical derivation of the governing equations of gas dynamics from first principles using the kinetic theory concepts. The prerequisite elementary concepts and notation of classical mechanics are introduced. The modeling procedure consists in deriving the Boltzmann- or Maxwell-Boltzmann equation determining the evolution of the microscopic single distribution function in phase space. This includes details of the collision operator derivation for elastic binary molecular interactions. The moment of equation of the Boltzmann equation results in the generic equation of change of molecular properties. From this equation the macroscopic conservation equations can be deduced. The closure laws for equilibrium—and non-equilibrium flows give rise to the Euler- and Navier-Stokes equations, respectively. For dilute gases brief surveys of the Enskog theory for solving the Boltzmann equation and the ultra simplified mean free path concept are provided, both shown to be useful methods deriving fundamental closures for the transport coefficients. The extended kinetic theory considering multi-component mixtures is sketched, and three different mass diffusion flux formulations are examined both on the mass and molar basis. An overview of the Enskog theory extending the Boltzmann equation by including volume—and finite molecular size corrections to denser gases is given. The modified Boltzmann equation derived by Enskog is called the *Enskog's equation*. The moment of equation of the Enskog equation constitutes the equation of change of molecular properties for dense gases. Because of the inherent corrections this moment equation contains two contributions to the dense gas fluxes, the flux due to the motion of molecules between collisions as for dilute gas and another flux associated with the collisional transfer which is important in dense gases but vanishes for dilute gas. The closure laws for non-equilibrium flows give rise to the dense gas dynamics equations. For dense gas the estimates of the transport coefficients obtained by use of the Enskog theory for solving the Enskog equation and the ultra simplified mean free path concept are also provided. The resulting set of dense gas conservation equations is the mathematical fundament for the theory of granular material flows considered in Chap. 4.

## 2.1 Introduction

The science of mechanics constitutes a vast number of sub-disciplines commonly considered beyond the scope of the standard chemical engineering education. However, when dealing with kinetic theory-, granular flow- and population balance modeling in chemical reactor engineering, basic knowledge of the principles of mechanics is required. Hence, a very brief but essential overview of the disciplines of mechanics and the necessary prescience on the historical development of kinetic theory are given before the more detailed and mathematical principles of kinetic theory are presented.

*Mechanics* is a branch of physics concerned with the motions of physical bodies and the interacting forces. The science of mechanics is commonly divided into two major disciplines of study called *classical mechanics* and *quantum mechanics*. Classical mechanics, which can be seen as the prime discipline of mechanics, describes the behavior of bodies with forces acting upon them. Quantum mechanics is a relatively modern field of science invented at about 1900. The term classical mechanics normally refers to the motion of relatively large objects, whereas the study of motion at the level of the atom or smaller is the domain of quantum mechanics. Classical mechanics is commonly divided into *statics* and *dynamics*. Statics deals with bodies at rest, while dynamics deals with bodies in motion. The study of dynamics is sometimes further divided into *kinematics* and *kinetics*. Kinematics denotes the description of motion without regard to its cause, while in kinetics one intends to explain the change in motion as a result of forces. A third and very recent branch of dynamics is *non-linear dynamics and chaos*, which denotes the study of systems in which small changes in a variable may have large effects. Frequently we also need to describe the behavior of large populations of interacting molecules in solids, gases and liquids, particulate systems, dense suspensions and dispersions. The science of classical mechanics may thus be grouped according to the state of matter being studied, into *solid mechanics* and *fluid mechanics*, both disciplines are often considered sub-disciplines of *continuum mechanics*<sup>1</sup> dealing with continuous matter. Hence, fluid mechanics or *fluid dynamics* denotes the study of the macroscopic physical properties and behavior of fluids. The continuity assumption, however, considers fluids to be continuous. That is, properties such as density, pressure, temperature, and velocity are taken to be well-defined at infinitely small points, and are assumed to vary continuously from one point to another. The discrete, molecular nature of a fluid is ignored. Hence, in many physical sciences this mathematical representation of the system is considered a simplifying engineering approach often useful in engineering practice, but of limited accuracy especially when the system considered doesn't allow sufficient inherent separation of scales. For those problems for which the continuity assumption does not give answers of desired accuracy we may (not always!)

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<sup>1</sup> Continuum mechanics is to a large degree based on the Leonhard Euler (1707–1783) axioms published in his book *Mechanica* in 1736–1737.

obtain better results using more fundamental concepts. *Statistical mechanics*<sup>2</sup> is the application of statistics, which includes mathematical tools for dealing with large populations, to the field of dynamics [47, 115, 116, 150]. Although the nature of each individual element of a system and the interactions between any pair of elements may both be well understood, the large number of elements and possible interactions present an infeasible problem to the investigators who seek to understand the behavior of the system. Statistical mechanics provides a mathematical framework upon which such an understanding may be built. There have apparently been two parallel developments of the statistical mechanics theory, which are typified by the work of Boltzmann [10] and Gibbs [47]. The main difference between the two approaches lies in the choice of statistical unit [23]. In the method of Boltzmann the statistical unit is the molecule and the statistical ensemble is a large number of molecules constituting a system, thus the system properties are said to be calculated as average over a phase space trajectory resembling time average properties [53]. In the method of Gibbs the entire system is taken as a single statistical unit and the statistics are those of an ensemble of such systems, hence the system properties are calculated as averages over a large collection of imaginary systems each of which is an independent replica of the system of interest. The collection of independent systems supposedly spans the assembly of all possible micro-states consistent with the constraints with which the system is characterized macroscopically. The very first steps developing the theory dealing with irreversible processes was principally in accordance with the method of Boltzmann as outlined shortly. In the more modern research in statistical mechanics the method of Gibbs [47] has achieved considerable attention as it can be extended in a relatively simple and general way to the description of irreversible processes. The discussion on the implications of choosing either of these methods usually goes along the following lines. If the positions and velocities of all the particles in a given system were known at any time, the behavior of the system could be determined by applying the laws of classical and quantum mechanics. This procedure is, of course, not feasible firstly because the actual positions and velocities of the individual particles are not known and secondly because the computational efforts needed calculating the macroscopic properties from the states of the individual particles are prohibitively great taking into consideration the large number of particles commonly present in the systems of interest. Instead, statistical methods are introduced with the object of predicting the most probable behavior of a large collection of particles without actually being concerned with the precise states of the individual particles. For this purpose the most probable particle states or a hypothetical ensemble of systems are considered calculating the macroscopic properties. Therefore, we may loosely say that the main reason for introducing the idea of an ensemble was to make it easier to accomplish averaging in statistical mechanics [80]. However, as the experimental characteristics are usually given as time average properties, the equivalence of the calculation and measurement data may be questionable. The ultimate question is whether the average over the ensemble of systems is the same as the average over

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<sup>2</sup> The expression *statistical mechanics* was apparently first used in 1902 by Josiah Willard Gibbs in the title of his book *Elementary Principles in statistical Mechanics* [47].

an infinite time for a single system. Time averages and micro-canonical ensemble averages are commonly assumed to be identical by the *ergodic hypothesis*.<sup>3</sup>

Statistical mechanics is normally further divided into two branches, one dealing with equilibrium systems, the other with non-equilibrium systems. Equilibrium statistical mechanics is sometimes called *statistical thermodynamics* [100]. *Kinetic theory* of gases is a particular field of non-equilibrium statistical mechanics that focuses on dilute gases which are only slightly removed from equilibrium [39]. The main objective of performing kinetic theory analyses is to explain physical phenomena that are measurable at the macroscopic level in a gas at—or near equilibrium in terms of the properties of the individual molecules and the intermolecular forces. For instance, one of the original aims of kinetic theory was to explain the experimental form of the ideal gas law from basic principles [95]. The kinetic theory of transport processes determines the transport coefficients (i.e., conductivity, diffusivity, and viscosity) and the mathematical form of the heat, mass and momentum fluxes. Nowadays the kinetic theory of gases originating in statistical mechanics is thus strongly linked with irreversible- or non-equilibrium thermodynamics which is a modern field in thermodynamics describing transport processes in systems that are not in global equilibrium.

In a series of impressive publications, Maxwell [95–98] provided most of the fundamental concepts constituting the statistical theory recognizing that the molecular motion has a random character. When the molecular motion is random, the absolute molecular velocity cannot be described deterministically in accordance with a physical law so a probabilistic (stochastic) model is required. Therefore, the conceptual ideas of kinetic theory rely on the assumption that the mean flow, transport and thermodynamic properties of a collection of gas molecules can be obtained from the knowledge of their masses, number density, and a probabilistic velocity distribution function. The gas is thus described in terms of the *distribution function*<sup>4</sup> which contains information of the spatial distributions of molecules, as well as about the molecular velocity distribution, in the system under consideration. An important introductory result was the Maxwellian velocity distribution function heuristically derived for a gas at equilibrium. It is emphasized that a gas at thermodynamic equilibrium contains no macroscopic gradients, so that the fluid properties like velocity, temperature and density are uniform in space and time. When the gas is out of equilibrium non-uniform spatial distributions of the macroscopic quantities occur, thus additional phenomena arise as a result of the molecular motion. The random movement of molecules from one region to another tend to transport with them the macroscopic properties of the region from which they depart. Therefore, at their destination the molecules find themselves out of equilibrium with the properties of the region in which they arrive. At the continuous macroscopic level the net effect

<sup>3</sup> In this context the *ergodic hypothesis* states that the time average of a property and the property average over a statistical ensemble of systems result in the same average property measure.

<sup>4</sup> The distribution function is sometimes given other names. Chapman [18, 19] and Chapman and Cowling [20], for example, introduced the name *velocity distribution function* which is also frequently used.

of these molecular transport processes is expressed through the non-equilibrium phenomena of viscosity, heat conduction and diffusion. Nowadays the phrase *transport processes* thus refers to the transport of mass, momentum and energy within a fluid smoothing out the macroscopic gradients in the physical variable fields enabling non-equilibrium systems to approach equilibrium states.

Analytical formulas quantifying the transport coefficients have been deduced in several ways, mostly based on the mean free path concept, the Maxwellian moment equations, and the Boltzmann equation.<sup>5</sup> A preliminary theory of transport processes was suggested by Maxwell [95] in which the transport coefficients were determined on the basis of Clausius' empirical mean free path hypothesis.<sup>6</sup> In a subsequent study by Maxwell [96] the *equation of transfer* for non-equilibrium gases was derived, describing the total rate of change of any mean property of a gas consisting of molecules having certain predefined properties, neatly simplifying the analytical solution. The so-called *Maxwellian molecules* are point centers of force repelling each other with forces which are inversely proportional to the fifth power of their mutual distance. The resulting *equations of change for the mean variables* (or moments of the distribution function), also called *moment equations* or equations of transfer, play an important role in kinetic theory (e.g., [157], p. 319 and p. 346; [109]). Based on these equations and the Maxwellian molecular model, Maxwell deduced more accurate analytical relationships for the transport coefficients.

A few years later Boltzmann [10] presented the derivation of a more general integro-differential equation which describes the evolution of the distribution function in phase space and time. Two approximate methods for the determination of the transport coefficients were proposed independently by Chapman [18, 19] and Enskog [35, 36], leading to almost the same novel relations. Enskog made the explicit solution of Boltzmann equation by successive approximation the basis for his work,<sup>7</sup> whereas Chapman followed Maxwell by using the (moment) equations of transfer rather than attempting to solve the Boltzmann equation explicitly [20, 39, 90]. The method by which Enskog solved the Boltzmann equation is considered a more complete formal solution and thus preferred compared to the Chapman method. However, as Chapman and Enskog did propose the same transport coefficient relations, Enskog's method is often referred to as the Chapman-Enskog expansion method. The first order solutions to the Boltzmann equation in the Chapman-Enskog procedure results in the equilibrium (Euler) equations. Each successive iterate in the Chapman-Enskog expansion yields a more detailed set of gas dynamics equations. The second iterate gives the non-equilibrium equations (or the set of Navier-Stokes equations). The third iterate gives the Burnett equations. Another important contribution by Boltzmann [10] was the H-theorem showing that the molecular collisions tend to increase entropy in an

<sup>5</sup> In order to indicate Maxwell's association with the ideas formulated by Boltzmann, the Boltzmann equation is sometimes termed the *Maxwell-Boltzmann equation* (e.g., see [20], p. 46).

<sup>6</sup> The mean free path is the average distance traveled by a molecule between successive collisions. The concept of mean free path was introduced by Clausius (1822–1888) in 1858 [14].

<sup>7</sup> Note that in 1949 Harold Grad (1923–1986) published an alternative method of solving the Boltzmann equation systematically by expanding the solution into a series of orthogonal polynomials [50].

irreversible manner providing a firm theoretical justification of the second law of thermodynamics which was already accepted at that time.<sup>8</sup>

A spin-off result of the foregoing analysis of Enskog [35, 36] determining the transport coefficients, a rigorous procedure deriving the governing equations of gas dynamics from first principles was established. It is stressed that in classical fluid dynamics the continuum hypothesis is used so that the governing equations of change are derived directly on the macroscopic scales applying the balance principle over a suitable control volume, as described in Chap. 1. Thereafter, closure laws are required relating the internal stresses and diffusive transport fluxes of mass and energy (heat) to the gradients of the macroscopic quantities (e.g., Newton's law of viscosity, Fick's law of mass diffusion, and Fourier's law of conduction are commonly adopted). By using these constitutive relationships we also introduce several unknown parameters, the so-called transport coefficients of viscosity, mass diffusivities and thermal conductivity into the governing equations. Unfortunately, fluid dynamics does neither provide any guidelines on how to determine the mathematical form of the constitutive relations nor the values of transport coefficients. Therefore, a unique application of kinetic theory emerges provided that an approximate solution of the Boltzmann equation is available. In this case particular moments of the distribution function can be obtained multiplying the Boltzmann equation by an invariant function (i.e., successively representing molecular mass, momentum and energy), and thereafter integrating the resulting equation over the whole velocity space. The moments of the distribution function (also called the probability-weighted average functions) represent macroscopic (ensemble) mean quantities like gas velocity, pressure, mass density, temperature and energy. In this way it is possible to derive rigorous equations of change for the evolution of the mean quantities starting out from the Boltzmann equation. Historically, the moment equation of the Boltzmann equation that was published in 1872 is equivalent to Maxwell's moment equation, originally called the *equation of transfer*, that was derived by Maxwell [96] in 1867, so the moment equation is sometimes named the *Maxwell's transport equation* [129]. The moment equation resulting from the Boltzmann equation is also frequently referred to as the *Enskog's equation of change* (e.g., [20], p. 49; [109], p. 232; [115], p. 527). The macroscopic moment equation of change by Enskog represents a generalization of the equation of transfer proposed by Maxwell [96]. The model generalization consists in the fact that Maxwell's equation refers to a function  $\psi(\mathbf{c})$  of  $\mathbf{c}$  alone whereas Enskog's equation is formulated for  $\psi(\mathbf{C}, \mathbf{r}, t)$  of  $\mathbf{C}, \mathbf{r}, t$  (see [20], p. 49). Moreover, since both Maxwell and Enskog did contribute to the development of the moment equation, the moment equation of change is also referred to as the *Maxwell-Enskog equation* (e.g., [93], p. 56). The resulting macroscopic moment conserva-

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<sup>8</sup> The pioneering work in the direction of the second law of thermodynamics is considered to be performed in 1825 by Sadi Carnot investigating the Carnot cycle [57, 80]. Carnot's main theoretical contribution was that he realized that the production of work by a steam engine depends on a flow of heat from a higher temperature to a lower temperature. However, Clausius (1822–1888) was the first that clearly stated the basic ideas of the second law of thermodynamics in 1850 [21] and the mathematical relationship called the *inequality of Clausius* in 1854 [80]. The word *entropy* was coined by Clausius in 1854 [80].

tion equations are recognized as being analogue to the conservation equations of continuum mechanics. In addition, in contrast to the continuum mechanic formulation the ensemble averaged equations obtained from kinetic theory do not contain any unknown coefficients. That is, a particular set of closure laws is established. Alternatively, by comparing the kinetic theory results with the classical fluid dynamic equations, we may verify both the form of the constitutive laws and the values of the transport coefficients.

The kinetic theory of multi-component non-reactive mixtures was first described by Maxwell [95, 97] and Stefan [142, 143] and later thoroughly described by Hirschfelder et al. [55]. Hirschfelder et al. [55] also considers reactive systems. The latest contributions are reviewed by Curtiss and Bird [26, 27].

The Boltzmann equation is considered valid as long as the density of the gas is sufficiently low and the gas properties are sufficiently uniform in space. Although an exact solution is only achieved for a gas at equilibrium for which the Maxwell velocity distribution is supposed to be valid, one can still obtain approximate solutions for gases near equilibrium states. However, it is evident that the range of densities for which a formal mathematical theory of transport processes can be deduced from Boltzmann's equation is limited to *dilute* gases, since this relation is reflecting an asymptotic formulation valid in the limit of no collisional transfer fluxes and restricted to binary collisions only. Hence, this theory cannot without ad hoc modifications be applied to dense gases and liquids.

Enskog [37] made the first heuristic attempt to extend the kinetic theory of dilute mono-atomic gases to higher density gas systems. Enskog introduced corrections to the Boltzmann equation accounting for the finite size of the colliding molecules (a free volume correction), and that the centers of the two colliding particles are no longer at the same point. These model extensions resulted in a novel flux accounting for the mechanisms of instantaneous momentum and energy transfer over the distance separating the centers of the two colliding molecules. The extended Boltzmann equation for dense gas is named the *Enskog's equation* (e.g., [39], p. 359). It is later stated that even at moderate densities the collisional transfer fluxes may become significant compared to the kinetic contribution, and they may dominate at slightly higher densities.

Nowadays the standard literature of kinetic theory of dilute gases usually refers to the books of Chapman and Cowling [20], Hirschfelder et al. [55], Huang [57], Reif [115], Present [109], Vincenti and Kruger [157], Ferziger and Kaper [39], Résibois and De Leener [117], Liboff [90], and Cercignani et al. [14]. Additional reviews on classical mechanics, for example the books of Goldstein [49], Arnold [4], McCall [99], Iro [60], and Panat [105], might also be useful deriving the elements of statistical mechanics, and in particular the dynamics of binary collisions. Moreover, the extensions of the elementary kinetic theory to liquid and polymeric liquid systems are examined by Hansen and McDonald [53] and Bird et al. [8], respectively. The contents of the this chapter are to a large extent based on these reviews and the pioneering work summarized in this introductory section. The reader is encouraged to consult this literature for further details of the kinetic theory.



## 2.2 Elementary Concepts in Classical Mechanics

This section is devoted to an outline of the pertinent principles of dynamics and classical statistical mechanics. Much of the notation required in order to present the kinetic theory concepts is thus established. It is important to recognize that several mathematical frameworks for the description of dynamic systems are in common use. In this context classical mechanics can be divided into three disciplines denoted by *Newtonian mechanics*, *Lagrangian mechanics* and *Hamiltonian mechanics* reflecting three conceptually different mathematical apparatus of model formulation [4, 8, 49, 53, 81, 89, 90, 147].

### 2.2.1 Newtonian Mechanics

The initial stage in the development of classical mechanics is often referred to as Newtonian mechanics, and is characterized by the mathematical methods invented by Newton, Galileo (the principle of relativity [4]), among others. Numerous books contain introductory synopses of the basic principles of the Newtonian mechanics, see for example the books by Arnold [4], Ferziger and Kaper [39] and Cercignani et al. [14].

Although some of the physical ideas of classical mechanics is older than written history, the basic mathematical concepts are based on Isaac Newton's axioms published in his book *Philosophiae Naturalis Principia Mathematica* or *principia* that appeared in 1687. Translated from the original Latin, the three axioms or the laws of motion can be approximately stated [13] (p. 13) :

Law I: *Every body continues in its state of rest, or of uniform motion in a right line, unless it is compelled to change that state by forces impressed on it.*

Law II: *The change of motion is proportional to the motive force impressed; and is made in direction of the right line in which that force is impressed.*

Law III: *To every action there is always an opposite and equal reaction: or, the mutual actions of two bodies upon each other are always equal, and directed to contrary parts.*

The basic concepts of Newtonian mechanics include the use of point masses or particles, which is an object with negligible size with respect to the typical length scales of the system considered [60]. Point masses are thus mathematical points having mass but no structure. The motion of a point particle is characterized by a small number of parameters, i.e., the particle position, mass, and the forces applied to it. For an ensemble of particles, the center of mass of a composite object behaves like a point particle. The position of a point particle is defined with respect to an arbitrary point in space, which is called the origin,  $O$ . A point is represented by the position vector  $\mathbf{r}$  from  $O$  to the particle. A vector  $\mathbf{r}_c$  representing the average of the radii vectors of the particles, weighted in portion to their mass as:



$$\mathbf{r}_c = \frac{\sum_i m_i \mathbf{r}_i}{\sum_i m_i} = \frac{\sum_i m_i \mathbf{r}_i}{M} \quad (2.1)$$

defines a point known as the center of mass, or more loosely as the center of gravity (see e.g., [105], p. 11).

Newton's second law relates the mass and velocity of a particle to a vector quantity known as a force. This fundamental law is also referred to as the equation of motion:

$$\frac{d(m\mathbf{c})}{dt} = \mathbf{F} \quad (2.2)$$

where the quantity  $m\mathbf{c}$  is called the momentum.

Given the initial coordinates and momenta of the particles, the particle position and velocity at any later time can in principle be obtained as the solution to Newton's equations of motion. Typically, the mass is constant in time, hence Newton's law can be written in the conventional form:

$$\mathbf{F} = m \frac{d\mathbf{c}}{dt} = m\mathbf{a} = m\dot{\mathbf{c}} = m\ddot{\mathbf{r}} \quad (2.3)$$

Newton used this equation as the basis of mechanics, hence it is sometimes called Newton's equation [4]. Note that Newton's 1. and 3. laws merely emerge as particular simplifications of the 2nd law and are thus not explicitly stated.

A particular class of forces, known as conservative forces,<sup>9</sup> can be expressed as the gradient of a scalar potential energy function (or potential) denoted by  $E_p$ :

$$m\ddot{\mathbf{r}} = \mathbf{F} = -\nabla E_p(\mathbf{r}) \quad (2.4)$$

It is noticed that Newton's second law of motion forms a set of second order differential equations.

In order to formulate Newton's laws, a suitable reference frame has to be chosen (as briefly sketched above). The inertial coordinate systems defined by the Galileo's principle of relativity are at rest or moving with a constant velocity [81]. In classical mechanics, Newton's laws are valid in all inertial coordinate systems, since the rate of change of velocity equals the absolute acceleration of the system. Moreover, all coordinate systems in uniform rectilinear motion with respect to an inertial frame are themselves inertial. Strictly speaking Newton's laws are no longer valid if a system undergoes accelerations [52]. However, the Newtonian formulation can be extended for systems with arbitrary relative motion [105]. The modified relations are obtained by establishing the equations of motion in a fixed system and thereafter transforming them into the accelerated system. In the non-inertial frame of reference additional

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<sup>9</sup> A force field  $\mathbf{F}$ , defined everywhere in space, is said to be a conservative force or conservative vector field if it meets any of the following three equivalent conditions [105]: (1) The curl of  $\mathbf{F}$  is zero,  $\nabla \times \mathbf{F} = 0$ . (2) There is zero net work ( $W$ ) done by the force  $\mathbf{F}$  when moving a particle through a trajectory constituting a closed curve  $C$ ,  $W = \oint_C \mathbf{F} \cdot d\mathbf{r} = 0$ . (3) The force can be written as the negative gradient of a potential energy function of position  $E_p(\mathbf{r})$ :  $\mathbf{F} = -\nabla E_p(\mathbf{r}) = 0$ .

fictitious forces (e.g., the Coriolis, centripetal and centrifugal forces) arise to account for the motion which is actually caused by the acceleration of the frame of reference.

Moreover, to understand the basic principles of kinetic theory, granular flows and population balances it is required to widen the knowledge of classical mechanics. Newton's mathematical formulation of the laws of motion is perhaps the most intuitive point of view considering familiar quantities like mass, force, acceleration, velocity and positions and as such preferred by chemical engineers. However, this framework is inconvenient for mathematical generalizations as required describing the motion of large populations of particles for which it is necessary to take into account the *constraints* that limit the motion of the system. In this book we restrict ourselves to holonomic constraints because most of the microscopic world has holonomic constraints. If the conditions of constraint can be expressed as equations connecting the coordinates of the particles and the time having the form:

$$f(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_1, \dots, t) = 0 \quad (2.5)$$

then the constraints are said to be *holonomic* [49, 105]. The constraints which cannot be expressed in the form of algebraic equations are non-holonomic constraints.<sup>10</sup>

Two types of difficulties in the solution of mechanical problems are introduced imposing constraints on the system. First, the coordinates of the  $N$  particles,  $\mathbf{r}_i$ ,  $i = 1, \dots, N$ , are no longer all independent as they are connected by the equations of constraint, hence the set of  $N$  equations determining the motion of the individual particles are no longer independent. Second, interacting forces may be created by the constraints and are thus not known a priori as required in the Newtonian concepts [60]. Therefore, after Newton the field of classical mechanics became more general, mathematical and abstract. In the case of holonomic constraints, the first difficulty is solved by the introduction of *generalized coordinates*. The second difficulty is avoided by re-formulating the original theory of motion and forces in accordance with the Lagrangian and Hamiltonian formalisms. These two alternative formulations circumvent the concept of force, instead they are referring to other quantities such as energy, generalized coordinates, generalized velocities and generalized momenta for describing mechanical systems. It is stressed that Lagrangian mechanics and Hamiltonian mechanics are equivalent to Newtonian mechanics, but these re-formulations are more convenient solving complex problems describing the behavior of a system of interacting particles. The main disadvantage of the Newtonian approach is that it is formally tied to the Cartesian coordinate system.<sup>11</sup> The Lagrangian and Hamiltonian formulations are independent of the coordinate system employed. That is, with the Lagrangian formalism one re-formulates the mechanical problem in terms of two scalar functions denoting the kinetic- and potential energy

<sup>10</sup> For the readers that are not familiar with the basics of Newtonian mechanics and the concepts of constraints, Chap. 1 of Goldstein [49] and Chaps. 1–4 of Panat [105] may serve as a understandable introduction to the subject.

<sup>11</sup> In principle, Newton regarded both space and time absolute entities, implying that they are the same for everyone [99]. No such frame does exist in nature, so in practice it is usually feasible to set up a coordinate system that comes as close to this idealization as may be required [49, 100, 105].

respectively, and this notation can greatly simplify the solution of many problems utilizing possible symmetries in the system in a better way. The Hamiltonian viewpoint is not particularly superior to the Lagrangian one for the direct solution of mechanical problems, but the Hamiltonian framework provides a better basis for theoretical generalizations in many areas of physics. In this context it is emphasized that the Hamiltonian formulation provides much of the language with which statistical mechanics and kinetic theory are constructed.

### 2.2.2 Lagrangian Mechanics

The Lagrange's equations can in general be expressed using either of two types of variational principles. These are called the differential and the integral principles. The latter group of methods is also referred to as the principles of minimum action, since in all these procedures the quantity to be varied has the dimension of an action ( $= \text{energy} \times \text{time}$ ) [4, 52]. As an example we consider the Hamiltonian integral principle,<sup>12</sup> because it is the most general method and especially useful for holonomic systems with forces derivable from particular potentials. In the context of kinetic theory of dilute gases the application of the Lagrangian formulation may be convenient for the solution of scattering problems, i.e., the two-body mutual central force problem as viewed in the center of mass coordinate system [49, 105]. Nevertheless, the derivation of the Lagrangian equations merely serves as an intermediate step examining basic elements of the Hamiltonian formulation.

Considering a mechanical system consisting of a collection of particles which are interacting with each other in accordance with the equations of motion, the state of the system is completely described by the set of all the positions and velocities of the particles. In mechanics the minimum number of *independent parameters* necessary to uniquely determine the location and orientation of any system in physical space is called the number of *degrees of freedom*.<sup>13</sup> These quantities need not be the Cartesian coordinates of the particle, as was the case in Newton's work. Rather, the conditions of the problem may render some other more convenient choice of parameters. Any  $N$  independent parameters  $\mathbf{q} = \{q_1, q_2, \dots, q_N\}$  which completely define the position of a system with  $N$  degrees of freedom are called *generalized coordinates* of the system. The corresponding derivatives  $\dot{\mathbf{q}} = \{\dot{q}_1, \dot{q}_2, \dots, \dot{q}_N\}$  are called *generalized*

<sup>12</sup> An example of the alternative differential method is the principle of Jean Le Rond d'Alembert (1717–1783). Perspicuous descriptions of the d'Alembert principle and the derivation of the Lagrangian equations are, for example, given by Greiner [52] and Panat [105].

<sup>13</sup> The phrase *degrees of freedom* is not interpreted identically when it is used in the different branches of science. In physics and chemistry, each independent mode in which a particle or system may move or be oriented is one degree of freedom. In mechanical engineering, degrees of freedom describes flexibility of motion. In statistics, the degrees of freedom are the number of parameter values in probability distributions that are free to be varied. In statistical mechanics the number of degrees of freedom a given system has is equal to the minimum number of independent parameters necessary to uniquely determine the location and orientation of the system in physical space.

*velocities*. For a system placed in a conservative force field an alternative form of the equations of motion is obtained by introducing a Lagrangian function defined as the difference between the kinetic energy,  $T(\dot{\mathbf{q}}, \mathbf{q})$ , and the potential energy,  $E_p(\mathbf{q}, t)$ :

$$L(\dot{\mathbf{q}}(t), \mathbf{q}(t), t) = T(\dot{\mathbf{q}}(t), t) - E_p(\mathbf{q}(t), t) = \frac{1}{2}m\dot{q}^2 - E_p(\mathbf{q}, t) \quad (2.6)$$

It is emphasized that Lagrangian mechanics is the description of a mechanical system in terms of generalized coordinates  $\mathbf{q}$  and generalized velocities  $\dot{\mathbf{q}}$ . The final task in the Lagrangian procedure is to derive a differential equation for  $L(\mathbf{q}, \dot{\mathbf{q}}, t)$  by use of rather complex variational principles. Briefly stated, we are considering the effect of small excursions along the path of the system. The variation denotes a virtual displacement and the trajectory of an object is derived by finding the path which minimizes the action, a quantity which is the integral of the Lagrangian over time. Just a brief outline of the method is given in this book, because the main aim is restricted to the introduction of elements of the notation to be used in kinetic theory analysis shortly. Further details on the technique are given elsewhere [49, 81, 90, 147].

The Hamiltonian variational principle states that the motion of the system between two fixed points, denoted by  $(q, t)_1$  and  $(q, t)_2$ , renders the action integral<sup>14</sup>:

$$S = \int_{t_1}^{t_2} L(q, \dot{q}, t) dt \quad (2.7)$$

a minimum. The necessary condition for  $S$  to have a minimum is that the variation of the integral is zero. Hence, the variational principle of least action is written in the form:

$$\delta S = \delta \int_{t_1}^{t_2} L(q, \dot{q}, t) dt = 0 \quad (2.8)$$

where  $\delta$  denotes a variation about the motion of the system.

Employing this concept to obtain a differential equation for  $L(q, \dot{q}, t)$ , which is defined by (2.6), the first variation of the action  $S$  is expressed by:

$$\delta S = \int_{t_1}^{t_2} L(q + \delta q, \dot{q} + \delta \dot{q}, t) dt - \int_{t_1}^{t_2} L(q, \dot{q}, t) dt = 0 \quad (2.9)$$

By expanding the first integral to first order, the variation can be expressed as:

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<sup>14</sup> For brevity we drop the vector font on the  $q$ 's and  $\dot{q}$ 's and assume a single degree of freedom.

$$\delta S = \int_{t_1}^{t_2} \left( \frac{\partial L}{\partial q} \delta q + \frac{\partial L}{\partial \dot{q}} \frac{d\delta q}{dt} \right) dt \quad (2.10)$$

Reformulating the second term of the integrand in accordance with:

$$\frac{d}{dt} \left( \frac{\partial L}{\partial \dot{q}} \delta q \right) = \frac{\partial L}{\partial \dot{q}} \frac{d\delta q}{dt} + \delta q \frac{d}{dt} \left( \frac{\partial L}{\partial \dot{q}} \right) \quad (2.11)$$

implies that:

$$\delta S = \frac{\partial L}{\partial \dot{q}} \delta q \Big|_{t_1}^{t_2} + \int_{t_1}^{t_2} \left( \frac{\partial L}{\partial q} - \frac{d}{dt} \left( \frac{\partial L}{\partial \dot{q}} \right) \right) \delta q dt \quad (2.12)$$

The first term on the RHS vanishes, since the end points of the trajectory are held fixed in the variation. The second integral must vanish for any arbitrary, infinitesimal variation  $\delta q$ , hence the integrand is zero. The result is:

$$\frac{d}{dt} \left( \frac{\partial L}{\partial \dot{q}} \right) - \frac{\partial L}{\partial q} = 0 \quad (2.13)$$

The above derivation can be generalized to a system of  $N$  particles, noting that the variation must be effected for each variable independently. Hence, in terms of  $L$ , the equations of motion are:

$$\frac{d}{dt} \left( \frac{\partial L}{\partial \dot{q}_i} \right) - \frac{\partial L}{\partial q_i} = 0 \quad i = 1, 2, 3, \dots, N \quad (2.14)$$

This set of equations are the famous Lagrangian equations.<sup>15</sup>

The second term on the LHS denotes the generalized forces defined by:

$$F_i = \frac{\partial L}{\partial q_i} \quad (2.15)$$

It can now be shown that the Lagrangian equations are equivalent to the more familiar Newton's second law of motion. If  $q_i = r_i$ , the generalized coordinates are simply the Cartesian coordinates. Introducing this definition of the generalized coordinates and the corresponding Lagrangian function (2.6) into the Lagrangian equations of motion (2.14), we get:

$$\frac{d}{dt} (m\dot{q}) = - \frac{\partial E_p}{\partial q} \quad (2.16)$$

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<sup>15</sup> The mathematical Lagrangian formalism in classical mechanics was first published in the book *Mécanique Analytique* by Joseph Louis Lagrange in 1788 [133].

in which the LHS and the RHS of the Lagrangian equations (2.14) have been reformulated by use of the Lagrangian function definition (2.6):

$$\begin{aligned} \frac{d}{dt} \left( \frac{\partial L}{\partial \dot{q}_i} \right) &= \frac{d}{dt} \left( \frac{\partial}{\partial \dot{q}_i} (T(\dot{q}_i, t) - E_p(q_i, t)) \right) = \frac{d}{dt} \left( \frac{\partial}{\partial \dot{q}_i} \left( \frac{1}{2} m \dot{q}_i^2 - E_p(q_i, t) \right) \right) \\ &= \frac{d}{dt} \left( \frac{\partial}{\partial \dot{q}_i} \left( \frac{1}{2} m \dot{q}_i^2 \right) \right) = \frac{d}{dt} (m \dot{q}_i) \end{aligned} \quad (2.17)$$

$$\begin{aligned} \frac{\partial L}{\partial q_i} &= \frac{\partial}{\partial q_i} (T(\dot{q}_i, \mathbf{q}) - E_p(q_i, t)) = \frac{\partial}{\partial q_i} \left( \frac{1}{2} m \dot{q}_i^2 - E_p(q_i, t) \right) \\ &= - \frac{\partial}{\partial q_i} (E_p(q_i, t)) \end{aligned} \quad (2.18)$$

Moreover, since the gradient of the time independent potential energy field denotes a conservative force [60], the relation can be expressed in terms of a force:

$$m \ddot{q}_i = F(q_i, t) \quad (2.19)$$

The resulting relation is identical to the equation obtained in the Newtonian representation (2.3).

Given the Lagrangian for a system of interacting particles, a number of fundamental system properties can be deduced. Among these properties are the basic conservation laws<sup>16</sup> which can be deduced invoking the principle of homogeneity of time and space for closed systems that do not interact with any external forces.

In this context examination of the total time derivative of the Lagrangian is informative. The relation can be expressed as:

$$\begin{aligned} \frac{d}{dt} (L(q_i(t), \dot{q}_i(t), t)) &= \sum_i \frac{\partial L}{\partial q_i} \dot{q}_i + \sum_i \frac{\partial L}{\partial \dot{q}_i} \ddot{q}_i + \frac{\partial L}{\partial t} \\ &= \sum_i \frac{d}{dt} \left( \dot{q}_i \frac{\partial L}{\partial \dot{q}_i} \right) + \frac{\partial L}{\partial t} \end{aligned} \quad (2.20)$$

or, by reorganizing the terms:

$$\sum_i \frac{d}{dt} \left( \dot{q}_i \frac{\partial L}{\partial \dot{q}_i} - L \right) = - \frac{\partial L}{\partial t} \quad (2.21)$$

Several classes of transformations between two frames or coordinate systems leave the Newtonian equation of motion invariant [60, 81]. The invariance of physical

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<sup>16</sup> During the motion of a mechanical system, the generalized coordinates and generalized velocities which specify the state of the system vary with time. However, a set of functions of these quantities exist whose values remain constant during the motion of the system and depend only on the initial conditions. These functions are referred to as integrals of motion, and the quantities represented by these integrals are said to be conserved [81].

systems under translations of the coordinate system is often referred to as the *homogeneity of space*. The analogue invariance under rotations of the coordinate system is named the *isotropy of space*. Translations of the time origin also make the equation of motion remain invariant, this property is called the *homogeneity of time*. By virtue of the homogeneity of time, the Lagrangian of a closed system does not depend explicitly on time. Therefore, using (2.21) with  $L$  as defined by (2.6), it is verified that the energy of the system is conserved, as the quantity:

$$\sum_i \dot{q}_i \frac{\partial L}{\partial \dot{q}_i} - L(q_i(t), \dot{q}_i(t), t) = T(\dot{q}_i(t), t) + E_p(q_i(t), t) = E(q_i(t), \dot{q}_i(t), t) \quad (2.22)$$

remains constant in time during the motion of the system.

In a similar manner the homogeneity in space leads to the law of conservation of linear momentum [60, 81]. In this case  $L$  does not depend explicitly on  $q_i$ , i.e., the coordinate  $q_i$  is said to be cyclic. It can then be seen exploring the Lagrange's equations (2.14) that the quantity  $\partial L / \partial \dot{q}_i$  is constant in time. By use of the Lagrangian definition (2.6), the relationship can be written in terms of more familiar quantities:

$$\frac{\partial L}{\partial \dot{q}_i} = m\dot{q}_i \quad (2.23)$$

It is stated that the momentum  $m\dot{q}_i$  is a constant of the motion, meaning that it is a conserved quantity. This result is, of course, only valid when all the interacting forces are conservative and there are no external forces acting on the system of particles. Note also that the isotropy of space is the basis for the derivation of the law of conservation of angular momentum [60, 81].

### 2.2.3 Hamiltonian Mechanics

Hamiltonian mechanics<sup>17</sup> is based on the description of mechanical systems in terms of generalized coordinates  $q_i$  and generalized momenta  $p_i$ . Starting out from Lagrangian mechanics in which the equations of motion are based on generalized coordinates  $q_i$  and the corresponding generalized velocities  $\dot{q}_i$ , ( $q_i, \dot{q}_i$ ),  $i = 1, 2, 3, \dots, N$ , the transformation of the problem to the Hamiltonian description can be performed adopting the Legendre's transformation technique. Hence, by replacing the generalized velocity variables  $\dot{q}_i$  with generalized momentum variables  $p_i$ , i.e., the latter quantities are also known as conjugate momenta, it is possible to further exploit the symmetry principles of mechanics. The concepts from

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<sup>17</sup> Hamiltonian mechanics refers to a mathematical formalism in classical mechanics invented by the Irish mathematician William Rowan Hamilton (1805–1865) during the early 1830s arising from Lagrangian mechanics which was introduced about 50 years earlier by Joseph-Louis Lagrange (1736–1813). The Hamiltonian equations can however be formulated on the basis of a variational principle without recourse to Lagrangian mechanics [4, 147].



Hamiltonian mechanics are pertinent to the phase space treatment of problems in dynamics.

The Hamiltonian formulation thus provides the view in which the statistical mechanics and modern kinetic theory are constructed. We define the Hamiltonian function by the Legendre transform of the Lagrangian function (2.6) [49, 52]:

$$H(\mathbf{p}, \mathbf{q}, t) = \sum_i \dot{q}_i p_i - L(\dot{\mathbf{q}}, \mathbf{q}, t) \quad (2.24)$$

in which  $p_i$  is defined as:

$$p_i = \frac{\partial L}{\partial \dot{q}_i} \quad (2.25)$$

Furthermore, substituting the  $p_i$  into the Lagrange's equations of motion (2.14) gives:

$$\dot{p}_i = \frac{\partial L}{\partial q_i} \quad (2.26)$$

Given the Lagrange's equations of motion (2.14) and the Hamiltonian function (2.24), the next task is to derive the Hamiltonian equations of motion for the system. This can be achieved by taking the differential of  $H$  defined by (2.24).

Each side of the differential of  $H$  produces a differential expressed as:

$$\begin{aligned} dH(\mathbf{q}, \mathbf{p}, t) &= \sum_i \frac{\partial H}{\partial q_i} dq_i + \sum_i \frac{\partial H}{\partial p_i} dp_i + \frac{\partial H}{\partial t} dt \\ &= d\left(\sum_i \dot{q}_i p_i\right) - dL(\dot{\mathbf{q}}, \mathbf{q}, t) \\ &= \sum_i \left(p_i - \frac{\partial L}{\partial \dot{q}_i}\right) d\dot{q}_i + \sum_i \dot{q}_i dp_i - \sum_i \frac{d}{dt} \left(\frac{\partial L}{\partial \dot{q}_i}\right) dq_i - \frac{\partial L}{\partial t} dt \\ &= \sum_i \left(p_i - \frac{\partial L}{\partial \dot{q}_i}\right) d\dot{q}_i + \sum_i \dot{q}_i dp_i - \sum_i \dot{p}_i dq_i - \frac{\partial L}{\partial t} dt \end{aligned} \quad (2.27)$$

in which the total differential of  $L$  is defined as:

$$dL(\dot{\mathbf{q}}, \mathbf{q}, t) = \sum_i \frac{\partial L}{\partial \dot{q}_i} d\dot{q}_i + \sum_i \frac{\partial L}{\partial q_i} dq_i + \frac{\partial L}{\partial t} dt \quad (2.28)$$

Substituting the definition of the conjugate momenta (2.25) and the manipulated form of the Lagrangian equations (2.26) into (2.27) and matching coefficients,  $\sum_i (p_i - \frac{\partial L}{\partial \dot{q}_i}) d\dot{q}_i = 0$ , we obtain the equations of motion of Hamiltonian mechanics (i.e., also known as the canonical equations of Hamilton):

$$\dot{p}_i = -\frac{\partial H}{\partial q_i} \quad (2.29)$$

$$\dot{q}_i = \frac{\partial H}{\partial p_i} \quad (2.30)$$

An additional relationship of importance for explicitly time-dependent system functions, can be deduced by the same procedure and expressed as:

$$\frac{\partial L}{\partial t} = -\frac{\partial H}{\partial t} \quad (2.31)$$

The total time derivative of the Hamiltonian is achieved from (2.27) as:

$$\frac{dH}{dt} = \frac{\partial H}{\partial t} + \sum_i \frac{\partial H}{\partial q_i} \dot{q}_i + \sum_i \frac{\partial H}{\partial p_i} \dot{p}_i \quad (2.32)$$

Substitution of the Hamiltonian equations (2.29) and (2.30) shows that the last two terms cancel,

$$\frac{dH(\mathbf{p}, \mathbf{q}, t)}{dt} = \frac{\partial H}{\partial t} - \sum_i \dot{p}_i \dot{q}_i + \sum_i \dot{q}_i \dot{p}_i \quad (2.33)$$

Thus:

$$\frac{dH}{dt} = \frac{\partial H}{\partial t} \quad (2.34)$$

In particular, if the Hamiltonian function does not depend explicitly on time, then:

$$\frac{dH}{dt} = 0 \quad (2.35)$$

This means that  $H$  represents a conserved quantity. Eliminating the Lagrangian from (2.24) using (2.22) shows that the Hamiltonian function equals the total energy of the system,  $H = E$ .

By use of the Hamiltonian description established in this subsection, it can be shown that the Hamiltonian equations are equivalent to the more familiar Newton's second law of motion in Newtonian mechanics, adopting a transformation procedure similar to the one used assessing the Lagrangian equations. In this case we set  $q_i = r_i$  and substitute both the Hamiltonian function  $H$  (2.24) and subsequently the Lagrangian function  $L$  (2.6) into one of Hamilton's equations of motion (2.29). The preliminary results can be expressed as:

$$\frac{\partial E_p}{\partial r_i} = -\dot{p}_i \quad (2.36)$$

and by use of (2.25) yields:

$$\frac{1}{m_i} p_i = \dot{r}_i. \quad (2.37)$$

Then, we combine these two equations and introduce the force on particle  $i$ , defined in terms of the potential  $E_p$  by  $F_i = -(\partial E_p / \partial r_i)$ . The final result is thus given by  $\mathbf{F}_i = m_i \ddot{\mathbf{r}}_i$  in 3D which corresponds to Newton's second law of motion for particle  $i$  as expressed in the Newtonian formalism (2.3).

The Hamiltonian formalism has a number of important properties and implications. In the following paragraphs a few of them are sketched in the context of a time-independent Hamiltonian function. Most important, the concepts of Hamiltonian mechanics are fundamental to the phase space treatment of problems in dynamics. For a system with  $N$  degrees of freedom the set of  $2N$  canonically conjugate variables  $(\mathbf{p}, \mathbf{q})$  define a  $2N$ -dimensional *phase space* sometimes called the  $\Gamma$ -space<sup>18</sup> of the system [81, 90]. It is sometimes convenient to regard the phase space for a system as a whole as constructed out of the *configuration space* that corresponds to the set of coordinates chosen for the system taken together with the *momentum space* that corresponds to the set of momenta conjugate to those coordinates. Each point in phase space corresponds to a definite state of the system. When the system moves, the point representing it describes a curve called the phase path or *phase trajectory*. The motion of the phase point along its phase trajectory is determined by the canonical equations. Since the Hamiltonian equations are first order differential equations in time, the path of the representative point in phase space is determined by the initial point.

### 2.2.3.1 Preservation of Phase Volume: Liouville Theorem

In the Hamiltonian formulation, the Liouville equation can be seen as a continuity or advection equation for the probability distribution function. This theorem is fundamental to statistical mechanics and requires further attention. Considering an *ensemble*<sup>19</sup> of initial conditions each representing a possible state of the system, we express the probability of a given ensemble or density distribution of system points

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<sup>18</sup> For a collection of  $N$  identical particles the state of the system may be specified by giving the coordinates of each particle so that the system as a whole is represented by a cloud of  $N$  points in phase space. Alternatively, the state of the system as a whole constituting the gas phase can be completely specified by a single point in phase space. The phase for the system as a whole is called a  $\gamma$ -space or sometimes a  $\Gamma$ -space, and the phase space for any individual kind of particles (molecules) contained in the system is called a  $\mu$ -space for that particle [39, 150]. These notations may be linked to the theory of Gibbs [47] and Boltzmann [10], respectively.

<sup>19</sup> Willard Gibbs (1839–1903) introduced the idea of an ensemble of systems in his book entitled *Elementary Principles in Statistical Mechanics* published in 1902 [47]. An ensemble is a large number of imaginary replicas of the system under consideration. Gibbs also introduced the ideas of canonical-, micro-canonical- and grand canonical ensembles which refer to ensembles having specific properties [80]. For example, the micro-canonical ensemble is the assembly of all states with fixed total energy  $E$ , and fixed size. The canonical ensemble, another example, considers all states with fixed size, but the energy can fluctuate [15].

in phase space  $\Gamma$  by a continuous function:

$$f = f(\mathbf{p}, \mathbf{q}, t) \quad (2.38)$$

which is a normalized quantity with the following property:

$$\int_{\text{all space}} f \Pi_i dp_i dq_i = 1, \quad (2.39)$$

where  $\Pi_i$  means product of all labeled variables and  $i$  runs from 1 to  $N$  degrees of freedom.

The distribution function  $f(\mathbf{q}, \mathbf{p}, t)$  is defined such that the product  $f(\mathbf{q}, \mathbf{p}, t) \Pi_i dp_i dq_i = f(\mathbf{q}, \mathbf{p}, t) d\Omega$  represents the number of system points in the phase volume  $d\Omega$  about the point  $(\mathbf{q}, \mathbf{p})$  at the time  $t$ . The product of differentials  $d\Omega = \Pi_i dp_i dq_i = dq_1 \dots dq_N dp_1 \dots dp_N$  may be regarded as an element of volume in phase space. It follows that the corresponding integral  $\int d\Omega$  taken over some region of phase space represents the volume of the particular region. This integral has the property of being invariant with respect to canonical transformations.<sup>20</sup> This means that the magnitude of a volume element in phase space is preserved under canonical transformations.<sup>21</sup> Therefore, at any given instant in time, the hypothetical ensemble points in the imaginary differential volume of  $\Gamma$ -space are consistently contained within a continuously closed surface. Thus, we let  $\Omega$  be an arbitrary volume element in  $\Gamma$ -space and  $S$  denotes its surface.

The rate of change of the number of phase points  $dN$ , within the infinitesimal phase space volume  $\Pi_i dp_i dq_i$  is obtained from a balance equation expressing that the system points in an ensemble are neither created nor destroyed [89]. Hence, the rate of change of the number of system points in the volume  $\Omega$ ,  $\int_{\Omega} f d\Omega$  is equal to the net flux of points that pass through the closed surface that bound  $\Omega$ :

$$\frac{\partial}{\partial t}(f d\Omega) + \sum_i \left\{ \frac{\partial}{\partial p_i} (\dot{p}_i f d\Omega) + \frac{\partial}{\partial q_i} (\dot{q}_i f d\Omega) \right\} = 0 \quad (2.40)$$

The rate of change of the density function at a fixed position in phase space is achieved dividing by a fixed element of volume in phase space  $d\Omega$ :

<sup>20</sup> The transformation from one pair of canonically conjugate coordinates  $\mathbf{q}$  and momenta  $\mathbf{p}$  to another set of coordinates  $\mathbf{Q} = \mathbf{Q}(\mathbf{p}, \mathbf{q}, t)$  and momenta  $\mathbf{P} = \mathbf{P}(\mathbf{p}, \mathbf{q}, t)$  is called a canonical transformation or point transformation. In this transformation it is required that the new coordinates  $(\mathbf{P}, \mathbf{Q})$  again satisfy the Hamiltonian equations with a new Hamiltonian  $H'(\mathbf{P}, \mathbf{Q}, t)$  [49, 60, 81].

<sup>21</sup> This theorem is known as the *Poincarè* theorem (1854–1912) [49, 60, 81], stating that:  $d\Omega = \Pi_i dp_i dq_i = \Pi_i dP_i dQ_i$ . The invariance rests on the property of the Jacobian determinant of a

canonical transformation:  $D = \det \left( \frac{\partial(\mathbf{Q}, \mathbf{P})}{\partial(\mathbf{q}, \mathbf{p})} \right) = 1$ . Consequently, the volume element is transformed as:  $\Pi_i dp_i dq_i = \Pi_i dP_i dQ_i = D \Pi_i dp_i dq_i$ . In particular, the evolution of a system in time also represents a canonical transformation which implies that the volume in phase space is conserved as it evolves in time. This is known as the *Liouville theorem* (1809–1882).

$$\frac{\partial f}{\partial t} = - \sum_i \left\{ \frac{\partial}{\partial p_i} (\dot{p}_i f) + \frac{\partial}{\partial q_i} (\dot{q}_i f) \right\} = \sum_i \left\{ \dot{p}_i \frac{\partial f}{\partial p_i} + f \frac{\partial \dot{p}_i}{\partial p_i} + \dot{q}_i \frac{\partial f}{\partial q_i} + f \frac{\partial \dot{q}_i}{\partial q_i} \right\} \quad (2.41)$$

Since the Hamiltonian equations satisfy the *incompressibility* condition,

$$\sum_i \left( \frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \dot{p}_i}{\partial p_i} \right) = \sum_i \left( \frac{\partial^2 H}{\partial p_i \partial q_i} - \frac{\partial^2 H}{\partial q_i \partial p_i} \right) = 0 \quad (2.42)$$

any volume element in phase space is preserved under Hamiltonian flow. This relation is called the *Liouville's theorem* which represents a fundamental property of Hamiltonian systems [60, 89].

This theorem further implies that the second and fourth terms in the summation on the RHS of (2.41) cancel to obtain:

$$\frac{\partial f}{\partial t} + \sum_i \left( \dot{p}_i \frac{\partial f}{\partial p_i} + \dot{q}_i \frac{\partial f}{\partial q_i} \right) = 0 \quad (2.43)$$

This result is known as the *Liouville's equations* [90].

Notice that this equation is commonly written in the Poisson bracket form:

$$\frac{\partial f}{\partial t} + [H, f] = 0 \quad (2.44)$$

The Poisson bracket operator is defined by:

$$[H, f] = \sum_{i=1}^N \left( \dot{q}_i \frac{\partial f}{\partial q_i} + \dot{p}_i \frac{\partial f}{\partial p_i} \right) = \sum_{i=1}^N \left( \frac{\partial H}{\partial p_i} \frac{\partial f}{\partial q_i} - \frac{\partial H}{\partial q_i} \frac{\partial f}{\partial p_i} \right) \quad (2.45)$$

The Poisson bracket is an operator in Hamiltonian mechanics which has convenient inherent properties considering the time evolution of dynamic variables [90, 105]. The most important property of the Poisson bracket is that it is invariant under any canonical transformation.

While this compact notation is convenient for the experienced user, to grasp the basic concepts a rough description may be preferable. Therefore, for the beginners that is not familiar with the concepts of statistical mechanics we reiterate the presentation of the abstract theory using an alternative notation equivalent to what is common in the fluid dynamic literature [57, 90]. The purpose is to provide introductory ideas about the practical implications of the Liouville equations describing the ensemble flow in  $\Gamma$ -space. For this reason, we let  $\mathbf{u}$  denote a generalized velocity vector of the system points in the neighborhood of the element of surface  $dS$ :

$$\mathbf{u} = \{\dot{q}_1, \dot{q}_2, \dots, \dot{q}_N; \dot{p}_1, \dot{p}_2, \dots, \dot{p}_N\} \quad (2.46)$$

In the particular case, where the volume  $\Omega$  is thought to be fixed in phase space, the corresponding continuity equation can be expressed as:

$$\frac{\partial}{\partial t} \int_{\Omega} f d\Omega = - \oint_S \mathbf{u} \cdot f d\mathbf{S} \quad (2.47)$$

where the net ‘convective’ flux out of the volume through the closed surface  $S$  is  $\oint_S \mathbf{u} \cdot f d\mathbf{S}$ .

Now, using a variant of Gauss theorem in  $\Gamma$ -space,

$$\oint_S \mathbf{u} \cdot f d\mathbf{S} = \int_{\Omega} \nabla \cdot (f\mathbf{u}) d\Omega \quad (2.48)$$

The continuity equation thus yields,

$$\int_{\Omega} \left[ \frac{\partial f}{\partial t} + \nabla \cdot (f\mathbf{u}) \right] d\Omega = 0 \quad (2.49)$$

Requiring that the integrand must be equal to zero for any volume  $d\Omega$ , the resulting differential equation is given by:

$$\frac{\partial f}{\partial t} + \nabla \cdot (f\mathbf{u}) = 0 \quad (2.50)$$

With (2.46) and (2.42), it is found that:

$$\nabla \cdot \mathbf{u} = \sum_{i=1}^N \left( \frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \dot{p}_i}{\partial p_i} \right) = \sum_{i=1}^N \left( \frac{\partial^2 H}{\partial q_i \partial q_i} - \frac{\partial^2 H}{\partial q_i \partial p_i} \right) = 0 \quad (2.51)$$

since the flow of system points is *incompressible*.

Introducing the *solenoidal* vector field into the continuity equation returns the Liouville equation, which now appears as:

$$\frac{\partial f}{\partial t} = -\mathbf{u} \cdot \nabla f - f \nabla \cdot \mathbf{u} = -\mathbf{u} \cdot \nabla f \quad (2.52)$$

In an engineering view, the ensemble of system points moving through phase space behaves much like a fluid in a multidimensional space, and there are numerous similarities between our imagination of the ensemble and the well known notions of fluid dynamics [49]. Then, the substantial derivative in fluid dynamics corresponds to a derivative of the density as we follow the motion of a particular differential volume of the ensemble in time. The material derivative is thus similar to the Lagrangian picture in fluid dynamics in which individual particles are followed in time. The partial derivative is defined at fixed  $(q, p)$ . It can be interpreted as if we consider a

particular fixed control volume in phase space and measure the time variation of the density as the ensemble of system points flows by us. The partial derivative at a fixed point in phase space thus resembles the Eulerian viewpoint in fluid dynamics.

### 2.2.3.2 BBGKY-Hierarchy

In the more theoretical fields of science the conventional derivation of the Boltzmann equation for the one-particle distribution function, assumed to be valid for dilute gases, is considered far too heuristic and accordingly does not form an adequate formal basis for rigorous analysis. In this point of view a formal derivation starts out from a complete knowledge of the probability density formulated in terms of a  $N$ -particle density function,<sup>22</sup>  $f_N(\mathbf{q}, \mathbf{p}, t)$ , providing a general way of deducing the Boltzmann equation from the laws of dynamics via approximations of this rigorous equation. Deriving the Boltzmann equation in this manner may also provide novel guidelines for the extension of Boltzmann equation to higher densities.

The time evolution of this phase space probability density is governed by the Liouville equation expressed as:

$$\frac{\partial f_N}{\partial t} = [H_N, f_N] \quad (2.53)$$

However, the description of the system governed by the complete phase space probability density is not feasible in practice for a large number of particles  $N$ . Therefore, one may rather consider the behavior of a subset of particles defining a reduced phase space distribution function. The unwanted information can be eliminated by integrating  $f_N$  over the coordinates and momenta of the remaining particles [53, 90] (i.e., resembling an averaging procedure). A particular system of integro-differential equations for such a reduced distribution function is known as the BBGKY-hierarchy (i.e., this abbreviation is written for N. N. Bogoliubov, M. Born, H. S. Greed, G. Kirkwood, and J. Yvon). Comprehensive discussions on this approach is given by Cercignani et al. [14] and Liboff [90]. Nevertheless, this approach is not very useful in practice since the BBGKY-hierarchy is not closed and an ad hoc problem contraction is required. It is noted that the first equation in this sequence is still most important as it governs the evolution of  $f_1(\mathbf{p}, \mathbf{q}, t)$  in time and space provided that an approximate closure for the pair density function  $f_2(\mathbf{p}', \mathbf{q}'; \mathbf{p}, \mathbf{q}, t)$  is available (i.e., this equation contains the lowest number of unknowns in the sequence), and it represents the generic form of all the kinetic equations. Much effort has been devoted to find approximate solutions to the BBGKY hierarchy on the basis of expressions that relate  $f_1(\mathbf{p}, \mathbf{q}, t)$  and  $f_2(\mathbf{p}', \mathbf{q}'; \mathbf{p}, \mathbf{q}, t)$ . The simplest approximation is to ignore the pair correlation altogether by writing:  $f_2(\mathbf{p}', \mathbf{q}'; \mathbf{p}, \mathbf{q}, t) = f_1(\mathbf{p}', \mathbf{q}', t) f_1(\mathbf{p}, \mathbf{q}, t)$ . This assumption implies that there is no statistical correlation between particles of states

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<sup>22</sup>  $f_N$  denotes the  $N$ -body joint-probability density for the  $N$ -body system. This function gives the probability density of finding, at time  $t$ , particle 1 in the state  $(\mathbf{p}_1, \mathbf{q}_1)$ , particle 2 in the state  $(\mathbf{p}_2, \mathbf{q}_2)$ , ..., and particle  $N$  in the state  $(\mathbf{p}_N, \mathbf{q}_N)$ .



$(\mathbf{p}', \mathbf{q}')$  and  $(\mathbf{p}, \mathbf{q})$  at any time  $t$ . Various efforts along these lines have attempted to derive the Boltzmann equation from first principles. However, a number of assumptions come into play in all these derivations, which renders even the more formal analyzes somewhat ad hoc. Therefore, many practitioners do not consider the classical formalism worthwhile.

## 2.3 Basic Concepts of Kinetic Theory

In this section the statistical theorems or mathematical tools needed to understand the Boltzmann equation in itself, and the mathematical operations performed developing the macroscopic conservation equations starting out from the microscopic Boltzmann equation, are presented. Introductory it is stressed that a heuristic theory, which resembles the work of Boltzmann [10] and the standard kinetic theory literature, is adopted in this section and the subsequent sections deriving the Boltzmann equation. Irrespective, the notation and concepts presented in Sect. 2.2 are often referred, or even redefined in a less formal wrapping, thus the underlying elements of classical mechanics are prescience of outmost importance understanding the true principles of kinetic theory.

### 2.3.1 Potential Energy of Molecular Interactions

In kinetic theory a binary molecular interaction is generally specified as a rather abrupt change in the trajectories of two molecules as a result of their mutual interaction. It is sometimes distinguished between interactions with and without contact between the molecular particles. The choice of molecular model determines the kind of interaction that will take place, thus only the hard sphere or billiard ball model gives rise to interactions with contact. The three phrases molecular interaction, encounter and collision are considered to be synonyms. Besides, attention is restricted to interactions between electrically neutral molecules in which the force between the molecules depends only on the distance between their centers. For monoatomic gases, the spacing between the particles is considered large enough so that we can approximate the particles as points, or point centers of force. For this reason, in kinetic theory, a gas molecule is characterized by its position  $\mathbf{r}$  and its velocity  $\mathbf{c}$ . However, the intermolecular force laws play a central role in the model determining the molecular interaction terms (i.e., related to the collision term on the RHS of the Boltzmann equation). Classical kinetic theory proceeds on the assumption that this law has been separately established, either empirically or from quantum theory. The force of interaction between two molecules is assumed to be conservative thus it can be related to the potential energy function (2.4):

$$\mathbf{F}(\mathbf{r}) = -\nabla E_p(\mathbf{r}) \quad (2.54)$$

where  $\mathbf{r}$  is the distance between the two molecules.

For most purposes it is chosen to specify the potential energy of interaction  $E_P(\mathbf{r})$  rather than the force of interaction  $\mathbf{F}(\mathbf{r})$ . Suppose that the particle moves from position  $\mathbf{r}$  to position  $\infty$  under the action of a conservative force  $\mathbf{F}$ . These two functions are then related as:

$$E_P(\mathbf{r}) = - \int_r^{\infty} \mathbf{F}(\mathbf{r}) \cdot d\mathbf{r} \quad (2.55)$$

Several models for the molecular potential energy of interaction have been considered, each of them having certain advantages either in their physical interpretations or giving simple mathematical representations of the laws of interaction. The *billiard ball model* is one such exploratory molecular potential energy of interaction model which is frequently used because of its simplicity. In this model a molecule is viewed as a microscopic particle and approximated by a small featureless sphere, possessing a spherically-symmetric force field. For neutral particles this force field has a very short range, and the particles can be pictured as being almost rigid spheres, with an effective diameter equal to the range of the force field. Therefore, in an average sense each gas molecule is assumed to be a rigid, spherical, non-attracting, particle with diameter equivalent to the range of molecular interaction  $d = r_0$ , and mass  $m$ . This molecular model is thus sometimes named the *rigid sphere model* or the *hard sphere model*. As they have no structure, these particles have only energy of translation. The gas is further assumed to be sufficiently dilute for collisions involving more than two particles at a time to be ignored, thus only binary collisions are considered. The collisions between these gas molecules are considered perfectly elastic. Considering a binary *elastic collision* two bodies collide and thereafter move apart again in such a way that both the overall momentum and the total kinetic energy of the center of mass of the two bodies are conserved ([148], p. 13) [60]. In a binary *in-elastic collision*, on the other hand, the two bodies collide and stick together. The overall momentum is normally conserved in these collisions too, but the overall kinetic energy of the center of mass of the two bodies is not conserved ([148], p. 13). It is noted that during real collisions, the colliding molecules (particles) undergo both elastic and in-elastic deformations.

The hard sphere potential is defined as:

$$E_P(r) = \begin{cases} \infty & \text{if } r \leq r_0 \\ 0 & \text{if } r > r_0 \end{cases} \quad (2.56)$$

in which  $r_0$  denotes the range of binary molecular interaction. The hard spheres are defined as impenetrable spheres that cannot overlap in space. The molecular energy interaction potential model mimic the extremely strong repulsion of spherical molecules at very close distances.

The hard sphere model is frequently used considering mono-atomic uncharged molecules. However, this model gives a very crude representation of the actual

physics (e.g., repulsive forces and volume of sphere), since molecules in fact are complicated electronic structures, and can by no means resemble rigid spheres. Alternatively, the energy interaction potential of the *Maxwellian molecules* might be useful in exploratory calculations in which a differentiable potential function is needed. For these molecules the intermolecular force between pairs at a distance  $r$  apart is of the form  $Kr^{-5}$ , where  $K$  is a constant [96]. Adopting this particular potential representation the solution of the equation of transfer reduces to a feasible problem, thereby Maxwell [96] obtained analytical expressions for the transport coefficients as outlined earlier. It is noted that many alternative potential functions have been proposed in the literature. The most frequently used model potentials are; rigid sphere, point center of repulsion, Sutherland's model, Lennard-Jones potential, modified Buckingham potential, Kihara potential, Morse potential. Their advantages and disadvantages are thoroughly discussed elsewhere [39, 55]. In the two models adopted in this work, the force is always repulsive and varies inversely as some power of the distance between the molecular centers. No redistribution of energy between the internal and the translational energy forms are allowed. Depending on the molecular energy interaction potential model chosen, the interacting force may arise only upon contact, or act when the molecules are at any distance away from each other.

### 2.3.2 Phase Space, Distribution Function, Means and Moments

A collection of mono-atomic gas molecules are characterized by their position  $\mathbf{r}$  in space and their velocity  $\mathbf{c}$  at time  $t$ . An infinitesimal spatial space containing the point  $\mathbf{r}$  is denoted by  $d\mathbf{r}$  (e.g., in Cartesian coordinates  $= dx dy dz$ ). In a similar manner, an infinitesimal element in a hypothetical velocity space containing the velocity  $\mathbf{c}$  is denoted by  $d\mathbf{c}$  (e.g., in Cartesian coordinates  $= dc_x dc_y dc_z$ ). The imaginary or hypothetical space containing both  $d\mathbf{r}$  and  $d\mathbf{c}$  constitutes the six-dimensional *phase space*.<sup>23</sup> Therefore, by a macroscopic point  $(\mathbf{r}, \mathbf{c}, t)$  in phase space is meant an infinitesimal volume,  $d\mathbf{r} d\mathbf{c}$ , centered at the point  $(\mathbf{r}, \mathbf{c}, t)$ , having an extension sufficient to contain a large number of molecules as required for a statistical description to be valid, but still small compared with the scale of the natural changes in the macroscopic quantities like pressure, gas velocity, temperature and density of mass.

A concept of principal importance in kinetic theory is the distribution function. The probabilistic *distribution function* containing the desired information about the spatial distribution of molecules and their velocity distribution is denoted by  $f(\mathbf{r}, \mathbf{c}, t)$ .

<sup>23</sup> The classical phase space is formally defined in terms of generalized coordinates and momenta following the Hamiltonian mechanics notation, because it is in terms of these variables that Liouville's theorem holds. However, in Cartesian coordinates as used in the present section it is usually still true that  $p_i = mc_i$  under the particular system conditions specified considering the kinetic theory of dilute gases, hence phase space can therefore be defined in terms of the coordinate and velocity variables in this particular case. Nevertheless, in the general case, for example in the presence of a magnetic field, the relation between  $p_i$  and  $c_i$  is more complicated and the classical formulation is required [115].

This probability function is defined in such a way that  $f(\mathbf{c}, \mathbf{r}, t) d\mathbf{c} d\mathbf{r}$  denotes the probable number of molecules in the volume element  $d\mathbf{r}$  located at  $\mathbf{r}$ , whose velocities lie in the range  $d\mathbf{c}$  about  $\mathbf{c}$  at time  $t$ . We treat  $f$  as being a continuous and differentiable function of its arguments. When the distribution function is given, the macroscopic properties of the gas are determined using the concept of moments (or probability-weighted averages). We may now define a molecular *state vector*  $(\mathbf{r}, \mathbf{c})$  denoting the independent variables needed to specify the rate of change of the macroscopic properties.

The macroscopic property obtained by integrating  $f d\mathbf{c}$  over the whole velocity space is the *number density*,  $n(\mathbf{r}, t)$ , which denotes the number of particles per unit volume at the location  $\mathbf{r}$  at time  $t$ :

$$n(\mathbf{r}, t) = \int_{-\infty}^{\infty} f(\mathbf{r}, \mathbf{c}, t) d\mathbf{c} \quad (2.57)$$

The mass *density* of the collection of gas molecules at  $\mathbf{r}$ , at time  $t$ , yields:

$$\rho(\mathbf{r}, t) = mn(\mathbf{r}, t) \quad (2.58)$$

Statistics means and moments are defined in terms of a suitable probability density function (PDF). Therefore, in the present context these statistical measures are expressed in terms of the normalized distribution function,  $P(\mathbf{r}, \mathbf{c}, t) = f(\mathbf{r}, \mathbf{c}, t)/n(\mathbf{r}, t)$ , having the important mathematical property of a PDF:

$$\int_{-\infty}^{\infty} P(\mathbf{r}, \mathbf{c}, t) d\mathbf{c} = \int_{-\infty}^{\infty} \frac{f(\mathbf{r}, \mathbf{c}, t)}{n} d\mathbf{c} = \frac{n}{n} = 1 \quad (2.59)$$

The mean (or expectation) of the random variable  $\mathbf{c}$  is defined by [107, 115, 116, 157]:

$$\mathbf{v}(\mathbf{r}, t) = \langle \mathbf{c}(\mathbf{r}, t) \rangle_M = \int_{-\infty}^{\infty} \mathbf{c} P(\mathbf{r}, \mathbf{c}, t) d\mathbf{c} \quad (2.60)$$

This measure is also referred to as the probability-weighted average of all possible values of  $\mathbf{c}$ .

More generally, let  $\psi(\mathbf{r}, \mathbf{c}, t)$  be a generalized physical function that denotes a property of the molecules located at time  $t$  near  $\mathbf{r}$  with a velocity near  $\mathbf{c}$ . Since  $\psi(\mathbf{r}, \mathbf{c}, t)$  is a function of  $\mathbf{c}$ , the mean of  $\psi$  is:

$$\langle \psi(\mathbf{r}, t) \rangle_M = \int_{-\infty}^{\infty} \psi(\mathbf{r}, \mathbf{c}, t) P(\mathbf{r}, \mathbf{c}, t) d\mathbf{c} = \frac{1}{n(\mathbf{r}, t)} \int_{-\infty}^{\infty} \psi(\mathbf{r}, \mathbf{c}, t) f(\mathbf{r}, \mathbf{c}, t) d\mathbf{c} \quad (2.61)$$

The  $n$ -th *moment about the origin* is defined to be:

$$\mu_n = \langle \mathbf{c}^n \rangle_M = \int_{-\infty}^{\infty} \mathbf{c}^n P(\mathbf{r}, \mathbf{c}, t) d\mathbf{c} \quad (2.62)$$

A first-order moment of  $\psi$  can thus be defined as:

$$\langle \psi(\mathbf{r}, t) \rangle_M = \int_{-\infty}^{\infty} \psi(\mathbf{r}, \mathbf{c}, t) P(\mathbf{r}, \mathbf{c}, t) d\mathbf{c} \quad (2.63)$$

It is noted that the first moment (2.63) equals the mean (2.61).

It follows that the mean or macroscopic *fluid velocity* at the position  $\mathbf{r}$  and time  $t$ , yields:

$$\mathbf{v}(\mathbf{r}, t) = \frac{1}{n(\mathbf{r}, t)} \int_{-\infty}^{\infty} \mathbf{c} f(\mathbf{r}, \mathbf{c}, t) d\mathbf{c} = \frac{1}{\rho(\mathbf{r}, t)} \int_{-\infty}^{\infty} m \mathbf{c} f(\mathbf{r}, \mathbf{c}, t) d\mathbf{c} \quad (2.64)$$

The translational motion of a particular collection of molecules can either be specified by their velocity  $\mathbf{c}$  relative to a standard frame of reference, or by their velocity relative to a frame moving with a specified velocity. The molecular velocity defined in the frame of reference which moves with the local fluid velocity  $\mathbf{v}$  is called the *peculiar velocity* of the collection of molecules. The peculiar velocity is defined by:

$$\mathbf{C} = \mathbf{c} - \mathbf{v} \quad (2.65)$$

It follows from the above definitions that the average peculiar velocity equals zero.

## 2.4 The Boltzmann Equation

The Boltzmann integro-differential equation is an equation of change for the one-particle (single) distribution function defined such that  $dN = f(\mathbf{r}, \mathbf{c}, t) d\mathbf{c} d\mathbf{r}$  represents the number of molecules that have velocities between  $\mathbf{c}$  and  $\mathbf{c} + d\mathbf{c}$  and positions between  $\mathbf{r}$  and  $\mathbf{r} + d\mathbf{r}$  at time  $t$ . All the derivations of the Boltzmann equation are based on a number of assumptions and hypotheses, making the analyzes somewhat ad hoc irrespective of the formal mathematical rigor and complexity accomplished. So in this book a heuristic theory, which is physically revealing and equally ad hoc to the more fundamental derivations of the Boltzmann equation, is adopted. It is stressed that the notation used resembles that introduced by Boltzmann [10] and is not strictly in accordance with the formal mathematical methods of classical mechanics. However, some aspects of the formal formulations and vocabulary outlined in

Sect. 2.2 are incorporated although somewhat based on intuition and empirical reasoning rather than fundamental principles as discussed in Sect. 2.3.

The Boltzmann equation can be derived using a procedure founded on the Liouville theorem. That is, a simplified interpretation of the Liouville theorem, outlined in Sect. 2.2, is employed intending to make the formulation more easily available for beginners. In this case the balance principle is applied to a control volume following a trajectory in phase space, expressed as:

$$\frac{\mathbb{D}}{\mathbb{D}t} \int \int f d\mathbf{r} d\mathbf{c} = \int \int \left( \frac{\partial f}{\partial t} \right)_{\text{Collision}} d\mathbf{r} d\mathbf{c} \quad (2.66)$$

This relation is denoting that the rate of change of  $f$  for a system of a number of particles moving with the phase space velocity vector  $(\frac{d\mathbf{r}}{dt}, \frac{d\mathbf{c}}{dt})$  equals the rate at which  $f$  is altered by collisions.

Applying numerous theorems, similar but not identical to those used in Chap. 1 deriving the governing equations in fluid dynamics, one arrives at the Boltzmann equation on the form:

$$\frac{\partial f}{\partial t} + \mathbf{c} \cdot \frac{\partial f}{\partial \mathbf{r}} + \mathbf{F} \cdot \frac{\partial f}{\partial \mathbf{c}} = \left( \frac{\partial f}{\partial t} \right)_{\text{Collision}} \quad (2.67)$$

where  $\mathbf{c}$  and  $\mathbf{r}$  are considered independent coordinates. In addition, the force  $\mathbf{F}$  per unit mass is assumed to be independent of  $\mathbf{c}$  and replaces the instantaneous acceleration.

Symbolically the Boltzmann equation can be written as [57]:

$$\frac{\mathcal{D}f}{\mathcal{D}t} = \left( \frac{\partial f}{\partial t} \right)_{\text{Collision}} \quad (2.68)$$

where the LHS denotes the translational motion and the RHS represents the impact of collisions.

The model derivation given above using the Liouville theorem is in many ways equivalent to the Lagrangian balance formulation [115]. Of course, a consistent Eulerian balance formulation would give the same result, but includes some more manipulations of the terms in the number balance (see Sect. 2.4.1). However, the Eulerian formulation is of special interest as we have adopted this framework in the preceding discussion of the governing equations of classical fluid dynamics, Chap. 1.

For binary collisions the RHS of the Boltzmann equation (2.68) assumes the form:

$$\left( \frac{\partial f}{\partial t} \right)_{\text{Collision}} = \int_{\mathbf{c}_1} \int_{4\pi} (f' f'_1 - f f_1) g \sigma_A(\boldsymbol{\Omega}) d\boldsymbol{\Omega} d\mathbf{c}_1 \quad (2.69)$$

where the un-primed distribution function refer to the state before collision, and the primed distribution function refer to the state after the collision. Moreover, for convenience, a shorthand notation is introduced for the distribution function:  $f' \equiv f(\mathbf{c}', \dots)$ ,  $f'_1 \equiv f(\mathbf{c}'_1, \dots)$ ,  $f \equiv f(\mathbf{c}, \dots)$ , and  $f_1 \equiv f(\mathbf{c}_1, \dots)$ .

A key contribution by Boltzmann was to determine the collision term solely due to two-body collisions between particles that are assumed to be uncorrelated prior to the collision (i.e., the Stosszahlansatz). Under this assumption the collision term can be written as a velocity-space integral over the product of one-particle (single) distribution functions. The velocities and the corresponding distribution functions of any two particles of the same type are conveniently distinguished by the labels  $\mathbf{c}$  and  $\mathbf{c}_1$  and  $f$  and  $f_1$ , respectively.

A survey of the kinetic theory required deriving the Boltzmann equation, for a dilute gas constituting identical molecular particles of mass  $m$ , is provided in the succeeding subsections. The translational part of the equation in the limit of no collisions is discussed first, before the more complex collision term closure is outlined.

### 2.4.1 The Boltzmann Equation in the Limit of No Collisions

Preliminarily, deriving the terms on the LHS of the Boltzmann equation, it is assumed that the effects of collisions are negligible. The molecular motion is thus purely translational. It is further assumed that in an average sense each molecule of mass  $m$  is subjected to an external force per unit mass,  $\mathbf{F}(\mathbf{r}, t)$ , which doesn't depend on the molecular velocity  $\mathbf{c}$ . This restriction excludes magnetic forces, while the gravity and electric fields which are more common in chemical and metallurgical reactors are retained. Two alternative approaches for deriving the generalized advection equation are available. These procedures are outlined in the subsequent paragraphs within this section.

#### 2.4.1.1 Ensemble of System Points Moving Along Their Trajectories in Phase Space

In this paragraph the translational motion of the distribution function is examined employing the framework of a generalized advection equation [20, 55, 57, 109, 115, 162]. The collection of molecules which at time  $t$  have positions and velocities in the range  $d\mathbf{r}d\mathbf{c}$  near  $\mathbf{r}$  and  $\mathbf{c}$  will, at an infinitesimal time  $dt$  later, have the positions and velocities in the range  $d\mathbf{r}'d\mathbf{c}'$  near  $\mathbf{r}'$  and  $\mathbf{c}'$  as a result of their motion under the influence of the force  $\mathbf{F}$ .

It follows that:

$$\mathbf{r}' = \mathbf{r} + \mathbf{c}dt \quad (2.70)$$

$$\mathbf{c}' = \mathbf{c} + \mathbf{F}dt \quad (2.71)$$

In mathematical terms the translational motion can be expressed as:



$$f(\mathbf{r}', \mathbf{c}', t) d\mathbf{r}' d\mathbf{c}' = f(\mathbf{r}, \mathbf{c}, t) d\mathbf{r} d\mathbf{c} \quad (2.72)$$

The Lagrangian like control volume  $d\mathbf{r} d\mathbf{c}$  in the six dimensional phase space may become distorted in shape as a result of the motion. But, in accordance with the Liouville's theorem, discussed in Sect. 2.2.3.1, the new volume is simply related to the old one by the relation (e.g., [109], p. 225):

$$d\mathbf{r}' d\mathbf{c}' = |J| d\mathbf{r} d\mathbf{c} \quad (2.73)$$

where  $J$  is the Jacobian determinant (value) of the transformation relations (2.70) and (2.71) from the old variables  $d\mathbf{r} d\mathbf{c}$  to the new variables  $d\mathbf{r}' d\mathbf{c}'$ . In this particular case where the force  $\mathbf{F}$  does not depend on the velocity  $\mathbf{c}$  of the molecules,  $J = 1$  due to the Poincarè theorem (see Sect. 2.2.3.1, p. 226). Hence,

$$f(\mathbf{r}', \mathbf{c}', t) = f(\mathbf{r}, \mathbf{c}, t) \quad (2.74)$$

or

$$f(\mathbf{r} + \mathbf{c} dt, \mathbf{c} + \mathbf{F} dt, t + dt) - f(\mathbf{r}, \mathbf{c}, t) = 0 \quad (2.75)$$

This means that in the limit of no molecular interactions, for which the collision term  $(\frac{\partial f}{\partial t})_{\text{Collision}}$  vanishes,  $f$  remains unchanged if the observer moves along with the system points in phase space.

Expanding the first term in (2.75) to the first order in  $dt$ , the generalized advection equation for the distribution function is obtained as  $dt \rightarrow 0$ :

$$\left[ \left( \frac{\partial f}{\partial x} c_x + \frac{\partial f}{\partial y} c_y + \frac{\partial f}{\partial z} c_z \right) + \left( \frac{\partial f}{\partial c_x} F_x + \frac{\partial f}{\partial c_y} F_y + \frac{\partial f}{\partial c_z} F_z \right) + \frac{\partial f}{\partial t} \right] dt = 0 \quad (2.76)$$

The terms in brackets equal an operator analogous to the substantial time derivative known from the transport phenomena literature. The total differential of  $f(\mathbf{r}, \mathbf{c}, t)$  is given by:

$$\begin{aligned} \mathcal{D}f &= \frac{\partial f}{\partial t} \mathcal{D}t + \left( \frac{\partial f}{\partial x} dx + \frac{\partial f}{\partial y} dy + \frac{\partial f}{\partial z} dz \right) + \left( \frac{\partial f}{\partial c_x} dc_x + \frac{\partial f}{\partial c_y} dc_y + \frac{\partial f}{\partial c_z} dc_z \right) \\ &= \frac{\partial f}{\partial t} \mathcal{D}t + \nabla_r f \cdot d\mathbf{r} + \nabla_c f \cdot d\mathbf{c} = \left[ \frac{\partial f}{\partial t} + \nabla_r f \cdot \mathbf{c} + \nabla_c f \cdot \mathbf{F} \right] \mathcal{D}t \end{aligned} \quad (2.77)$$

where  $\mathcal{D}t$  is taken to be infinitesimal and represents the total change in  $f$  resulting from changes in the seven variables on which  $f$  depends explicitly by means of the first partial derivatives.

Equation (2.76) can thus be written more compactly on the vector form:

$$\frac{\mathcal{D}f}{\mathcal{D}t} \equiv \frac{\partial f}{\partial t} + \mathbf{c} \cdot \frac{\partial f}{\partial \mathbf{r}} + \mathbf{F} \cdot \frac{\partial f}{\partial \mathbf{c}} = 0 \quad (2.78)$$

where  $\nabla_{\mathbf{r}} \equiv \frac{\partial}{\partial \mathbf{r}}$ ,  $\nabla_{\mathbf{c}} \equiv \frac{\partial}{\partial \mathbf{c}}$  are the gradient operators with respect to  $\mathbf{r}$  and  $\mathbf{c}$ , respectively.

### 2.4.1.2 Ensemble of System Points Moving Through a Fixed Volume in Phase Space

In this paragraph the translational motion of the distribution function is examined employing the framework of a generalized continuity equation [115, 117, 157]. Consider a fixed 6-dimensional control volume in phase space (i.e., an imaginary extension of the Eulerian control volume known from fluid dynamics, Fig. 1.2), containing a given range of molecular positions between  $\mathbf{r}$  and  $\mathbf{r} + d\mathbf{r}$  and of velocities between  $\mathbf{c}$  and  $\mathbf{c} + d\mathbf{c}$ . The number of molecules in the control volume  $d\mathbf{r}d\mathbf{c}$  of phase space changes as the positions and velocities of the molecules change. The net accumulation of molecules in this range in time  $dt$  is given by  $(\frac{\partial f}{\partial t})d\mathbf{r}d\mathbf{c}dt$ . The net change in the number of molecules within the control volume is determined by the number of molecules entering and leaving this range  $d\mathbf{r}d\mathbf{c}$  as a result of the random molecular motion. In Cartesian coordinates the number of molecules entering the control volume,  $d\mathbf{r}d\mathbf{c}$ , in time  $dt$  through the face  $x = \text{constant}$  equals  $f(c_x dt)dydzdc_xdc_ydc_z$ . The corresponding number of molecules leaving through the face  $x + dx = \text{constant}$  is given by  $[fc_x + \frac{\partial}{\partial x}(fc_x)dx]dtdydzdc_xdc_ydc_z$  where both  $f$  and  $c_x$  are evaluated at  $x + dx$  and thereafter approximated using a first order Taylor expansion. Hence, the number of molecules entering the control volume  $d\mathbf{r}d\mathbf{c}$  in time  $dt$  through the different control volume faces are approximated by:

Net inflow in x- direction:

$$f(c_x dt)dydzdc_xdc_ydc_z - [fc_x + \frac{\partial}{\partial x}(fc_x)dx]dtdydzdc_xdc_ydc_z = -\frac{\partial}{\partial x}(fc_x)d\mathbf{r}d\mathbf{c}dt \quad (2.79)$$

Net inflow in y- direction:

$$f(c_y dt)dx dz dc_x dc_y dc_z - [fc_y + \frac{\partial}{\partial y}(fc_y)dy]dtdx dz dc_x dc_y dc_z = -\frac{\partial}{\partial y}(fc_y)d\mathbf{r}d\mathbf{c}dt \quad (2.80)$$

Net inflow in z- direction:

$$f(c_z dt)dx dy dc_x dc_y dc_z - [fc_z + \frac{\partial}{\partial z}(fc_z)dz]dtdx dy dc_x dc_y dc_z = -\frac{\partial}{\partial z}(fc_z)d\mathbf{r}d\mathbf{c}dt \quad (2.81)$$

Net inflow through the  $c_x$  face of the velocity space:

$$\begin{aligned}
& f(F_x dt) dx dy dz dc_y dc_z - [f F_x + \frac{\partial}{\partial c_x}(f F_x) dc_x] dt dx dy dz dc_y dc_z \\
& = -\frac{\partial}{\partial c_x}(f F_x) d\mathbf{r} d\mathbf{c} dt
\end{aligned} \tag{2.82}$$

Net inflow through the  $c_y$  face of the velocity space:

$$\begin{aligned}
& f(F_y dt) dx dy dz dc_x dc_z - [f F_y + \frac{\partial}{\partial c_y}(f F_y) dc_y] dt dx dy dz dc_x dc_z \\
& = -\frac{\partial}{\partial c_y}(f F_y) d\mathbf{r} d\mathbf{c} dt
\end{aligned} \tag{2.83}$$

Net inflow through the  $c_z$  face of the velocity space:

$$\begin{aligned}
& f(F_z dt) dx dy dz dc_x dc_y - [f F_z + \frac{\partial}{\partial c_z}(f F_z) dc_z] dt dx dy dz dc_x dc_y \\
& = -\frac{\partial}{\partial c_z}(f F_z) d\mathbf{r} d\mathbf{c} dt
\end{aligned} \tag{2.84}$$

Overall, the net inflow of molecules into the phase space  $d\mathbf{r} d\mathbf{c}$  is balanced by the transient term, hence:

$$\begin{aligned}
\left(\frac{\partial f}{\partial t}\right) d\mathbf{r} d\mathbf{c} dt & = -\left[\frac{\partial}{\partial x}(f c_x) + \frac{\partial}{\partial y}(f c_y) + \frac{\partial}{\partial z}(f c_z)\right] d\mathbf{r} d\mathbf{c} dt \\
& \quad -\left[\frac{\partial}{\partial c_x}(f F_x) + \frac{\partial}{\partial c_y}(f F_y) + \frac{\partial}{\partial c_z}(f F_z)\right] d\mathbf{r} d\mathbf{c} dt
\end{aligned} \tag{2.85}$$

Or, after dividing by  $d\mathbf{r} d\mathbf{c} dt$  and adopting Einsteins summation index notation:

$$\begin{aligned}
\left(\frac{\partial f}{\partial t}\right) & = -\frac{\partial}{\partial x_i}(f c_i) - \frac{\partial}{\partial c_i}(f F_i) \\
& = -\left[c_i \frac{\partial f}{\partial x_i} + F_i \frac{\partial f}{\partial c_i}\right] - f\left[\frac{\partial c_i}{\partial x_i} + \frac{\partial F_i}{\partial c_i}\right]
\end{aligned} \tag{2.86}$$

Further simplification can be achieved as we recall that the variables  $\mathbf{r}$  and  $\mathbf{c}$  are independent, hence:

$$\frac{\partial c_i}{\partial x_i} = 0 \tag{2.87}$$

In a similar manner,

$$\frac{\partial F_i}{\partial c_i} = 0 \tag{2.88}$$

since  $\mathbf{F}$  does not depend on  $\mathbf{c}$ .

Using the latter two relations the terms within the last bracket in (2.86) vanish, so the Boltzmann equation reduces to:

$$\frac{\partial f}{\partial t} = -\mathbf{c} \cdot \frac{\partial f}{\partial \mathbf{r}} - \mathbf{F} \cdot \frac{\partial f}{\partial \mathbf{c}} \quad (2.89)$$

This relation is known as the Liouville theorem as discussed in Sect. 2.2.3.1.

Introducing a generalized form of the substantial derivative, measuring the rate of change as the observer moves along with the system points in phase space, a compact form similar to (2.78) is achieved. Note also that it is common in the mechanics literature to assume that there always exists a sufficiently differentiable and single-valued function defining the position vector, even though it is unknown. In this interpretation the molecular positions and velocities changes in accordance with (2.70) and (2.71) [92] (Sect. 4.3).

### 2.4.2 The Boltzmann Equation Collision Term Approximation

To determine the rate of change of  $f$  caused by molecular collisions a number of simplifying assumptions concerning the molecular motion and collisions are introduced. The most important assumptions are [20, 39, 115]:

- The system under consideration in the classical kinetic theory is a dilute gas of  $N$  mono-atomic molecules enclosed in a box of volume  $V$ . It is assumed that the particles in the system are identical having mass  $m$ .
- The gas density is assumed to be very low so that only elastic binary collisions need to be taken into account. At higher densities, ternary and higher order interactions become significant.
- The interactions with the external boundaries of the system are ignored. That is, the physical walls of the container are replaced by idealized surfaces which reflect the particles by elastic collisions.
- All possible effects which can be exerted by the external force per unit mass,  $\mathbf{F}$ , on the magnitude of the collisional cross section are neglected.
- The *local equilibrium* assumption is imposed. This means that the distribution function  $f(\mathbf{r}, \mathbf{c}, t)$  does not vary appreciably (homogeneous) during a time interval of the order of the duration of a molecular collision, nor does it vary appreciably over a spatial distance of the order of the range of intermolecular forces.
- The *molecular chaos* assumption is imposed. This assumption implies that the dilute gas point particles are uncorrelated outside the range of interaction  $r_0$ . Moreover, the range of interaction is considered infinitesimal relative to the mean free path of the molecular particles  $l$ , thus  $r_0/l \ll 1$ . Equivalently, the interaction volume  $V_0 \propto r_0^3$  and the interaction time  $\tau_0$  is considered infinitesimal relative to the average volume per particle and the mean free time between the interactions. This constraint ensures rectilinear particle trajectories before and after a collision. This assumption is sometimes referred to as the Stosszahlansatz. In the original paper by

Boltzmann [10], it is rather assumed that in a given volume element the expected number of collisions between molecules that belong to different velocity ranges can be computed statistically. This assumption was then referred to as the Boltzmann *Stosszahlansatz* (German for: Collision number assumption). This assumption is difficult to justify because it introduces statistical arguments into a problem that is in principle purely mechanical [117]. Criticism against the Boltzmann equation was raised in the past related to this problem. Nowadays it is apparently accepted that the molecular chaos assumption is needed only for the molecules that are going to collide. After the collision the scattered particles are of course strongly correlated, but this is considered irrelevant for the calculation since the colliding molecules come from different regions of space and have met in their past history other particles and are therefore entirely uncorrelated. Furthermore, the molecular chaos assumption also implies that the pair distribution function can be approximated by the product of two single distribution functions. If the pair distribution function can be expressed as the sum of the product of two single distribution functions and a pair correlations function, the following approximation holds:

$$\begin{aligned} f^{(2)}(\mathbf{r}, \mathbf{c}_1, \mathbf{r}, \mathbf{c}_2, t) &= \frac{N-1}{N} \left[ f^{(1)}(\mathbf{r}, \mathbf{c}_1, t) f^{(2)}(\mathbf{r}, \mathbf{c}_2, t) + f_{\text{Correlation}} \right] \\ &\approx f^{(1)}(\mathbf{r}, \mathbf{c}_1, t) f^{(2)}(\mathbf{r}, \mathbf{c}_2, t) \end{aligned} \quad (2.90)$$

The chaos assumption thus allows the pair correlation to be neglected outside the range of molecular interaction, thus  $f_{\text{Correlation}} \approx 0$  when  $|\mathbf{r}_2 - \mathbf{r}_1| > r_0$ .

A result of the Boltzmann *H-theorem* analysis is that the latter statistical assumption makes Boltzmann's equation irreversible in time (e.g., [39], Sect. 4.2).

No exact expression for  $(\frac{\partial f}{\partial t})_{\text{Collision}}$  has been obtained since the nature of the interaction between the colliding molecules is not known in sufficient details. It is rather assumed by hypothesis some laws of interaction which are validated comparing the overall results with experimental data. Nevertheless, detailed experimental analysis of gases shows that, at distances large compared to the molecular dimensions, weak intermolecular forces exist, whereas at distances of the order of the molecular dimensions the molecules repel each other strongly. Moreover, collisions between complex molecules may in general also redistribute energy between the translational and internal energy forms but as the present analysis is restricted to mono-atomic gases it is presupposed that no energy is redistributed between these energy forms. To close the statistical Boltzmann equation determining the evolution of the distribution function, it is considered advantageous to derive constitutive relations for the collision term based on mechanistic analysis of simplified images or models of binary particle collisions. In this context simplifying assumptions about the nature of the forces between the two molecules during collisions must be made. Several molecular models have been considered, as already mentioned in Sect. 2.3.1. In the following, the molecules of the gas are approximated as hard spheres resembling billiard balls. Moreover, all the particles have the same mass and the particle collisions are elastic. Taking into account the molecular interactions a mathematical expression for the

rate at which the distribution function  $f$  is being altered by collisions is required. In the Boltzmann equation, these phenomena are represented by the net rate at which collisions increase or decrease the number of molecules entering the phase volume  $d\mathbf{r}d\mathbf{c}$ :

$$\left(\frac{\partial f}{\partial t}\right)_{\text{Collision}} = \left(\frac{\partial f}{\partial t}\right)_{\text{Collision}}^+ - \left(\frac{\partial f}{\partial t}\right)_{\text{Collision}}^- \quad (2.91)$$

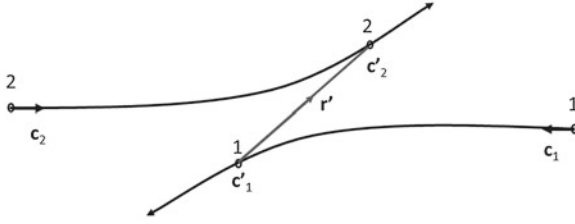
where the number of particles injected into  $d\mathbf{r}d\mathbf{c}$  due to collisions during the time  $dt$  is denoted by  $\left(\frac{\partial f}{\partial t}\right)_{\text{Collision}}^+ d\mathbf{r}d\mathbf{c}dt$ , while the number of particles ejected is  $\left(\frac{\partial f}{\partial t}\right)_{\text{Collision}}^- d\mathbf{r}d\mathbf{c}dt$ . It is in specifying these terms the assumption that the system is a dilute gas becomes relevant.

The conventional collision term  $\left(\frac{\partial f}{\partial t}\right)_{\text{Collision}}$  closure is further discussed in the paragraph called *generalized collision term* in the current subsection, presenting an outline of the derivation of the approximate constitutive relations for  $\left(\frac{\partial f}{\partial t}\right)_{\text{Collision}}^+$  and  $\left(\frac{\partial f}{\partial t}\right)_{\text{Collision}}^-$ . Meanwhile, the prerequisite understanding of the fundamental nature of the dynamics of binary particle collisions, and the mechanical relations between the velocities before and after the interaction, the scattering cross sections, the symmetry properties of the collision, the concept of solid angle, and an estimate of the expected number of molecular collisions are outlined in the subsequent paragraphs within this section.

#### 2.4.2.1 Dynamics of Elastic Binary Molecular Interactions

It is required to express either pair of molecular velocities before and after the interaction in terms of the other pair, and of two independent geometrical variables ( $b$  and  $\phi$ ) in order to complete the specification of the encounter. The original Boltzmann equation derivation considers elastic collisions in free space between two spin-less molecules of equal mass. However, due to the major interest in multicomponent mixtures, the theory outline consider elastic collisions between two spin-less mono-atomic molecules in an ideal gas mixture. The theory may be useful even if the molecules are not mono-atomic, provided that their states of internal motion (i.e., rotation and vibration) are not affected by the collisions. The two molecules under consideration are treated as point particles with respective masses  $m_1$  and  $m_2$ . In the *laboratory frame*, the incoming molecule positions are denoted by  $\mathbf{r}_1$  and  $\mathbf{r}_2$ , and the particle velocities are indicated by  $\mathbf{c}_1$  and  $\mathbf{c}_2$ . The corresponding positions and velocities after the encounter are  $\mathbf{r}'_1$ ,  $\mathbf{r}'_2$  and  $\mathbf{c}'_1$ ,  $\mathbf{c}'_2$ , respectively. The classical trajectories for two interacting molecules presented in the laboratory system frame are viewed in Fig. 2.1. It is supposed that the particle interaction is determined by conservative potential interaction forces only. Any external forces which might act on the molecules are considered negligible compared to the potential forces involved locally in the collision. The relative position vectors in the laboratory frame are defined by:

$$\mathbf{r} = \mathbf{r}_2 - \mathbf{r}_1 \text{ and } \mathbf{r}' = \mathbf{r}'_2 - \mathbf{r}'_1 \quad (2.92)$$



**Fig. 2.1** A binary particle interaction or scattering event as viewed in the laboratory coordinate system

Accordingly, the relative displacements are:

$$r = |\mathbf{r}_2 - \mathbf{r}_1| \text{ and } r' = |\mathbf{r}'_2 - \mathbf{r}'_1| \quad (2.93)$$

To express the dynamics of a binary interaction in mathematical terms, a more precise definition of an encounter is needed. A molecular interaction, or particle scattering event, is divided into three epochs: before, during, and after the interaction. Both before and after the interaction, molecules are free and do not interact with one another. We may then introduce a measure  $r_0$  that denotes the range of interaction. In the present analysis of an ideal gas mixture, the hard sphere molecular model (2.56), given at page 232, is employed. This parameter is thus defined so that, when the particles are sufficiently far away from each other ( $r > r_0$ ), the interaction vanishes. By definition, when the particles enter the interaction domain ( $r \leq r_0$ ), they experience a collision. The meaning of before and after collision is thus given in terms of the potential of interaction  $E_P(r)$  or the range of interaction  $r_0$ . Before interaction denotes the interval in which the particles are approaching one another and  $r > r_0$  or, equivalently,  $E_P(r) = 0$ . After collision denotes the interval in which the particles are receding from one another and, again,  $E_P(r) = 0$  and  $r > r_0$ . Before the particles are entering the interaction region,  $r > r_0$ , the two particles move freely with constant momenta towards each other. The total energy of the system equals the sum of the kinetic energies:

$$E_{\text{Total}} = \frac{\mathbf{p}_1^2}{2m_1} + \frac{\mathbf{p}_2^2}{2m_2} \quad (2.94)$$

After the particles are exiting the interaction region,  $r > r_0$ , they again move freely with constant momenta but now away from each other.

The energy after interaction is:

$$E'_{\text{Total}} = \frac{\mathbf{p}'_1{}^2}{2m_1} + \frac{\mathbf{p}'_2{}^2}{2m_2} = E_{\text{Total}} \quad (2.95)$$



In the interaction region,  $r \leq r_0$ , the kinetic energy of the particles is generally converted partly into potential energy. The total energy of the two particles is still conserved<sup>24</sup>:

$$E'_{\text{Total}} = \frac{\mathbf{p}_1'^2}{2m_1} + \frac{\mathbf{p}_2'^2}{2m_2} + E_p(r) = E_{\text{Total}} \quad (2.97)$$

It is assumed that the interaction force is conservative. A conservative force is a force with the property that the work done in moving a particle between two points is independent of the path taken. For this reason the force depends only on the position of the particle.

In the laboratory frame<sup>25</sup> the equations of motion (i.e., Newtons 2. law) for each of the interacting particles are:

$$m_1 \frac{d^2 \mathbf{r}_1}{dt^2} = \mathbf{F}_{12} \quad (2.98)$$

$$m_2 \frac{d^2 \mathbf{r}_2}{dt^2} = \mathbf{F}_{21} \quad (2.99)$$

where the force exerted on molecule 1 by molecule 2 is denoted by  $\mathbf{F}_{12}$ , and the force exerted on molecule 2 by molecule 1 is denoted by  $\mathbf{F}_{21}$ . The Newtons laws and the total energy balance, including an approximate molecular energy interaction potential model, determine the movement of point centers with specified masses thus the corresponding position vector trajectories reproduce the movement of actual molecules of finite size.

The law of conservation of total energy for the binary particle system can be derived from the equations of motion in the following manner. In the first step we multiply, by the scalar vector product, the particle velocity  $\mathbf{c}_1 = \dot{\mathbf{r}}_1$  with the vector equation (2.98), and the particle velocity  $\mathbf{c}_2 = \dot{\mathbf{r}}_2$  with the vector equation (2.99). Second, the LHS terms are manipulated using simple derivation rules. Finally, the resulting two equations are added and the forces are eliminated using the definition (2.54):

$$m_1 \frac{d(\frac{1}{2}c_1^2)}{dt} + m_2 \frac{d(\frac{1}{2}c_2^2)}{dt} = -\nabla E_p(|\mathbf{r}_1 - \mathbf{r}_2|) \cdot \frac{d\mathbf{r}_1}{dt} - \nabla E_p(|\mathbf{r}_2 - \mathbf{r}_1|) \cdot \frac{d\mathbf{r}_2}{dt} \quad (2.100)$$

---

<sup>24</sup> Note that the Hamiltonian of two particles interacting under an energy potential  $E_p(r)$ , in the laboratory frame, is written [90]:

$$H(\mathbf{r}_1, \mathbf{r}_2, \mathbf{p}_1, \mathbf{p}_2) = \frac{\mathbf{p}_1^2}{2m_1} + \frac{\mathbf{p}_2^2}{2m_2} + E_p(r = |\mathbf{r}_2 - \mathbf{r}_1|) = E_{\text{Total}}. \quad (2.96)$$

<sup>25</sup> In physics, the laboratory frame of reference is the reference frame in which the laboratory is at rest. The laboratory frame name is obtained as the experiment is presumed to be made by laboratory instruments.

Since  $dt$  vanishes by multiplication, undetermined integrations provide the result denoting the law of conservation of total energy [60]:

$$E_{\text{Total}} = \frac{1}{2}m_1c_1^2 + \frac{1}{2}m_2c_2^2 + \Delta E_p(|\mathbf{r}_2 - \mathbf{r}_1|) = \text{Constant} \quad (2.101)$$

where the kinetic theory regards the range  $r \leq r_0$  over which  $\Delta E_p(|\mathbf{r}_2 - \mathbf{r}_1|)$  is effective as being small (i.e., both  $E_p(|\mathbf{r}_2 - \mathbf{r}_1|) \rightarrow 0$  and  $E_p(|\mathbf{r}_1 - \mathbf{r}_2|) \rightarrow 0$  for  $r = |\mathbf{r}_2 - \mathbf{r}_1| \geq r_0$ ). Equivalently, the time duration of the interactions is assumed to be so small that we may consider them instantaneous compared to the time period between successive collisions. Moreover, considering elastic collisions of hard sphere – billiard ball particles (2.56), there are no loss in kinetic energy (i.e.,  $\Delta E_p(|\mathbf{r}_2 - \mathbf{r}_1|) \rightarrow 0$  for  $r \leq r_0$ ). For these reasons, henceforth our interest lies on the particles' dynamics before and after the interaction takes place.

For an ideal gas mixture only elastic collisions take place, hence the kinetic energy is conserved and the kinetic energy before and after a collision equals:

$$\frac{1}{2}m_1c_1^2 + \frac{1}{2}m_2c_2^2 = \frac{1}{2}m_1c_1'^2 + \frac{1}{2}m_2c_2'^2 = E_{\text{Total}} \quad (2.102)$$

Similarly, the sum of the cross products of (2.98) and (2.99) with  $\dot{\mathbf{r}}_1$  and  $\dot{\mathbf{r}}_2$ , respectively, leads to the law of conservation of total angular momentum:

$$L_{\text{Total}} = m_1\mathbf{r}_1 \times \dot{\mathbf{r}}_1 + m_2\mathbf{r}_2 \times \dot{\mathbf{r}}_2 = \text{Constant} \quad (2.103)$$

In the laboratory frame the coordinate  $\mathbf{r}_c$  of the center of mass of two point particles is given by the weighted average of their coordinates  $\mathbf{r}_1$  and  $\mathbf{r}_2$ :

$$\mathbf{r}_c = \frac{m_1\mathbf{r}_1 + m_2\mathbf{r}_2}{m_1 + m_2} \quad (2.104)$$

where  $m_c = m_1 + m_2$  is the total mass. The coordinates of the center of mass point  $\mathbf{r}_c$  lies on the straight line connecting the positions  $\mathbf{r}_1$  and  $\mathbf{r}_2$  of point masses  $m_1$  and  $m_2$ , respectively.

In the laboratory frame, the velocity of the center of mass is given by:

$$\mathbf{G} = \dot{\mathbf{r}}_c = \frac{d\mathbf{r}_c}{dt} \quad (2.105)$$

It follows that the center of mass acceleration vanishes as:

$$m_c \frac{d\mathbf{G}}{dt} = m_c \frac{d^2\mathbf{r}_c}{dt^2} = m_1 \frac{d^2\mathbf{r}_1}{dt^2} + m_2 \frac{d^2\mathbf{r}_2}{dt^2} = \mathbf{F}_{12} + \mathbf{F}_{21} = 0 \quad (2.106)$$

since the Newton 3. law of action and reaction states that  $\mathbf{F}_{12} = -\mathbf{F}_{21}$ . Note also that when the forces are given by the molecular energy interaction potential  $E_p(r)$ , the local problem is spherically symmetric [60].

It follows from (2.106), when integrated in time, that the conservation of linear momentum yields:

$$m_c \mathbf{G} = m_1 \mathbf{c}_1 + m_2 \mathbf{c}_2 = m_1 \mathbf{c}'_1 + m_2 \mathbf{c}'_2 = \mathbf{P} = \text{Constant} \quad (2.107)$$

This relation is showing that the velocities are not independent. In fact (2.107) states that the total mass  $m_c$  of the two molecules moves uniformly throughout the collision. That is, the center of mass velocity  $\mathbf{G}$  remains unchanged since  $\mathbf{P}$  is conserved (constant) for elastic collisions.

The ratio between the kinetic energy (2.102) and momentum (2.107) is:

$$\frac{m_1(\mathbf{c}'_1{}^2 - \mathbf{c}_1^2)}{m_1(\mathbf{c}'_1 - \mathbf{c}_1)} = -\frac{m_2(\mathbf{c}'_2{}^2 - \mathbf{c}_2^2)}{m_2(\mathbf{c}_2 - \mathbf{c}'_2)} \quad (2.108)$$

and, after simple manipulations

$$\mathbf{c}'_1 + \mathbf{c}_1 = \mathbf{c}_2 + \mathbf{c}'_2 \text{ or equivalently } \mathbf{g}'_{21} = -\mathbf{g}_{21} \quad (2.109)$$

Accordingly, by integration in time we also get:  $\mathbf{r}' = -\mathbf{r}$ .

It is noticed that *in-elastic* collisions are characterized by the degree to which the relative speed is no longer conserved. For this reason, the coefficient of restitution  $e$  in a collision is defined (i.e., with basis in (2.109)) as the ratio of the relative velocity after collision, divided by the relative velocity of approach [63, 99]:

$$\mathbf{c}'_2 - \mathbf{c}'_1 = -e(\mathbf{c}_2 - \mathbf{c}_1) \quad (2.110)$$

where  $e = 1$  denotes elastic collisions, whereas  $e = 0$  for totally inelastic collisions.

Another quantity of interest is the relative velocity. Let  $\mathbf{g}_{21}$  and  $\mathbf{g}'_{21}$ , and  $\mathbf{g}_{12}$  and  $\mathbf{g}'_{12}$  denote respectively the relative velocities before and after the interaction either defined as the second molecule relative to the first, or of the first relative to the second:

$$\mathbf{g}_{21} = \mathbf{c}_2 - \mathbf{c}_1 = -\mathbf{g}_{12} \text{ and } \mathbf{g}'_{21} = \mathbf{c}'_2 - \mathbf{c}'_1 = -\mathbf{g}'_{12} \quad (2.111)$$

The magnitudes of the relative velocities before collision are equal and denoted by  $g$ , likewise the relative velocities after collision are equal and denoted  $g'$ .

Thus, for elastic collisions the following relations hold:

$$g_{21} = g_{12} = g \text{ and } g'_{21} = g'_{12} = g' \quad (2.112)$$

By means of (2.107) and (2.111) we can express  $\mathbf{c}_1$  and  $\mathbf{c}_2$ , and  $\mathbf{c}'_1$  and  $\mathbf{c}'_2$  in terms of  $\mathbf{G}$  and  $\mathbf{g}_{21}$ , as given by:

$$\begin{aligned}
\mathbf{c}_1 &= \mathbf{G} - \frac{\mu}{m_1} \mathbf{g}_{21} \\
\mathbf{c}'_1 &= \mathbf{G} - \frac{\mu}{m_1} \mathbf{g}'_{21} \\
\mathbf{c}_2 &= \mathbf{G} + \frac{\mu}{m_2} \mathbf{g}_{21} \\
\mathbf{c}'_2 &= \mathbf{G} + \frac{\mu}{m_2} \mathbf{g}'_{21}
\end{aligned} \tag{2.113}$$

in which is a hypothetical mass quantity,  $\mu$ , named the reduced mass of the binary particle system has been introduced.

The *reduced mass* is defined as:

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \tag{2.114}$$

These relations (2.113) thus show that a knowledge of  $\mathbf{G}$  and  $\mathbf{g}_{21}$  is equivalent to a knowledge of  $\mathbf{c}_1$  and  $\mathbf{c}_2$  or  $\mathbf{c}'_1$  and  $\mathbf{c}'_2$  denoting the state of motion before and after the interaction.

By experience, it proves convenient in discussing scattering events to transform the model into a frame of reference that moves along with the center of mass in which  $\mathbf{r}_c = 0$  is taken as origin. In this coordinate system, the center of mass motion is eliminated in accordance with the definition (2.105):

$$\mathbf{G}_c = \left. \frac{d\mathbf{r}_c}{dt} \right|_{\mathbf{r}_c=0} = 0 \tag{2.115}$$

Since the problem has been formulated in terms of the relative velocity vectors before and after an interaction, it is revealed that in the center of mass frame the collision process can be described by simple relationships. From (2.113), we get:

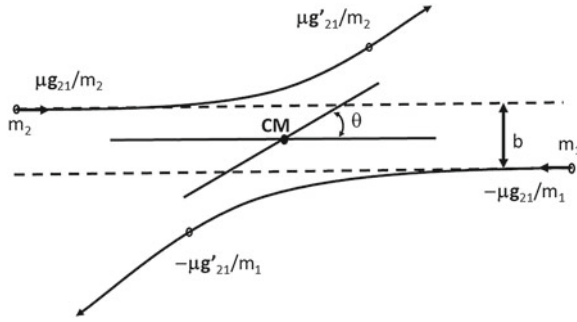
$$\mathbf{c}_{1c} = \mathbf{c}_1 - \mathbf{G} = -\frac{\mu}{m_1} \mathbf{g}_{21} \tag{2.116}$$

$$\mathbf{c}_{2c} = \mathbf{c}_2 - \mathbf{G} = \frac{\mu}{m_2} \mathbf{g}_{21} \tag{2.117}$$

$$\mathbf{c}'_{1c} = \mathbf{c}'_1 - \mathbf{G} = -\frac{\mu}{m_1} \mathbf{g}'_{21} \tag{2.118}$$

$$\mathbf{c}'_{2c} = \mathbf{c}'_2 - \mathbf{G} = \frac{\mu}{m_2} \mathbf{g}'_{21} \tag{2.119}$$

The binary particle collision presented in the center of mass frame is depicted in Fig. 2.2. The center of mass frame is 1D in the symmetric case.



**Fig. 2.2** Scattering in the center of mass frame illustrating the relative velocities of masses  $m_1$  and  $m_2$

By the definition of the center of mass frame, (2.107) might be manipulated as:

$$\mathbf{P}_c = m_c \mathbf{G}_c = m_1 \mathbf{c}_{1c} + m_2 \mathbf{c}_{2c} = m_1 \mathbf{c}'_{1c} + m_2 \mathbf{c}'_{2c} = 0 \quad (2.120)$$

By use of the relations given in (2.113), the kinetic energy equation (2.102) becomes:

$$E_c = \frac{1}{2} m_c (G_c^2 + \frac{\mu}{m_c} g^2) = \frac{1}{2} m_c (G_c^2 + \frac{\mu}{m_c} g'^2) \quad (2.121)$$

The relative velocity changes from the value  $\mathbf{g}_{21}$  before the collision to the value  $\mathbf{g}'_{21}$  after the collision. Since the collision is assumed to be elastic so that the internal energies of the molecules remain unchanged, the total kinetic energy  $E_c$  remains unchanged in a collision. It follows from (2.121) and (2.115) that the kinetic energy equation can be simplified as:

$$E_c = \frac{\mu}{m_c} g^2 = \frac{\mu}{m_c} g'^2 \quad (2.122)$$

Hence, it is revealed that the magnitude of the relative velocity is the same before and after the collision:

$$g = g' \quad (2.123)$$

This result shows that the relative velocity is changed only in direction and not in magnitude by the collision. The dynamical effect of a collision is therefore known when the change in direction of  $\mathbf{g}_{21}$  is determined.

Further knowledge on the direction of  $\mathbf{g}_{21}$  is obtained by examining the simultaneous positions (or velocities) of the two particles in the center of mass framework. The position vectors  $\mathbf{r}_{1c}$ ,  $\mathbf{r}_{2c}$  and  $\mathbf{r}'_{1c}$ ,  $\mathbf{r}'_{2c}$  of the particles relative to the center of mass are defined by:

$$\mathbf{r}_{1c} = \mathbf{r}_1 - \mathbf{r}_c = -\frac{\mu}{m_1} \mathbf{r} \quad (2.124)$$

$$\mathbf{r}_{2c} = \mathbf{r}_2 - \mathbf{r}_c = \frac{\mu}{m_2} \mathbf{r} \quad (2.125)$$

$$\mathbf{r}'_{1c} = \mathbf{r}'_1 - \mathbf{r}'_c = -\frac{\mu}{m_1} \mathbf{r}' \quad (2.126)$$

$$\mathbf{r}'_{2c} = \mathbf{r}'_2 - \mathbf{r}'_c = \frac{\mu}{m_2} \mathbf{r}' \quad (2.127)$$

in which the definition of  $\mathbf{r}_c$  is given by (2.104), p. 246.

Eliminating the relative position vectors  $\mathbf{r}$  and  $\mathbf{r}'$  from these relations, yield:

$$m_1 \mathbf{r}_{1c} = -m_2 \mathbf{r}_{2c} \quad (2.128)$$

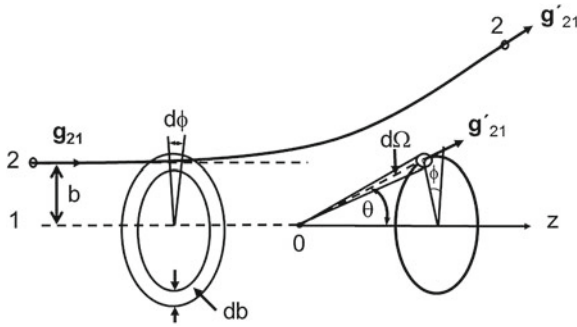
$$m_1 \mathbf{r}'_{1c} = -m_2 \mathbf{r}'_{2c} \quad (2.129)$$

This means that in the frame of reference which moves with the center of mass, the position vectors are at all times oppositely directed along a line, and their magnitudes have a fixed ratio. Moreover, the vector  $\mathbf{r}$  joining the molecules passes always through their center of mass. The impact parameter  $b$  is now to be interpreted as the hypothetical distance of closest approach if both particles were to continue undeflected along their original trajectories ( $r_m$  is the actual distance of closest approach) [109], Chap. 8. No further information about the collision can be obtained from the laws of conservation of momentum and energy. Instead, a geometrical analysis of the interaction between molecules reveals that the direction of  $\mathbf{g}'_{21}$  depends not only on the initial velocities  $\mathbf{c}_1$  and  $\mathbf{c}_2$  (or in  $\mathbf{G}$  and  $\mathbf{g}_{21}$ ), but also on two independent geometrical variables constituting an angle  $\phi$  and a displacement  $b$ . In the center of mass system it suffices to focus on one of the molecules, due to the prior result that the other molecule always moves in the opposite direction. Thus, the problem reduces to an equivalent problem of the scattering of a molecule by a fictitious fixed center of force, represented by the point  $O$  in Figs. 2.3 and 2.4. Using (2.113), the equation of motion for particle 2 (2.99) can be expressed as:

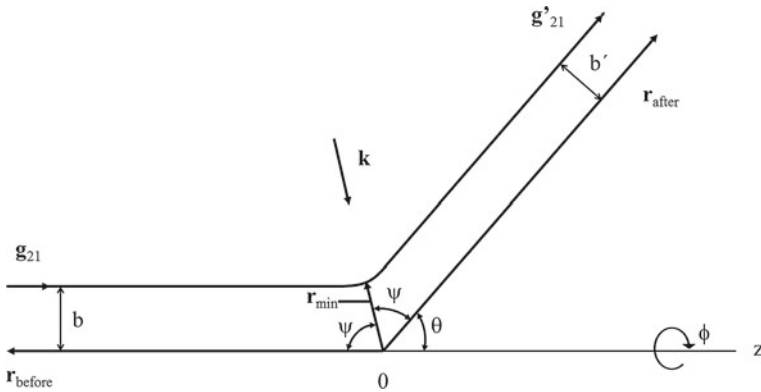
$$m_2 \frac{d^2 \mathbf{r}_2}{dt^2} = \mu \frac{d^2 \mathbf{r}}{dt^2} = \mathbf{F}_{21} \quad (2.130)$$

It follows that the motion  $\mathbf{r}$  of molecule 2 relative to molecule 1 is the same as if the particle had a mass  $\mu$  and were acted on by the force  $\mathbf{F}_{21}$ . The discussion of the two-molecule problem is thus reduced to the solution of a simple one-molecule problem.

We naturally chose to work in a polar coordinate frame of reference where the trajectory is represented by the polar coordinates  $(r, \theta, \phi)$ . Moreover, it is convenient to define a frame of reference with  $O$  located at the origin of the coordinate system with  $z$  axis parallel to  $\mathbf{g}_{21}$ . The 2 molecule approaches  $O$  with velocity  $\mathbf{g}_{21}$ , whose perpendicular distance to  $O$  is called the impact parameter  $b$ . The polar coordinates of the point molecule 2 thus give its position relative to a fixed reference point  $O$  and a given polar axis  $z$ . The radial coordinate  $r$  is the distance from  $O$  to the molecule



**Fig. 2.3** Scattering of a molecule by a fixed center of force  $O$ . Molecule 1 is at rest with its center at the origin



**Fig. 2.4** Scattering in the frame of the relative vector  $\mathbf{r}$ . The scattering angle  $\theta$  is related to  $\psi$  through the relation  $\theta + 2\psi = \pi$

2. For elastic collisions in which  $g' = g$ , the final state after collision is specified by the two scattering angles  $\theta$  and  $\phi$ , collectively denoted by  $\Omega'$ , with  $\theta$  the angle between  $\mathbf{g}'_{21}$  and the  $z$  axis and  $\phi$  the azimuth (rotational) angle of  $\mathbf{g}'_{21}$  about the  $z$  axis, as shown in Fig. 2.4. Specifying  $\mathbf{G}$ ,  $\mathbf{g}_{21}$ , the angle  $\phi$ , and the impact parameter  $b$ , uniquely determines  $\mathbf{g}'_{21}$ . Thus, the kinetic description of the binary molecular collision is complete.

#### 2.4.2.2 Relative Velocity Difference

The main aim in this paragraph is to close the inverse collision terms in the Boltzmann equation. Consider a scattering event, as sketched in Fig. 2.4. In the following analysis the particle collision is viewed in a frame where the origin of the relative vector  $\mathbf{r}$  is fixed. This framework is also known as a fixed center of force. The line joining the

two molecules when at the points of closest approach,  $\mathbf{r}_{\min}$ , is called *the apse-line*. This apse-line passes through  $O$ , the intersection of the two asymptotes  $\mathbf{g}_{21}$  and  $\mathbf{g}'_{21}$ . The unit vector  $\mathbf{k}$  of the apse-line bisects the angle between  $-\mathbf{g}_{21}$  and  $\mathbf{g}'_{21}$ , as the orbit of the second molecule relative to the first is symmetrical about the apse-line. This symmetry is a consequence of the conservation of angular momentum [49, 90]:

$$L = \mu g b = \mu g' b' \quad (2.131)$$

Previous results revealed that the components of  $\mathbf{g}_{21}$  and  $\mathbf{g}'_{21}$  are equal in magnitude, but opposite in sign, hence from simple vector analysis it follows that:  $\mathbf{g}_{21} \cdot \mathbf{k} = -\mathbf{g}'_{21} \cdot \mathbf{k}$ . Moreover, simple vector subtraction shows that  $\mathbf{g}_{21}$  and  $\mathbf{g}'_{21}$  differ by twice the component of  $\mathbf{g}_{21}$  in the direction of  $\mathbf{k}$ , thus:

$$\mathbf{g}_{21} - \mathbf{g}'_{21} = 2(\mathbf{g}_{21} \cdot \mathbf{k})\mathbf{k} = -2(\mathbf{g}'_{21} \cdot \mathbf{k})\mathbf{k} \quad (2.132)$$

With the help of (2.132) and the relationships given in (2.113), two useful relations between the particle velocities before and after a collision are established:

$$\mathbf{c}'_1 - \mathbf{c}_1 = \frac{\mu}{m_2}(\mathbf{g}_{21} - \mathbf{g}'_{21}) = 2\frac{\mu}{m_2}(\mathbf{g}_{21} \cdot \mathbf{k})\mathbf{k} = -2\frac{\mu}{m_2}(\mathbf{g}'_{21} \cdot \mathbf{k})\mathbf{k} \quad (2.133)$$

$$\mathbf{c}'_2 - \mathbf{c}_2 = \frac{\mu}{m_1}(\mathbf{g}_{21} - \mathbf{g}'_{21}) = 2\frac{\mu}{m_1}(\mathbf{g}_{21} \cdot \mathbf{k})\mathbf{k} = -2\frac{\mu}{m_1}(\mathbf{g}'_{21} \cdot \mathbf{k})\mathbf{k} \quad (2.134)$$

Thereby it has been shown that when  $\mathbf{k}$ ,  $\mathbf{c}_1$  and  $\mathbf{c}_2$  are given, the velocities after the collision,  $\mathbf{c}'_1$  and  $\mathbf{c}'_2$ , can be determined.

These two formulas make it possible to calculate the distribution function quantities in the collision term of the Boltzmann equation associated to the inverse collisions (2.69):

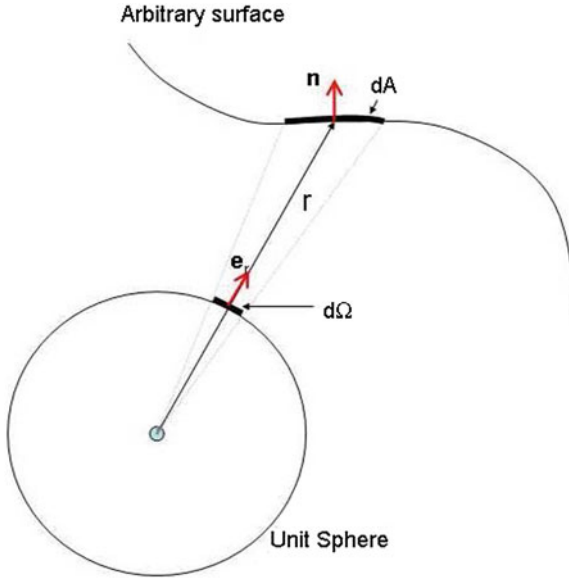
$$f'_1[\mathbf{c}'_1] = f'_1[\mathbf{c}_1 + 2\frac{\mu}{m_2}(\mathbf{g}_{21} \cdot \mathbf{k})\mathbf{k}] \quad (2.135)$$

$$f'_2[\mathbf{c}'_2] = f'_2[\mathbf{c}_2 - 2\frac{\mu}{m_1}(\mathbf{g}'_{21} \cdot \mathbf{k})\mathbf{k}] \quad (2.136)$$

### 2.4.2.3 Concept of Solid Angle

The concept of solid angle, commonly used in kinetic theory, radiation and other scattering problem descriptions, is defined before the molecular scattering process is described in further details in the subsequent section. Basically, the solid angle is the three dimensional analog of an ordinary angle. A differential plane angle  $d\chi$  is defined as the ratio of the element of arc length  $dl$  on the circle to the radius  $r$  of the circle, hence  $d\chi = dl/r$ . Analogous, the differential solid angle  $d\Omega$  subtended





**Fig. 2.5** An illustration of the differential solid angle,  $d\Omega = \sin\theta d\theta d\phi$ . The solid angle has the units of the steradian (sr) or  $\text{radian}^2$  ( $\text{rad}^2$ )

by an arbitrary differential surface  $dA$  is defined as the differential surface area  $d\Omega$  of a unit sphere covered by the arbitrary surface's projection onto the unit sphere [59, 109, 131]:

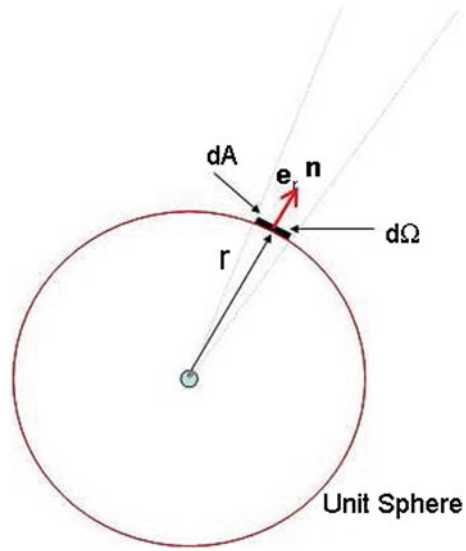
$$d\Omega = \frac{\mathbf{e}_r \cdot d\mathbf{A}}{|\mathbf{r}|^2} = \frac{\mathbf{e}_r \cdot \mathbf{n} dA}{r^2} \quad (2.137)$$

where  $\mathbf{e}_r = \frac{\mathbf{r}}{|\mathbf{r}|}$  denotes a unit vector in the direction of  $\mathbf{r}$ ,  $|\mathbf{r}|$  is the distance from the origin to the arbitrary differential area  $dA$ , and  $\mathbf{n}$  is the unit normal vector of the differential surface area  $dA$  as sketched in Fig. 2.5.

In kinetic theory we are using the solid angle to indicate the direction of the outgoing particles after the collision. In principle, we can calculate the solid angle from any given surface. We chose to use the particular surface that coincides with the unit sphere making the mathematical complexity feasible. In this particular case we observe that  $\mathbf{n} = \mathbf{e}_r$  and  $|\mathbf{r}| = r = 1$ , and from (2.137) we get:  $d\Omega = \sin\theta d\theta d\phi$ . Hence, as illustrated in Fig. 2.6, in spherical coordinates the differential solid angle,  $d\Omega$ , subtended by a surface element on the sphere,  $dA = (r d\theta)(r \sin\theta d\phi)$ , can be expressed as:

$$d\Omega = \frac{\mathbf{e}_r \cdot \mathbf{e}_r dA}{r^2} = \frac{\mathbf{e}_r \cdot \mathbf{e}_r (r d\theta)(r \sin\theta d\phi)}{r^2} = \sin\theta d\theta d\phi \quad (2.138)$$

**Fig. 2.6** A sketch of the solid angle in the special case when the arbitrary surface coincides with the unit sphere. In this particular case  $\mathbf{n} = \mathbf{e}_r$ ,  $|\mathbf{r}| = r = 1$ , hence from (2.137) it follows that  $d\Omega = \sin\theta d\theta d\phi$



#### 2.4.2.4 Scattering Cross Sections and Symmetry Properties

In engineering practice we are often concerned with the scattering of a beam of identical particles incident with uniform velocity on the scattering center rather than with the deflection of a single particle. The different particles in the beam have different impact parameters and are therefore scattered through different angles. Hence, in these applications the complexity of the scattering processes involved cannot be described with the classical methods due to the prohibitive computational costs. Instead, the scattering of the particles in the incident beam are calculated in a statistical manner considering the distribution of the deflected particles to be proportional to the density of the incident beam. The corresponding proportionality factor is the *differential scattering cross section*. Due to the symmetry properties of a binary collision, it is convenient to illustrate the basic ideas considering a one body scattering problem that is concerned with the scattering of particles by a fixed center of force. We first state that as a particle approaches the center of force, its orbit will deviate from the incident straight line trajectory. After passing the center of force, the force acting on the particle will eventually diminish so that the orbit once again approaches a straight line (as sketched in Fig. 2.4). In general the final direction of motion is not the same as the incident direction, and the particle is said to be scattered. To calculate the differential scattering cross section we need to define a particular system of reference for the differential solid angle (see Chapman and Cowling [20], p. 60). For this purpose the unit vectors  $\mathbf{e}_g$  and  $\mathbf{e}_{g'}$  in the directions of  $\mathbf{g}_{21}$  and  $\mathbf{g}'_{21}$  might be defined so that  $\mathbf{g}_{21} = g\mathbf{e}_g$  and  $\mathbf{g}'_{21} = g'\mathbf{e}_{g'}$ , respectively. The element of the surface  $d\Omega_g$  includes the point in a perpendicular plane with unit normal  $\boldsymbol{\Omega} \equiv \mathbf{e}_g$ , whereas the element of the surface  $d\Omega_{g'}$  includes the point in a perpendicular plane with unit normal  $\boldsymbol{\Omega}' \equiv \mathbf{e}_{g'}$ , respectively. The differential scattering cross section

can then be defined in the following manner. Imagine a uniform beam of particles of energy  $E(g)$  and flux (intensity)  $\mathbf{I}$ , which is incident upon a scatterer particle denoting a scattering center of force located at the origin  $O$ . The incident flux (intensity) of this beam of particles denotes the number of molecules in the incident beam crossing a unit area normal to the beam per unit time. The number of particles scattered into the element of solid angle  $d\Omega_{g'}$  about  $\Omega'$  is proportional to the incident flux  $\mathbf{I}$  and the element of solid angle  $d\Omega_{g'}$ . The differential scattering cross section,  $\sigma_A(\Omega'; g')$ , thus represents a statistical proportionality factor, defined by:

$$\mathbf{I}\sigma_A(\Omega'; g')d\Omega_{g'} = \text{the number of molecules scattered into the solid angle element } d\Omega_{g'} \text{ about } \Omega' \text{ per unit time}(s),$$

where  $\sigma_A(\Omega'; g')d\Omega_{g'}$  denotes a surface in a plane perpendicular to the incident flux defined such that the molecules that cross this surface end up with a velocity  $\mathbf{g}'$  within the solid angle  $d\Omega_{g'}$ .

Performing a trigonometrical analysis of the particle interaction problem sketched in Fig. 2.3, it can be shown that the number of deflected molecules considered equals the number of molecules that passed through the differential cylinder collision cross section area,  $bd\phi db$ . A rigorous derivation of this relationship for rigid spheres are provided shortly (2.142)–(2.150). Hence, the number of molecules scattered into the solid angle element  $d\Omega_{g'}$  about  $\Omega'$  per unit time (s) can be expressed in terms of the differential cylinder collision cross section area  $b(\theta)db(\theta)d\phi$ :

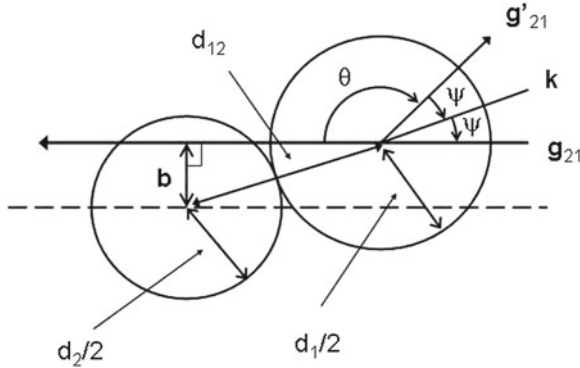
$$\mathbf{I}\sigma_A(\Omega'; g')d\Omega_{g'} = \mathbf{I}\sigma_A(\theta; g)d\Omega = \mathbf{I}b(\theta)db(\theta)d\phi \quad (2.139)$$

The azimuthal angle  $\phi$ , which locates a section of the incident beam, is the same angle that appears in the spherical coordinate frame fixed with origin at the target particle denoting the center of force.

The relationship between  $\sigma_A(\Omega', g')$  and the deflection angle  $\theta$  is established by trigonometry since with central forces there must be complete symmetry around the axis of the incident beam. It is then observed that all the particles with an impact parameter in the range  $(b, b+db)$  are deflected in the range  $(\theta, \theta+d\theta)$ , independently of  $\phi$ , hence  $\sigma_A(\Omega', g') = \sigma_A(\theta, g')$  [117]. Henceforth the differential scattering cross section notation is simplified as  $g' = g$  from (2.123). The detailed form of  $\sigma_A(\theta; g)$  depends on the intermolecular potential.<sup>26</sup> Besides, the impact parameter  $b$  is generally considered a function of the energy and the corresponding scattering angle, thus (2.139) together with the solid angle relation in polar angles (2.138) constitute the classical formula for the differential scattering cross section,

$$\sigma_A(\theta, E(g)) = \frac{b(\theta, E(g))}{\sin \theta} \left| \frac{db(\theta, E(g))}{d\theta} \right| \quad (2.140)$$

<sup>26</sup> The differential cross section is a measurable quantity [57]. If the intermolecular potential is known,  $\sigma_A(\theta, g)$  can also be calculated using techniques from quantum mechanics. In this book we regard  $\sigma_A(\theta, g)$  as a specified property of the gas.



**Fig. 2.7** A sketch defining the geometrical variables in scattering of rigid spheres

where  $E(g) = \frac{1}{2}\mu g^2$ , and  $\theta$  is the scattering angle. The absolute signs are required as  $b$  and  $\theta$  can vary in opposite directions, thus we avoid negative particle numbers.

The *total scattering cross section* is another statistical quantity that can be derived from the differential cross section, defined as the integral of  $\sigma_A(\mathbf{\Omega}'; g)$  over all solid angle elements, hence:

$$\sigma_{AT} = \int_{4\pi} \sigma_A(\mathbf{\Omega}', g') d\mathbf{\Omega}_{g'} = \int_{2\pi} \int_{\pi} \sigma_A(\theta, g) \sin \theta d\theta d\phi \quad (2.141)$$

In other words,  $\sigma_A(\mathbf{\Omega}'; g)$  denotes the proportionality factor for the number of particles scattered into a specific direction, whereas  $\sigma_{AT}$  represents the proportionality factor for the total number of molecules scattered out of the incident beam. For example, in the particular case when the molecules are rigid elastic spheres the apse-line becomes identical with the line of center at collision. In this case the distance  $d_{12}$  between the centers of the spheres at collision is connected with their diameters  $d_1, d_2$  by the relation [109]:

$$d_{12} = \frac{1}{2}(d_1 + d_2), \quad (2.142)$$

Note also that since  $\psi$  is the angle between the  $\mathbf{g}_{21}$  and  $\mathbf{k}$ , as sketched in Fig. 2.7, it is shown that:  $\psi = \frac{1}{2}(\pi - \theta)$ .

Since the plane through  $\mathbf{k}$  and  $\mathbf{g}_{21}$  makes an angle  $\psi$  with a reference plane through  $\mathbf{g}_{21}$ ,  $\psi$  and  $\theta$  are polar coordinates specifying the direction of  $\mathbf{k}$  on the unit sphere. Thereby,

$$b = d_{12} \sin \psi = d_{12} \sin\left[\frac{1}{2}(\pi - \theta)\right] = d_{12} \cos \frac{1}{2}\theta \quad (2.143)$$

The billiard ball model is unique in that  $\theta$  depends only on  $b$ , and not on  $g$ .

From the previous result, the quantity  $b db$  can be determined:

$$b db = d_{12} \sin \psi \times d(d_{12} \sin \psi) = d_{12}^2 \sin \psi \cos \psi d\psi \quad (2.144)$$

In order to relate the differential cross section to the solid angle, some geometry and manipulation of the trigonometric functions are required. By use of standard formulas from trigonometry the following relationships are obtained [120]:

$$\begin{aligned} \cos \theta &= \cos(\pi - 2\psi) = \cos(\pi) \cos(2\psi) - \sin(\pi) \sin(2\psi) \\ &= -1[\cos^2 \psi - \sin^2 \psi] - 0[2 \sin \psi \cos \psi] = \sin^2 \psi - \cos^2 \psi \\ &= 1 - \cos^2 \psi - \cos^2 \psi = 1 - 2 \cos^2 \psi \end{aligned} \quad (2.145)$$

By differentiation of this trigonometric relationship yields:

$$\sin \theta d\theta = 4 \cos \psi \sin \psi d\psi \quad (2.146)$$

Therefore, (2.144) can be manipulated as:

$$b db = d_{12}^2 \sin \psi \cos \psi d\psi = \frac{d_{12}^2}{4} \sin \theta d\theta \quad (2.147)$$

Hence, the differential cylinder collision cross sectional area  $b db d\phi$  can be expressed in terms of the differential element of the solid angle:

$$b db d\phi = d_{12}^2 \sin \psi \cos \psi d\psi d\phi = \frac{d_{12}^2}{4} \sin \theta d\theta d\phi = \frac{d_{12}^2}{4} d\Omega \quad (2.148)$$

in which  $d\Omega = \sin \theta d\theta d\phi$  denotes the differential element of solid angle, which is the small area through which the unit vector  $\mathbf{e}_{g'}$  passes through.

The differential collision cross section is defined as a positive proportionality factor (e.g., [20], p. 60; [117], p. 81), in accordance with (2.140), hence:

$$\sigma_{A12} = \left| \frac{b db}{\sin \theta d\theta} \right| = \frac{b}{\sin \theta} \left| \frac{db}{d\theta} \right| = \frac{d_{12}^2}{4} \quad (2.149)$$

Combining (2.148) and (2.149) an important relationship between the differential cylinder collision cross sectional area  $b db d\phi$  and differential collision cross section  $\sigma_{A12}$  is obtained:

$$b db d\phi = \sigma_{A12} d\Omega_{g'} = \sigma_{A12} d\Omega \quad (2.150)$$

The corresponding total scattering cross section can be computed from (2.141):

$$\sigma_{A_{T12}} = 2\pi \int_{-1}^1 \frac{d_{12}^2}{4} d \cos \theta = \pi d_{12}^2 \quad (2.151)$$

The molecular collisions have specific symmetry properties which are consequences of the electromagnetic nature of the molecular interactions. For this reason, the differential cross section parameter must reflect the same symmetry properties. Two such collisions symmetry properties are particularly relevant in kinetic theory deriving the Boltzmann equation. In describing these symmetries, it proves convenient to speak of a collision in terms of two-particle relative velocities before  $(\mathbf{c}_1, \mathbf{c}_2)$  and after  $(\mathbf{c}'_1, \mathbf{c}'_2)$  the collision. For this purpose it is convenient to introduce the notation:

$$\sigma_A(\mathbf{c}_1, \mathbf{c}_2 | \mathbf{c}'_1, \mathbf{c}'_2) = \sigma_A(\mathbf{\Omega}_{g'}, g') = \sigma_A(\mathbf{\Omega}_g, g) \quad (2.152)$$

where  $\mathbf{\Omega}_{g'}$  denotes the angles between  $\mathbf{g}_{21}$  and  $\mathbf{g}'_{21}$ .

The relevant symmetries are outlined in the following two point paragraphs:

- Invariance Under Time Reversal:

$$\sigma_A(\mathbf{c}_1, \mathbf{c}_2 | \mathbf{c}'_1, \mathbf{c}'_2) = \sigma_A(-\mathbf{c}'_1, -\mathbf{c}'_2 | -\mathbf{c}_1, -\mathbf{c}_2) \quad (2.153)$$

The invariance of physical laws under time reversal<sup>27</sup> makes the cross sections for the original and *reverse* collisions equal [57, 115, 150]. This means that if we reverse the time each molecule will retrace its original trajectory, as sketched in Fig. 2.8.

- Invariance Under Rotation and Reflection:

$$\sigma_A(\mathbf{c}_1, \mathbf{c}_2 | \mathbf{c}'_1, \mathbf{c}'_2) = \sigma_A(\mathbf{c}^*_1, \mathbf{c}^*_2 | \mathbf{c}'^*_1, \mathbf{c}'^*_2) \quad (2.154)$$

where  $\mathbf{c}^*$  denotes the vector obtained from  $\mathbf{c}$  after performing a given rotation in space or a reflection with respect to a given plane, or a combination of both [57, 115, 150].

It is of particular interest to consider an *inverse* collision which is obtained from the original collision by interchanging the initial and final states, as sketched in Fig. 2.9. As a consequence of the symmetries outlined above, the inverse collision has the same differential cross section as the original collision [57]:

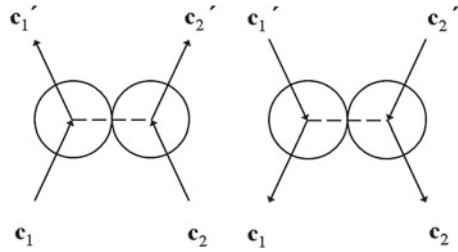
$$\sigma_A(\mathbf{c}_1, \mathbf{c}_2 | \mathbf{c}'_1, \mathbf{c}'_2) = \sigma_A(\mathbf{c}'_1, \mathbf{c}'_2 | \mathbf{c}_1, \mathbf{c}_2) \quad (2.155)$$

Prove for this relationship was given by Huang [57], p. 63, among others.

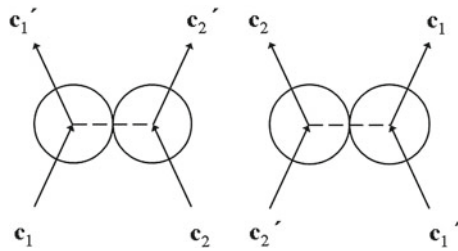
In Hamiltonian mechanics the Liouville's law for elastic collisions states that phase space volumes are conserved as it evolves in time [60, 90]. Since time-evolution is a canonical transformation, it follows that when the Jacobian is unity the differential cross sections of the original, reverse and inverse collisions are all equal. From this result, it can be concluded that [39, 115, 163]:

<sup>27</sup> From the definition of the Lagrangian function (2.6) it can be shown that the time coordinate is both homogeneous and isotropic meaning that its properties are the same in both directions [81]. For, if  $t$  is replaced by  $-t$ , the Lagrangian is unchanged, and therefore so are the equations of motion. In this sense all motions which obey the laws of classical mechanics are reversible.

**Fig. 2.8** A sketch illustrating an original collision (*left*) and an reverse collision (*right*). The scattering cross section are the same for both types of collision



**Fig. 2.9** A sketch illustrating an original collision (*left*) and an inverse collision (*right*). The scattering cross section are the same for both types of collision



$$\sigma_A(\Omega, g) = \sigma_A(\Omega', g') \quad (2.156)$$

#### 2.4.2.5 Expected Number of Molecular Collisions

To determine the rate of change of the distribution function  $f$  due to molecular collisions, an expression for the expected number of molecular collisions must be derived. In the statistical analysis of molecular collisions, it is necessary to consider small but finite ranges of the velocities,  $d\mathbf{c}_1$ ,  $d\mathbf{c}_2$  rather than specific values  $\mathbf{c}_1$ ,  $\mathbf{c}_2$  because the probability is about zero that at a given instant, in a finite volume of gas,  $d\mathbf{r}$ , there is any molecule whose velocity is exactly equal to any specific values  $\mathbf{c}_1$ ,  $\mathbf{c}_2$  out of the whole continuous range of velocities. In a similar manner, it is necessary to consider small but finite ranges of the geometrical collision variables  $db$ ,  $d\phi$  rather than specific values  $b$  and  $\phi$  because the probable number of collisions in  $d\mathbf{r}$ , during a small time-interval  $dt$ , between molecules in the velocity ranges  $d\mathbf{c}_1$ ,  $d\mathbf{c}_2$  will be about zero if the geometrical collision variables  $b$ ,  $\phi$  are exactly assigned at specific values. The average number of collisions of the type considered is thus proportional to the product  $d\mathbf{c}_1 d\mathbf{c}_2 db d\phi d\mathbf{r} dt$ .

The probable number of molecules of the first kind  $\mathbf{c}_1$ , in  $\mathbf{r}$ , having velocities in the small range  $d\mathbf{c}_1$ , is  $f_1 d\mathbf{c}_1 d\mathbf{r}$ , and the probable number of molecules of the second kind  $\mathbf{c}_2$ , in  $\mathbf{r}$ , having velocities within the range  $d\mathbf{c}_2$ , is  $f_2 d\mathbf{c}_2 d\mathbf{r}$ . The incident flux of particles may thus be approximated by:

$$\mathbf{I} = f_2 d\mathbf{c}_2 g \quad (2.157)$$

In order to determine the expected number of molecular collisions, consider the motion of molecules 2 relative to the center of force molecule 1 as sketched in Fig. 2.3. A collision between two molecules in which the impact parameter is in the range  $db$  about  $b$  and the azimuthal angle is in the range  $d\phi$  about  $\phi$  can occur provided that the extension of the vector  $\mathbf{g}_{21}$  cut the plane through  $O$  perpendicular to the polar axis within the area bounded by circles of radii  $db$ ,  $b + db$  and center  $O$ , and by radii from  $O$  including an angle  $d\phi$ . If such a collision is to occur in a time interval  $dt$ , then at the beginning of  $dt$  the center of molecule 2 must be within a cylinder having an area  $bd\phi db$  as base and generators equal to  $-\mathbf{g}_{21}dt$  (i.e., the length of the cylinder generators in the  $\mathbf{e}_g$  direction is given by the scalar product:  $(\mathbf{g}_{21} \cdot \mathbf{e}_g)dt = |\mathbf{g}_{21}||\mathbf{e}_g| \cos(0)dt = gdt$ ). The volume,  $dV_{\text{cylinder}} = (gdt)(bd\phi db)$ , is commonly referred to as *the collision cylinder*, as sketched in Fig. 2.10. It is imagined that such a cylinder is associated with each of the  $f_1 d\mathbf{c}_1 d\mathbf{r}$  molecules of the first kind  $\mathbf{c}_1$ , within a specific velocity range  $d\mathbf{c}_1$ , in  $\mathbf{r}$ . Moreover, if  $db$  and  $d\phi$  are small, it might be assumed that these cylinders do not overlap to any significant extent, so that the total volume  $dV_{\text{total}}$  of all the cylinders can be approximated by:

$$dV_{\text{total}} = \{f_1 d\mathbf{c}_1 d\mathbf{r}\} \times \{(gdt)(bdbd\phi)\} \quad (2.158)$$

In many of these tiny cylinders there might be no molecule of the second kind  $\mathbf{c}_2$ , having a velocity in the range  $d\mathbf{c}_2$ . If  $db$ ,  $d\phi$  and  $d\mathbf{c}_2$  are sufficiently small, the possibility that in any one cylinder there are two such molecules  $\mathbf{c}_2$  might be neglected. The total number of molecules of the second kind  $\mathbf{c}_2$ , with velocities in the range  $d\mathbf{c}_2$  about  $\mathbf{c}_2$ , in the whole combined volume  $dV_{\text{total}}$  of all the collision cylinders is  $(f_2 d\mathbf{c}_2) \times dV_{\text{total}}$ , which by the assumptions made correspond to the number of occupied cylinders in which such a molecule occurs. Moreover, it follows that each occupied cylinder corresponds to a binary collision of the specified type, occurring within  $d\mathbf{r}$  during the time  $dt$ . Inserting the above expression for  $dV_{\text{total}}$  into  $f_2 d\mathbf{c}_2 dV_{\text{total}}$ , the number of binary molecular collisions is found to be:

$$f_1 f_2 g b d b d \phi d\mathbf{c}_1 d\mathbf{c}_2 d\mathbf{r} dt = (f_2 d\mathbf{c}_2)(f_1 d\mathbf{c}_1 d\mathbf{r}) \times \{(gdt)(bdbd\phi)\} \quad (2.159)$$

On substituting  $\sigma_A(\mathbf{\Omega}, g) d\mathbf{\Omega}_g = bd\phi db$ , in accordance with (2.150), an alternative expression for the number of collisions is obtained:

$$f_1 f_2 g \sigma_A(\mathbf{\Omega}, g) d\mathbf{\Omega}_g d\mathbf{c}_1 d\mathbf{c}_2 d\mathbf{r}_1 dt \quad (2.160)$$

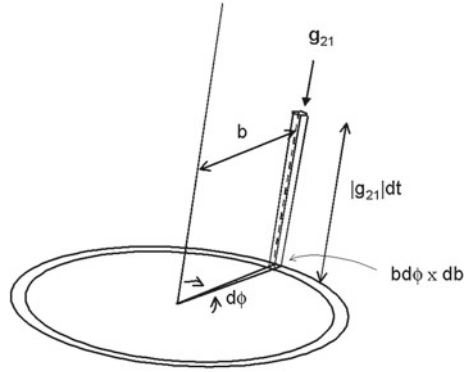
For completeness it is noted that these relations rely on the molecular chaos assumption (see Sect. 2.4.2), anticipating that the collisional pair distribution function can be approximated by [53, 90]:

$$f^{(2)}(\mathbf{r}, \mathbf{c}_1, \mathbf{r}, \mathbf{c}_2, t) \approx f_1(\mathbf{r}, \mathbf{c}_1, t) f_2(\mathbf{r}, \mathbf{c}_2, t) \quad (2.161)$$

There by a more general expression for the expected number of collisions is obtained:



**Fig. 2.10** Collision cylinder. Scattering in the  $\mathbf{c}_1$  molecular frame, where the  $\mathbf{c}_2$  molecules have velocity  $\mathbf{g}_{21}$



$$f^{(2)}(\mathbf{r}, \mathbf{c}_1, \mathbf{r}, \mathbf{c}_2, t) g \sigma_A(\mathbf{\Omega}, g) d\mathbf{\Omega}_{g'} d\mathbf{c}_1 d\mathbf{c}_2 d\mathbf{r} dt \quad (2.162)$$

#### 2.4.2.6 Molecular Collision Density and Frequency

The molecular collision density and frequency, that are two frequently used quantities in models deduced from kinetic theory principles, can be plainly derived from the expected number of molecular collision formula (2.160). Based on the foregoing modeling results determining the expected number of molecular collisions, different estimates of the *molecular collision density and frequency* can be deduced. Adopting the molecular billiard ball model considering molecules that are smooth and symmetric rigid elastic spheres, and requiring that the molecules are not affected by other potential field forces, the molecules interact only during the collision events. Moreover, considering such binary collisions between billiard ball molecules of masses  $m_1$  and  $m_2$  in a gas mixture at rest in a uniform steady state, the number of collisions per unit volume and time can be deduced from (2.160) after dividing by  $d\mathbf{r}$  and  $dt$ . Integrating the resulting relation over all values of  $\mathbf{\Omega}$ ,  $\mathbf{c}_1$  and  $\mathbf{c}_2$ , the *collision density* representing the total number of collisions per unit volume and time between molecules of type  $m_1$  and molecules of type  $m_2$  is obtained:

$$\begin{aligned} Z_{12} &= \int_{\mathbf{c}_2} \int_{\mathbf{c}_1} \int_{4\pi} f_1 f_2 g \sigma_A(\mathbf{\Omega}, g) d\mathbf{\Omega}_{g'} d\mathbf{c}_1 d\mathbf{c}_2 \\ &= \sigma_{A12} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_0^{2\pi} \int_0^{\pi} f_1 f_2 g \sin \theta d\theta d\phi d\mathbf{c}_1 d\mathbf{c}_2 \end{aligned} \quad (2.163)$$

where  $\sigma_{A12}$  is the differential cross section for rigid spheres defined in accordance with (2.150).

Adopting the absolute Maxwellian distribution function (anticipated at this point, it is further discussed in Sect. 2.7.2), substituting  $f_1$  and  $f_2$  by the appropriate forms

of the distribution function (2.243), p. 285:

$$\begin{aligned} f_1 &= n_1(m_1/2\pi kT)^{3/2} \times \exp(-m_1 c_1^2/2kT) \\ f_2 &= n_2(m_2/2\pi kT)^{3/2} \times \exp(-m_2 c_2^2/2kT) \end{aligned}$$

gives [20] (p. 87):

$$Z_{12} = 2n_1 n_2 d_{12}^2 \left( \frac{2\pi kT m_c}{m_1 m_2} \right)^{1/2} = 2n_1 n_2 d_{12}^2 \left( \frac{2\pi kT}{\mu} \right)^{1/2} \quad (2.164)$$

This quantity is named the *bi-molecular collision rate*. The  $\mu$  denotes the reduced mass and  $m_c = m_1 + m_2$  represents the total mass associated with the center of mass of a two particle system.

Note that the number of collisions between pairs of similar molecules  $m_1$  cannot be calculated by simply changing the suffix 2 to 1 in the given collision density relation for unlike molecules (2.164), because in this case one counts each collision between a pair of  $m_1$  molecules twice. The correct number of collisions between pairs of molecules  $m_1$  per unit volume and time is thus only half the value given by the formula for pairs of unlike molecules. Hence, for similar molecules the collision density is given by:

$$Z_{11} = 2n_1^2 d_1^2 \left( \frac{\pi kT}{m_1} \right)^{1/2} = \frac{1}{\sqrt{2}} \pi d_1^2 \langle c_1 \rangle_M n_1^2 \quad (2.165)$$

It is anticipated that the mean value of the speed of a gas which consists of molecules of type  $m_1$  in the Maxwellian state is given by  $\langle c_1 \rangle_M = \left( \frac{8kT}{\pi m_1} \right)^{1/2}$ . The derivation of this relationship is explained at page 370 in association to (2.609) and (2.610).

The *collision frequency* denotes the average number of collisions undergone by each molecule of a certain type per unit time. The frequency of collisions between any one molecule of type  $m_1$  with other  $m_1$  molecules, is:

$$Z_{1-1} = \frac{2Z_{11}}{n_1} = 4n_1 d_1^2 \left( \frac{\pi kT}{m_1} \right)^{1/2} \quad (2.166)$$

since each collision affects two molecules at once. The type of target species considered calculating the frequency is indicated by the last index of  $Z_{1-1}$  that is separated by the hyphen [157].

The frequency of collisions between any one molecule of type  $m_1$  and a  $m_2$  molecule is given by:

$$Z_{1-2} = \frac{Z_{12}}{n_1} = 2n_2 d_{12}^2 \left( \frac{2\pi kT m_c}{m_1 m_2} \right)^{1/2} \quad (2.167)$$

The collision frequency for a molecule of type  $m_1$  colliding with all kinds of molecules in the mixture is:

$$Z_1 = \frac{Z_{11} + \sum_{j=2} Z_{1j}}{n_1} = Z_{1-1} + \sum_{j=2} Z_{1-j} \quad (2.168)$$

### 2.4.2.7 The Collision Term Closure Formulation

In this section an explicit expression for the collision source term  $(\frac{\partial f}{\partial t})_{\text{Collision}}$  in the Boltzmann equation (2.67) is derived. An expression for the rate  $(\frac{\partial f}{\partial t})_{\text{Collision}} d\mathbf{r} d\mathbf{c}_1 dt$  at which the velocity distribution function  $f(\mathbf{r}, \mathbf{c}_1, t)$  is being altered by molecular collisions can be obtained by focus attention on molecules with velocity between  $\mathbf{c}_1$  and  $\mathbf{c}_1 + d\mathbf{c}_1$  located in the volume element  $d\mathbf{r}$  located between  $\mathbf{r}$  and  $\mathbf{r} + d\mathbf{r}$ , and consider the collisions which occurs there in the time between  $t$  and  $t + dt$ . In the same spatial volume there are molecules of any velocity  $\mathbf{c}_2$  that pose as an incident beam of molecules incident on the molecule  $\mathbf{c}_1$ . The volume  $d\mathbf{r}$  is taken to be large compared to the range of intermolecular forces and  $dt$  to be large compared to the duration of a collision. Nevertheless, they can be considered infinitesimally small with respect to variations in  $f$  by virtue of the assumption that the distribution function  $f(\mathbf{r}, \mathbf{c}, t)$  does not vary appreciably during a time interval of the order of the duration of a molecular collision, nor does it vary appreciably over a spatial distance of the order of the range of intermolecular forces. First, the molecules in  $d\mathbf{r}$  can be thrown out of the velocity range  $\mathbf{c}_1$  and  $\mathbf{c}_1 + d\mathbf{c}_1$  by virtue of collisions with other molecules with any velocity  $\mathbf{c}_2$ . The resulting decrease in time  $dt$  of the number of such molecules is denoted by  $(\frac{\partial f}{\partial t})_{\text{Collision}}^- d\mathbf{r} d\mathbf{c}_1 dt$ . Second, molecules in  $d\mathbf{r}$  whose velocity is originally not in the range between  $\mathbf{c}_1$  and  $\mathbf{c}_1 + d\mathbf{c}_1$  can be thrown into this velocity range by virtue of collisions with other molecules with any velocity  $\mathbf{c}_2$ . The resulting increase in time  $dt$  of the number of molecules scattered into the velocity range  $\mathbf{c}_1$  and  $\mathbf{c}_1 + d\mathbf{c}_1$  is denoted by  $(\frac{\partial f}{\partial t})_{\text{Collision}}^+ d\mathbf{r} d\mathbf{c}_1 dt$ .

To derive an approximate closure relation for the rate  $(\frac{\partial f}{\partial t})_{\text{Collision}}^- d\mathbf{r} d\mathbf{c}_1 dt$ , we need to determine the flux of incident molecules of any velocity  $\mathbf{c}_2$  that pose as an incident beam of molecules on the center of force molecule with velocity  $\mathbf{c}_1$  in the same spatial volume  $d\mathbf{r}$  about  $\mathbf{r}$ , as defined (2.139). The incident flux  $\mathbf{I}$  of this incident beam is generally approximated by:

$$\mathbf{I} = f(\mathbf{r}, \mathbf{c}_2, t) d\mathbf{c}_2 g_{21} \quad (2.169)$$

Moreover, the number of binary collisions, in which the velocities of the colliding molecules are  $\mathbf{c}_1$  and  $\mathbf{c}_2$  and the velocities of the molecules after the collision are  $\mathbf{c}'_1$  and  $\mathbf{c}'_2$ , is given by (2.139):

$$\mathbf{I} \sigma_A(\boldsymbol{\Omega}', g') d\boldsymbol{\Omega}_{g'} dt = f(\mathbf{r}, \mathbf{c}_2, t) d\mathbf{c}_2 g_{21} \sigma_A(\boldsymbol{\Omega}', g') d\boldsymbol{\Omega}_{g'} dt \quad (2.170)$$

where  $\sigma_A(\boldsymbol{\Omega}', g')$  is the differential cross section in the center of mass system and  $\boldsymbol{\Omega}'$  denotes the angles between  $\mathbf{g}_{21}$  and  $\mathbf{g}'_{21}$ .

The rate  $(\frac{\partial f}{\partial t})_{\text{Collision}}^- d\mathbf{r}d\mathbf{c}_1 dt$  is obtained by subsequent integration over all  $\mathbf{c}_2$  velocities and multiplication by the spatial density of molecules  $f(\mathbf{r}, \mathbf{c}_1, t)$  in  $d\mathbf{c}_1$ :

$$(\frac{\partial f}{\partial t})_{\text{Collision}}^- d\mathbf{r}d\mathbf{c}_1 dt = f(\mathbf{r}, \mathbf{c}_1, t) \int \int g_{21} f(\mathbf{r}, \mathbf{c}_2, t) \sigma_A(\boldsymbol{\Omega}', g') d\boldsymbol{\Omega}_g d\mathbf{r}d\mathbf{c}_2 d\mathbf{c}_1 dt \quad (2.171)$$

By arguments identical with those used above, an approximate closure relation for the rate  $(\frac{\partial f}{\partial t})_{\text{Collision}}^+ d\mathbf{r}d\mathbf{c}'_1 dt$  can be deduced examining *inverse collisions* where  $\mathbf{c}_1$  is fixed. We may first consider a molecule  $c'_1$  with a beam of molecules  $c'_2$  incident upon it. The incident flux of the beam of molecules  $\mathbf{c}'_2$  incident upon  $\mathbf{c}'_1$  can be approximated by:

$$\mathbf{I}' = f(\mathbf{r}, \mathbf{c}'_2, t) d\mathbf{c}'_2 |g'_{21}| \quad (2.172)$$

From this incident flux of molecules, we only want to consider all molecules in the same volume element  $d\mathbf{r}$  with arbitrary initial velocities  $\mathbf{c}'_1$  and  $\mathbf{c}'_2$  which are such that, after collision, one of the two molecules acquires a velocity in the range of interest between  $\mathbf{c}_1$  and  $\mathbf{c}_1 + d\mathbf{c}_1$ , while the other molecule out of the two acquires some velocity between  $\mathbf{c}_2$  and  $\mathbf{c}_2 + d\mathbf{c}_2$ . This scattering process is described by the scattering probability  $\sigma_A(\boldsymbol{\Omega}, g) = \sigma_A(c'_1, c'_2 | c_1, c_2)$ , which equals  $\sigma_A(\boldsymbol{\Omega}', g') = \sigma_A(c_1, c_2 | c'_1, c'_2)$  according to (2.155). The number of collisions of this type during  $dt$  can be approximated by:

$$\mathbf{I}' \sigma_A(\boldsymbol{\Omega}, g) d\boldsymbol{\Omega}_g dt = f(\mathbf{r}, \mathbf{c}'_2, t) d\mathbf{c}'_2 |g'_{21}| \sigma_A(\boldsymbol{\Omega}, g) d\boldsymbol{\Omega}_g dt \quad (2.173)$$

It follows that the rate  $(\frac{\partial f}{\partial t})_{\text{Collision}}^+ d\mathbf{r}d\mathbf{c}'_1 dt$  is given by:

$$(\frac{\partial f}{\partial t})_{\text{Collision}}^+ d\mathbf{r}d\mathbf{c}'_1 dt = \int \int f(\mathbf{r}, \mathbf{c}'_1, t) f(\mathbf{r}, \mathbf{c}'_2, t) |g'_{21}| \sigma_A(\boldsymbol{\Omega}, g) d\boldsymbol{\Omega}_g d\mathbf{r}d\mathbf{c}'_1 d\mathbf{c}'_2 dt \quad (2.174)$$

It is noted that the vectors  $(\mathbf{c}_1, \mathbf{c}_2)$ ,  $(\mathbf{c}'_1, \mathbf{c}'_2)$  refer to collisions that are inverse of each other, thus since  $\sigma_A(\boldsymbol{\Omega}', g') = \sigma_A(\boldsymbol{\Omega}, g)$ ,  $g_{21} = g'_{21}$ , and the transformation of the differential element  $d\boldsymbol{\Omega}_g d\mathbf{c}_1 d\mathbf{c}_2 = J \boldsymbol{\Omega}_g d\mathbf{c}'_1 d\mathbf{c}'_2$  by the Liouville theorem (e.g., [20], pp. 61–64; [39], Sect. 3.1; [57], p. 66; [90], pp. 17–18; [115], p. 52). The rate expression can be rewritten as:

$$(\frac{\partial f}{\partial t})_{\text{Collision}}^+ d\mathbf{r}d\mathbf{c} dt = \int \int f(\mathbf{r}, \mathbf{c}'_1, t) f(\mathbf{r}, \mathbf{c}'_2, t) g_{21} \sigma(\boldsymbol{\Omega}', g') d\boldsymbol{\Omega}_g d\mathbf{r}d\mathbf{c}_1 d\mathbf{c}_2 dt \quad (2.175)$$

### 2.4.2.8 Deriving the Boltzmann Equation from First Principles

Due to the approximate relation between the pair distribution function and the two associated single distribution functions (2.161) imposing the assumption of molecular chaos and the associated expression for the expected number of collisions in  $d\mathbf{r}$  (2.162), several scientists investigated the feasibility of deriving the Boltzmann equation from first principles with a higher degree of rigor. In the following paragraphs in this section, the Boltzmann equation is thus re-derived based on a more compact and mathematically formal notation. A drawback is that the numerous inherent assumptions are not easy to grasp making this analysis somewhat ad hoc.

In the formal derivation, the number of particles which is thrown out of the phase element is determined by:

$$\left(\frac{\partial f}{\partial t}\right)_{\text{Collision}}^- d\mathbf{r} d\mathbf{c} dt = \int_1 f^{(2)}(\mathbf{r}, \mathbf{c}, \mathbf{r}_1, \mathbf{c}_1, t) d\mathbf{r}_1 d\mathbf{c}_1 d\mathbf{r} d\mathbf{c} dt \quad (2.176)$$

In this model derivation it is convenient and thus common practice to divide the velocity of all particles in the gas into two groups, the small range of velocities that fall into the interval  $d\mathbf{c}$  about  $\mathbf{c}$  and all other velocities denoted by  $\mathbf{c}_1$ . Considering that the  $\mathbf{c}_1$  particles in  $d\mathbf{r}_1$  undergo a collision with the  $\mathbf{c}$  particles in  $d\mathbf{r}$  in the time  $dt$ ,  $d\mathbf{r}_1$  must be determined in terms of designable quantities. Such a model can be derived with the aid of the sketch showing a scattering event in the frame of the  $\mathbf{c}$  particles (equivalent to Fig. 2.10), revealing that all  $\mathbf{c}_1$  particles in the collision cylinder of height  $gdt$  and base area  $bd\phi db$  undergo a collision with the  $\mathbf{c}$  particles in the time  $dt$ . Hence, the volume of the collision cylinder is given by  $d\mathbf{r}_1 = gdt bd\phi db$ .

It follows that the number of particles removed in  $dt$  is determined by:

$$\begin{aligned} \left(\frac{\partial f}{\partial t}\right)_{\text{Collision}}^- d\mathbf{r} d\mathbf{c} dt &= \int_1 f^{(2)}(\mathbf{r}, \mathbf{c}, \mathbf{r}_1, \mathbf{c}_1, t) (gbd\phi db) d\mathbf{c}_1 d\mathbf{r} d\mathbf{c} dt \\ &= \int_1 f^{(2)}(\mathbf{r}, \mathbf{c}, \mathbf{r}_1, \mathbf{c}_1, t) g\sigma_A(\boldsymbol{\Omega}', g') d\boldsymbol{\Omega}_{g'} d\mathbf{c}_1 d\mathbf{r} d\mathbf{c} dt \end{aligned} \quad (2.177)$$

where  $\sigma_A(\boldsymbol{\Omega}', g') d\boldsymbol{\Omega}_{g'} = \sigma_A(\theta, g) d\boldsymbol{\Omega} = bd\phi db$  in accordance with (2.150).

Dividing by  $d\mathbf{r} d\mathbf{c} dt$  yields:

$$\left(\frac{\partial f}{\partial t}\right)_{\text{Collision}}^- = \int_1 f^{(2)}(\mathbf{r}, \mathbf{c}, \mathbf{r}_1, \mathbf{c}_1, t) g\sigma_A(\boldsymbol{\Omega}', g') d\boldsymbol{\Omega}_{g'} d\mathbf{c}_1 \quad (2.178)$$

in which the integration is over the solid angle,  $d\boldsymbol{\Omega}_{g'}$ , and  $\mathbf{c}_1$  to sum up the rate of decrease for all the collisions occurring during  $dt$ .

The number of particles injected into  $d\mathbf{c} d\mathbf{r}$  due to collisions in the interval  $dt$ ,  $\left(\frac{\partial f}{\partial t}\right)_{\text{Collision}}^+ d\mathbf{r} d\mathbf{c} dt$ , considers all the binary collisions that can send one particle into the velocity interval  $d\mathbf{c}$  about  $\mathbf{c}$ . This kind of collision is recognized as being the inverse of the original collision, hence:

$$\begin{aligned}
\left(\frac{\partial f}{\partial t}\right)_{\text{Collision}}^+ d\mathbf{r}d\mathbf{c}dt &= \int_1 f'^{(2)}(\mathbf{r}', \mathbf{c}', \mathbf{r}'_1, \mathbf{c}'_1, t) d\mathbf{r}'_1 d\mathbf{c}'_1 d\mathbf{r}d\mathbf{c}' \\
&= \int_1 f'^{(2)}(\mathbf{r}', \mathbf{c}', \mathbf{r}'_1, \mathbf{c}'_1, t) g' \sigma_A(\mathbf{\Omega}, g) d\mathbf{\Omega}_g d\mathbf{c}'_1 d\mathbf{r}d\mathbf{c}' dt
\end{aligned} \tag{2.179}$$

where the primed variables refer to the inverse collision of the un-primed variables in (2.178). That is, a collision of the type (2.155) is considered in a frame where the origin of the relative vector is fixed denoting a fixed center of force.

To express (2.179) in terms of known variables the Liouville law for elastic collisions can be adopted, as several investigators (e.g., [20], pp. 61–64; [39], Sect. 3.1; [57], p. 66; [90], pp. 17–18; [115], p. 52) have shown that by symmetry (i.e.,  $\mathbf{G} = \mathbf{G}'$  and  $d\mathbf{g}_{21} = d\mathbf{g}'_{21}$ ) the Jacobian is unity, hence:

$$d\mathbf{\Omega}_g d\mathbf{c}'_1 d\mathbf{c}' = d\mathbf{\Omega}_{g'} d\mathbf{c}_1 d\mathbf{c} \tag{2.180}$$

Note also that from the law of conservation of angular momentum (2.131), the impact parameters  $b$  and  $b'$  before and after the collisions, respectively, are equal as  $L = \mu gb = \mu gb'$ . It follows that the number of particles added in  $dt$  is:

$$\left(\frac{\partial f}{\partial t}\right)_{\text{Collision}}^+ d\mathbf{r}d\mathbf{c}dt = \int_1 f'^{(2)}(\mathbf{r}', \mathbf{c}', \mathbf{r}'_1, \mathbf{c}'_1, t) g \sigma_A(\mathbf{\Omega}, g) d\mathbf{\Omega}_{g'} d\mathbf{c}_1 d\mathbf{r}d\mathbf{c}dt \tag{2.181}$$

Dividing by  $d\mathbf{r}d\mathbf{c}dt$  yields:

$$\left(\frac{\partial f}{\partial t}\right)_{\text{Collision}}^+ = \int_1 f'^{(2)}(\mathbf{r}', \mathbf{c}', \mathbf{r}'_1, \mathbf{c}'_1, t) g \sigma_A(\mathbf{\Omega}, g) d\mathbf{\Omega}_{g'} d\mathbf{c}_1 \tag{2.182}$$

and again the integration is over the solid angle,  $d\mathbf{\Omega}_g$ , and  $\mathbf{c}_1$ , but this time to sum up the rate of increase for all the collisions occurring during  $dt$ .

Substituting these results into (2.91), yields the net collision rate:

$$\begin{aligned}
\left(\frac{\partial f}{\partial t}\right)_{\text{Collision}} &= \int_1 f'^{(2)}(\mathbf{r}', \mathbf{c}', \mathbf{r}'_1, \mathbf{c}'_1, t) g \sigma_A(\mathbf{\Omega}') d\mathbf{\Omega}_{g'} d\mathbf{c}_1 \\
&\quad - \int_1 f^{(2)}(\mathbf{r}, \mathbf{c}, \mathbf{r}_1, \mathbf{c}_1, t) g \sigma_A(\mathbf{\Omega}') d\mathbf{\Omega}_{g'} d\mathbf{c}_1
\end{aligned} \tag{2.183}$$

Substituting all these results and the approximation of the pair distribution function (2.161) into (2.67), gives the *Boltzmann* equation:

$$\begin{aligned}
\frac{\partial f}{\partial t} + \mathbf{c} \cdot \frac{\partial f}{\partial \mathbf{r}} + \mathbf{F} \cdot \frac{\partial f}{\partial \mathbf{c}} &= \int_1 [f'(\mathbf{r}, \mathbf{c}', t) f'_1(\mathbf{r}, \mathbf{c}'_1, t) \\
&\quad - f(\mathbf{r}, \mathbf{c}, t) f_1(\mathbf{r}, \mathbf{c}_1, t)] g \sigma_A(\mathbf{\Omega}', g') d\mathbf{\Omega}_{g'} d\mathbf{c}_1
\end{aligned} \tag{2.184}$$

It is noted that this substitution is not strictly rigorous as a number of unspecified approximations are introduced as well [10].

The collision term may be further manipulated in terms of  $\mathbf{k}$  [117] (pp. 83–85), but for convenience the fundamental form is retained at this point. For denser gases and rigid spheres the collision term is normally further reformulated in terms of  $\mathbf{k}$  [117] (pp. 83–85), as outlined in Sect. 2.12.

## 2.5 Flux Vectors

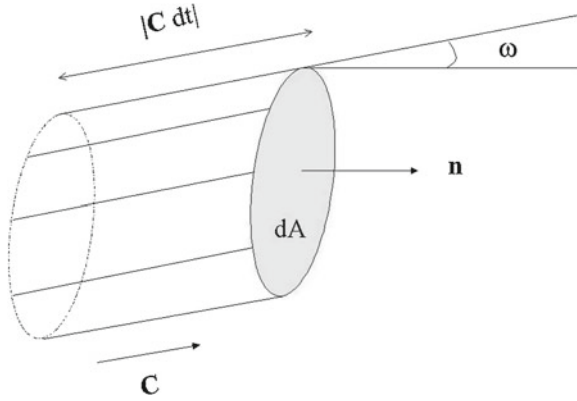
In a non-equilibrium gas system there are gradients in one or more of the macroscopic properties. In a mono-atomic gas the gradients of density, fluid velocity, and temperature induce molecular transport of mass, momentum, and kinetic energy through the gas. The mathematical theory of transport processes enables the quantification of these macroscopic fluxes in terms of the distribution function on the microscopic level. It appears that the mechanism of transport of each of these molecular properties is derived by the same mathematical procedure, hence they are collectively represented by the generalized property  $\psi$ . In the gas we consider an infinitesimal element of surface area  $dA$  as sketched in Fig. 2.11. The orientation of the surface area is defined by a unit vector  $\mathbf{n}$  normal to the surface, and  $\omega$  is the angle between  $\mathbf{C}$  and  $\mathbf{n}$ . Imagine further that the element of surface area moves along with the fluid having the velocity  $\mathbf{v}(\mathbf{r}, t)$ . The collection of molecules will then move back and forth across this element area with their peculiar velocities  $\mathbf{C}$  about the mean velocity  $\mathbf{v}$ , in accordance with (2.65). Ignoring any molecular collisions the number of molecules crossing the surface area  $dA$  during the infinitesimal time interval  $(t, t + dt)$  equals the number of molecules contained within an infinitesimal cylinder volume with cross-sectional area  $dA$  and length  $|\mathbf{C}|dt$  at time  $t$ . The volume of this cylinder,  $\mathbf{n} \cdot \mathbf{C} dt dA$ , contains  $f(\mathbf{r}, \mathbf{c}, t) d\mathbf{c} (\mathbf{n} \cdot \mathbf{C} dt dA)$  molecules.

Assuming that each molecule in an average sense carries with them the physical property  $\psi(\mathbf{r}, \mathbf{c}, t)$ , the amount of  $\psi$  transported by the molecules with velocities in the range  $d\mathbf{C}$  about  $\mathbf{C}$  across the area  $dA$  in the time  $dt$  is given by  $f(\mathbf{r}, \mathbf{c}, t) d\mathbf{c} (\mathbf{n} \cdot \mathbf{C} dt dA) \psi(\mathbf{r}, \mathbf{c}, t)$ . Accordingly, the flux of  $\psi$  denoting the amount which crosses  $dA$  per unit area per unit time is expressed as  $f\mathbf{n} \cdot \mathbf{C}\psi d\mathbf{c}$ .

The total flux of  $\psi$  across the elementary surface area  $dA$  is obtained by adding the contributions from molecules within all velocity ranges<sup>28</sup>:

$$\Phi_n(\mathbf{r}, t) = \int_{-\infty}^{\infty} f\mathbf{n} \cdot \mathbf{C}\psi d\mathbf{c} \quad (2.185)$$

<sup>28</sup> The integration over  $\mathbf{c}$  is equivalent to integrating over  $\mathbf{C}$  since these two velocities differ by a constant (i.e., independent of  $\mathbf{c}$ ) only, and the integration is over the entire velocity space [55] (p. 457).



**Fig. 2.11** A cylinder containing all molecules with peculiar velocity  $\mathbf{C}$  which cross the surface element  $dA$  during the time interval  $dt$

where  $\Phi_n(\mathbf{r}, t)$  denotes the  $\mathbf{n}$ -component of the *flux vector*, thus  $\Phi_n(\mathbf{r}, t) = \mathbf{n} \cdot \Phi(\mathbf{r}, t) = n \langle C_n \psi(\mathbf{r}, t) \rangle_M$ .

The complete flux vector of the property  $\psi$  is give by:

$$\Phi(\mathbf{r}, t) = \int_{-\infty}^{\infty} f \mathbf{C} \psi d\mathbf{c} \quad (2.186)$$

The physical interpretation of this vector is that the  $\mathbf{n}$ -component of the vector equals the flux of  $\psi$  across a surface normal to  $\mathbf{n}$ .

At this point it is appropriate to introduce the particular flux vectors associated with the transport of mass, momentum, and kinetic energy.

### 2.5.1 Transport of Mass

In this case we set  $\psi = m$ :

$$\Phi(\mathbf{r}, t) = m \int_{-\infty}^{\infty} f \mathbf{C} d\mathbf{c} = mn \langle \mathbf{C} \rangle_M = 0 \quad (2.187)$$

### 2.5.2 Transport of Momentum

In this case we set  $\psi = mC_i$ , hence:



$$\Phi(\mathbf{r}, t) = m \int_{-\infty}^{\infty} f C_i \mathbf{C} d\mathbf{c} = mn \langle C_i \mathbf{C} \rangle_M = \mathbf{p}_i \quad (2.188)$$

This flux vector denotes the transport of momentum relative to  $\mathbf{v}$  in the  $i$ -direction. In a 3D system the direction index  $i$  takes three different values, so there are a total of three flux vectors associated with momentum transfer.

Together the three flux vectors constitute a symmetric second-order tensor with nine components. This tensor is usually referred to as the pressure tensor,  $\mathbf{p}$ . The pressure tensor is expressed by:

$$\mathbf{p} \equiv m \int_{-\infty}^{\infty} f \mathbf{C} \mathbf{C} d\mathbf{c} \equiv \rho \langle \mathbf{C} \mathbf{C} \rangle_M = \rho \begin{pmatrix} \langle C_x^2 \rangle_M & \langle C_x C_y \rangle_M & \langle C_x C_z \rangle_M \\ \langle C_y C_x \rangle_M & \langle C_y^2 \rangle_M & \langle C_y C_z \rangle_M \\ \langle C_z C_x \rangle_M & \langle C_z C_y \rangle_M & \langle C_z^2 \rangle_M \end{pmatrix} \quad (2.189)$$

The diagonal elements  $\langle C_i^2 \rangle_M$  represent the *normal stresses*, in general denoting the sum of the static and the viscous forces per unit area acting on a surface at an instant in time. The non-diagonal elements, denoted by  $\langle C_i C_j \rangle_M$  for  $i \neq j$ , represent the *shear stresses* or the viscous shear forces per unit area.

We define the deviatoric—or viscous stresses as the negative thermal flux, determined by the difference between the thermodynamic pressure and the pressure tensor elements, as follows:

$$\sigma_{ij} \equiv [p \delta_{ij} - \rho \langle C_i C_j \rangle_M] \quad (2.190)$$

where the  $\delta_{ij}$  is the Kronecker delta.

The *mean pressure* (or *pressure*) is defined as the mean value of the normal stresses across any three orthogonal planes. The mean pressure,  $\bar{p}$ , is thus one third of the trace of the pressure tensor:

$$\bar{p} = \frac{1}{3} \rho \langle C^2 \rangle_M = \frac{1}{3} \mathbf{p} : \mathbf{e} \quad (2.191)$$

where the  $\mathbf{e}$  is the unit tensor.

The trace of the pressure tensor can be expressed in terms of the peculiar velocity:

$$\mathbf{p} : \mathbf{e} = p_{xx} + p_{yy} + p_{zz} = nm (\langle C_x^2 \rangle_M + \langle C_y^2 \rangle_M + \langle C_z^2 \rangle_M) = \rho \langle C^2 \rangle_M \quad (2.192)$$

In particular, when the system is at equilibrium (no macroscopic gradients), the viscous stresses vanish (i.e.,  $\sigma_{ij} = 0$ ) and the pressure tensor can be expressed in terms of the mean pressure or alternatively in terms of the *thermodynamic pressure*,  $p$ , as:

$$\mathbf{p} = \bar{p} \mathbf{e} = p \mathbf{e} \quad (2.193)$$

where  $P_{xx} = P_{yy} = P_{zz} = p$ . Since these conditions are satisfied in the static case only, such a pressure system is called *static*.

In general the net macroscopic pressure tensor is determined by two different molecular effects: One pressure tensor component associated with the pressure and a second one associated with the viscous stresses.<sup>29</sup> For a fluid at rest, the system is in an equilibrium static state containing no velocity or pressure gradients so the average pressure equals the static pressure everywhere in the system. The static pressure is thus always acting normal to any control volume surface area in the fluid independent of its orientation. For a compressible fluid at rest, the static pressure may be identified with the pressure of classical thermodynamics as may be derived from the diagonal elements of the pressure tensor expression (2.189) when the equilibrium distribution function is known. On the assumption that there is local thermodynamic equilibrium even when the fluid is in motion this concept of stress is retained at the macroscopic level. For an incompressible fluid the thermodynamic, or more correctly thermostatic, pressure cannot be defined except as the limit of pressure in a sequence of compressible fluids. In this case the pressure has to be taken as an independent dynamical variable [2] (Sects. 5.13–5.24).

The macroscopic relationship between the *pressure tensor*, which includes both the *hydrostatic*- or *thermodynamic pressure* and the *viscous stresses* is expressed as:

$$\mathbf{p} = p\mathbf{e} + \boldsymbol{\sigma} \quad (2.194)$$

or in matrix notation:

$$\mathbf{p} = \begin{pmatrix} p + \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & p + \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & p + \sigma_{zz} \end{pmatrix} \quad (2.195)$$

In practice the local pressure variable is assumed to be independent on the state of the fluid. If the gradients in the flow field of a mono-atomic gas are sufficiently large, viscous stresses and heat conduction phenomena emerge, and the Maxwellian distribution function is no longer adequate. Therefore, when the fluid is in real motion, additional viscous normal stresses appear as denoted by  $\sigma_{ii}$ .

Adopting the Newton's viscosity law (1.77) derived from continuum mechanical principles [160] (Sect. 2-4.2), the thermodynamic pressure deviates slightly from the mean pressure. It follows that the mean pressure is approximated as:

$$\bar{p} = \frac{1}{3}(P_{xx} + P_{yy} + P_{zz}) = p - (\mu_B + \frac{2}{3}\mu)\nabla \cdot \mathbf{v} \quad (2.196)$$

---

<sup>29</sup> The viscous stresses only come into play for systems containing significant velocity gradients within the fluid. Nevertheless, very large gradients are not required as the Navier-Stokes equations can be derived from the Chapman-Enskog perturbation theory. On the other hand, for the non-equilibrium boundary layer and shock wave systems, i.e., systems which deviates considerably from equilibrium, higher order expansions are apparently needed [39]. Actually, at least for shock waves the validity of the Maxwell-Boltzmann equation becomes questionable.

This law is showing that the mean pressure in a deforming viscous fluid is not exactly equal to the thermodynamic property called pressure (i.e., apparently the constitutive relation is not consistent with the local equilibrium assumption). This distinction is rarely important, as  $\nabla \cdot \mathbf{v}$  is normally very small in typical reactor flow problems, nevertheless adopting the rigorous form of the constitutive relation (1.77) the bulk viscosity  $\mu_B$  appears as an undetermined system parameter. Stokes [144] solved this problem by introducing the novel assumption that  $\mu_B + \frac{2}{3}\mu = 0$ . Adopting this hypothesis we simply avoid the problem. Alternatively, when the incompressible flow limit  $\nabla \cdot \mathbf{v} = 0$  is applicable,  $\bar{p}$  equals  $p$ . Even for high speed compressible flows, i.e., for which  $\nabla \cdot \mathbf{v} \neq 0$ , we avoid the problem since the viscous normal stresses are normally negligible for such flows. Still a third assumption is often put forth, i.e., that the kinetic theory of gases proves that  $\mu_B + \frac{2}{3}\mu = 0$  for a mono-atomic gas<sup>30</sup> (e.g., Hirschfelder et al. [55], p. 521; Vincenti and Kruger [157], p. 391; Ferziger and Kaper [39]). However, White [160] (p. 70) states that this is a specious argument since the kinetic theory actually assumes rather than proves this relationship to be valid. The discussion reported by Truesdell [153] also states that the theory is vague on this issue, as the different perturbation methods proposed in kinetic theory for solving the Maxwell-Boltzmann equation do not give consistent results even for mono-atomic gases. For polyatomic gases no formal theory exist determining this parameter value. It appears, apparently, that there exists no exact interpretation of Newton's viscosity law.

### 2.5.3 Transport of Kinetic Energy

In this case we set  $\psi = \frac{1}{2}m\mathbf{C} \cdot \mathbf{C}$  and get:

$$\Phi(\mathbf{r}, t) = \int_{-\infty}^{\infty} f \frac{1}{2}mC^2 C d\mathbf{c} = \frac{1}{2}mn\langle C^2 \mathbf{C} \rangle_M = \mathbf{q}(\mathbf{r}, t) \quad (2.197)$$

By use of (2.65), the kinetic energy of the collection of particles may be expressed as:

$$\frac{1}{2}m\mathbf{c} \cdot \mathbf{c} = \frac{1}{2}m(\mathbf{C} + \mathbf{v}) \cdot (\mathbf{C} + \mathbf{v}) = \frac{1}{2}m(C^2 + 2\mathbf{v} \cdot \mathbf{C} + v^2) \quad (2.198)$$

The average of the second term on the RHS,  $\langle m\mathbf{v} \cdot \mathbf{C} \rangle_M$ , vanishes, whereas the average of the last term on the RHS,  $\langle \frac{1}{2}mv^2 \rangle_M$ , denotes the kinetic energy of the macroscopic

<sup>30</sup> For example, the proof given by Vincenti and Kruger [157] (p. 391) is based on a comparison between the result obtained solving the Maxwell-Boltzmann equation using the Enskog expansion method and the corresponding expressions for the stress tensor derived in continuum gas dynamics. From this inter-comparison it is seen that for mono-atomic gases the kinetic theory result does not contain any terms corresponding to the bulk viscosity, thus it is concluded that this parameter equals zero.

fluid motion. The average of the first term on the RHS,  $\langle \frac{1}{2}mC^2 \rangle_M$ , is thus interpreted as the internal energy of the gas. It follows that the *internal energy per unit mass* of the gas,  $e(\mathbf{r}, t)$ , is defined as:

$$e(\mathbf{r}, t) = \frac{1}{n(\mathbf{r}, t)} \int_{-\infty}^{\infty} \frac{1}{2}C^2 f(\mathbf{r}, \mathbf{c}, t) d\mathbf{c} = \frac{1}{\rho(\mathbf{r}, t)} \int_{-\infty}^{\infty} \frac{1}{2}mC^2 f(\mathbf{r}, \mathbf{c}, t) d\mathbf{c} \quad (2.199)$$

The translational kinetic gas *temperature*,  $T$ , is defined in terms of  $e$  by the relation:

$$\rho e = \frac{1}{2}nm\langle C^2 \rangle_M = \frac{3}{2}nkT \quad (2.200)$$

It is noted that for point particles equipartition of energy gives the relation:  $\frac{1}{2}m\langle C^2 \rangle_M = \frac{3}{2}kT$ .  $k$  is the universal Boltzmann constant,  $k = 1.380 \times 10^{-23}$  (J/K).

In classical statistical mechanics the principle of equipartition of energy states that the internal energy of a system composed of a large number of particles at thermal equilibrium will distribute itself evenly among each of the quadratic degrees of freedom allowed to the particle system [49, 150]. In particular, for any part of the internal molecular energy that can be expressed as the sum of square terms, each term contributes an average energy of  $\frac{1}{2}kT$  per molecule [100, 157]. The phrase *square term* refers to a term that is quadratic in some appropriate variable used to describe energy. It follows that for a dilute mono-atomic gas, the mean energy associated with the translational motion of the  $c$ -th molecule in each of the three space directions is  $\frac{1}{2}m\langle C_i^2 \rangle_M$ , for  $i = 1, 2, 3$ . The mean energy of the gas is obtained by adding the contributions from all the three directions:  $\frac{1}{2}m\langle C^2 \rangle_M = \langle \frac{1}{2}m(C_1^2 + C_2^2 + C_3^2) \rangle_M = \frac{3}{2}kT$ .

The equipartition principle was initially proposed by Maxwell [96] in 1867 who stated that the energy of a gas is equally divided between linear and rotational energy. The original theorem was later generalized by Boltzmann [10] in 1872 by showing that the internal energy is actually equally divided among all the independent components of motion in the system.

## 2.6 The Equation of Change in Terms of Mean Molecular Properties

The emphasis in this section is to derive an equation of change for the average property  $\langle \psi \rangle_M$ . The mean value of the property function  $\psi(\mathbf{r}, \mathbf{c}, t)$  was defined by (2.61) in Sect. 2.3.2 at p. 207, considering any property function  $\psi$  of a type of molecules that has position  $\mathbf{r}$  and velocity  $\mathbf{c}$  at time  $t$ .

The equation of change can be derived in two ways, either by analyzing the situation directly on the macroscopic moment scales, or by starting out from the

continuum microscopic Boltzmann equation (2.184) and thereafter apply a suitable averaging procedure to obtain the corresponding average—or moment equation. In this section, an analysis based on the Boltzmann equation will be given. It is noted that the translational terms on the LHS of the Boltzmann equation can be derived adopting one out of two slightly different frameworks, i.e., considering either a fixed control volume (i.e., in which  $\mathbf{r}$  and  $\mathbf{c}$  are fixed and independent of time  $t$ ) or a control volume that is allowed to move following a trajectory in phase space (i.e., in which  $\mathbf{r}(t)$  and  $\mathbf{c}(t)$  are dependent of time  $t$ ) both, of course, in accordance with the Liouville theorem. The pertinent moment equations can be derived based on either of these two frameworks. The fixed control volume approach is adopted in this book because this procedure is normally simplest mathematically and most commonly used. The alternative derivation based on the moving control volume framework is described by de Groot and Mazur [32] (pp. 167–170) among others. By virtue of the fixed control volume framework, introductory a generalized moment equation for the moment  $\langle \psi \rangle_M$  is derived. The average quantity  $\langle \psi \rangle_M$  is defined by (2.61), p. 209. To find the equation that  $\langle \psi \rangle_M$  satisfies, both sides of the Boltzmann equation (2.184) is multiplied by the property  $\psi$  and integrated over all velocities  $\mathbf{c}$ . The result is:

$$\int_{-\infty}^{\infty} \frac{\mathcal{D}f}{\mathcal{D}t} \psi d\mathbf{c} = \int_{-\infty}^{\infty} \left( \frac{\partial f}{\partial t} \right)_{\text{Collision}} \psi d\mathbf{c} \quad (2.201)$$

where

$$\int_{-\infty}^{\infty} \frac{\mathcal{D}f}{\mathcal{D}t} \psi d\mathbf{c} \equiv \underbrace{\int_{-\infty}^{\infty} \frac{\partial f}{\partial t} \psi d\mathbf{c}}_1 + \underbrace{\int_{-\infty}^{\infty} \mathbf{c} \cdot \frac{\partial f}{\partial \mathbf{r}} \psi d\mathbf{c}}_2 + \underbrace{\int_{-\infty}^{\infty} \mathbf{F} \cdot \frac{\partial f}{\partial \mathbf{c}} \psi d\mathbf{c}}_3 \quad (2.202)$$

Thereafter, all the integrals in (2.202) must be transformed into quantities which are direct averages of the density function  $f$ , i.e., into integrals which involve  $f$  itself rather than its derivatives.

Term 1 is manipulated as:

$$\int_{-\infty}^{\infty} \frac{\partial f}{\partial t} \psi d\mathbf{c} = \int_{-\infty}^{\infty} \left[ \frac{\partial}{\partial t} (f\psi) - f \frac{\partial \psi}{\partial t} \right] d\mathbf{c} = \frac{\partial}{\partial t} \int_{-\infty}^{\infty} f \psi d\mathbf{c} - \int_{-\infty}^{\infty} f \frac{\partial \psi}{\partial t} d\mathbf{c} \quad (2.203)$$

In this manipulation we have utilized that the order of differentiation with respect to  $t$  and integration over  $\mathbf{c}$  can be interchanged when the integration limits of  $\mathbf{c}$  is not a function of  $t$  (i.e., applied to the first term of the RHS as the local time differentiation acts on the whole argument of the integral). Term 1 in (2.202) thus yields:

$$\int_{-\infty}^{\infty} \frac{\partial f}{\partial t} \psi d\mathbf{c} = \frac{\partial}{\partial t} (n \langle \psi \rangle_M) - n \langle \frac{\partial \psi}{\partial t} \rangle_M \quad (2.204)$$

The integral term 2 in (2.202) can be manipulated in a similar manner, keeping in mind that  $\mathbf{r}$  and  $\mathbf{c}$  are *independent* dynamic variables:

$$\begin{aligned} \int_{-\infty}^{\infty} \mathbf{c} \cdot \frac{\partial f}{\partial \mathbf{r}} \psi d\mathbf{c} &= \int_{-\infty}^{\infty} \left[ \frac{\partial}{\partial \mathbf{r}} \cdot (f \mathbf{c} \psi) - f \mathbf{c} \cdot \frac{\partial \psi}{\partial \mathbf{r}} \right] d\mathbf{c} \\ &= \frac{\partial}{\partial \mathbf{r}} \cdot \int_{-\infty}^{\infty} f \mathbf{c} \psi d\mathbf{c} - \int_{-\infty}^{\infty} f \mathbf{c} \cdot \frac{\partial \psi}{\partial \mathbf{r}} d\mathbf{c} \\ &= \frac{\partial}{\partial \mathbf{r}} \cdot (n \langle \mathbf{c} \psi \rangle_M) - n \langle \mathbf{c} \cdot \frac{\partial \psi}{\partial \mathbf{r}} \rangle_M \end{aligned} \quad (2.205)$$

Finally, since it is imposed that the force,  $\mathbf{F}$ , is independent of the velocity  $\mathbf{c}$ , the integral term 3 in (2.202) can be manipulated as:

$$\begin{aligned} \int_{-\infty}^{\infty} \mathbf{F} \cdot \frac{\partial f}{\partial \mathbf{c}} \psi d\mathbf{c} &= \int_{-\infty}^{\infty} \left[ \frac{\partial}{\partial \mathbf{c}} \cdot (\mathbf{F} f \psi) - \mathbf{F} \cdot f \frac{\partial \psi}{\partial \mathbf{c}} \right] d\mathbf{c} \\ &= [\mathbf{F} f \psi]_{\mathbf{c}} - \mathbf{F} \cdot \int_{-\infty}^{\infty} f \frac{\partial \psi}{\partial \mathbf{c}} d\mathbf{c} \end{aligned} \quad (2.206)$$

The first term on the RHS of (2.206) vanishes, because for each direction (e.g., in Cartesian coordinates,  $i = 1, 2, 3$ ),  $f \rightarrow 0$  as  $|c_i| \rightarrow \infty$ , thus  $[F_i f \psi]_{c_i=-\infty}^{c_i=+\infty} \rightarrow 0$ . Hence, term 3 in (2.206) becomes:

$$\int_{-\infty}^{\infty} \mathbf{F} \cdot \frac{\partial f}{\partial \mathbf{c}} \psi d\mathbf{c} = -\mathbf{F} \cdot n \langle \frac{\partial \psi}{\partial \mathbf{c}} \rangle_M \quad (2.207)$$

Introducing the expressions from (2.204) through (2.206) into (2.202), the following result is achieved:

$$\begin{aligned} \int_{-\infty}^{\infty} \frac{\mathcal{D}f}{\mathcal{D}t} \psi d\mathbf{c} &= \frac{\partial}{\partial t} (n \langle \psi \rangle_M) + \frac{\partial}{\partial \mathbf{r}} \cdot (n \langle \mathbf{c} \psi \rangle_M) - \\ &\quad n \left[ \langle \frac{\partial \psi}{\partial t} \rangle_M + \langle \mathbf{c} \cdot \frac{\partial \psi}{\partial \mathbf{r}} \rangle_M + \mathbf{F} \cdot \langle \frac{\partial \psi}{\partial \mathbf{c}} \rangle_M \right] \\ &= \frac{\partial}{\partial t} (n \langle \psi \rangle_M) + \frac{\partial}{\partial \mathbf{r}} \cdot (n \langle \mathbf{c} \psi \rangle_M) - n \langle \frac{\mathcal{D}\psi}{\mathcal{D}t} \rangle_M \end{aligned} \quad (2.208)$$

in which, for convenience, a novel operator is defined:

$$\frac{\mathcal{D}\psi}{\mathcal{D}t} = \frac{\partial\psi}{\partial t} + \mathbf{c} \cdot \frac{\partial\psi}{\partial \mathbf{r}} + \mathbf{F} \cdot \frac{\partial\psi}{\partial \mathbf{c}} \quad (2.209)$$

At this point, the collision term given in (2.201) is examined. From (2.184) it is seen that the collision term takes the form:

$$\begin{aligned} \mathcal{J}(\psi(\mathbf{c})) = & \int \int \int \psi[f'(\mathbf{r}, \mathbf{c}', t) f'_1(\mathbf{r}, \mathbf{c}'_1, t) \\ & - f(\mathbf{r}, \mathbf{c}, t) f_1(\mathbf{r}, \mathbf{c}_1, t)] g \sigma_A(\boldsymbol{\Omega}, g) d\boldsymbol{\Omega}_g d\mathbf{c}_1 d\mathbf{c} \end{aligned} \quad (2.210)$$

Unfortunately, this relation is not particularly useful for a general  $\psi$  because of the very complex integrals. However, since mass ( $m$ ), momentum ( $m\mathbf{c}$ ), or kinetic energy ( $mc^2$ ) are conserved during a collision, it can be shown that:

$$\begin{aligned} \mathcal{J}(\psi(\mathbf{c})) = & \int \int \int \psi[f'(\mathbf{r}, \mathbf{c}', t) f'_1(\mathbf{r}, \mathbf{c}'_1, t) \\ & - f(\mathbf{r}, \mathbf{c}, t) f_1(\mathbf{r}, \mathbf{c}_1, t)] g \sigma_A(\boldsymbol{\Omega}') d\boldsymbol{\Omega}' d\mathbf{c}_1 d\mathbf{c} = 0 \end{aligned} \quad (2.211)$$

By use of the relation (2.211), the formulation of the general equation of change is considerably simplified. Fortunately, the fundamental gas dynamic conservation equations of continuity, momentum, and energy are thus derived from the Boltzmann equation without actually determining the form of either the collision term or the distribution function  $f$ .

It is convenient to introduce the notion of *collisional invariants* (or *summational invariants*) (e.g., [55], p. 460; [90], p. 150). The validity of (2.211) is commonly justified by the following arguments: Due to the symmetry properties of the collision term expression, interchanging variables gives the following equalities:

$$\begin{aligned} \mathcal{J}(\psi(\mathbf{c})) &= \mathcal{J}(\psi_1(\mathbf{c}_1)), \text{ for } (\mathbf{c}, \mathbf{c}_1) \rightarrow (\mathbf{c}_1, \mathbf{c}), \\ \mathcal{J}(\psi'(\mathbf{c}')) &= -\mathcal{J}(\psi(\mathbf{c})), \text{ for } (\mathbf{c}, \mathbf{c}_1) \rightarrow (\mathbf{c}', \mathbf{c}'_1), \text{ and} \\ \mathcal{J}(\psi'(\mathbf{c}')) &= \mathcal{J}(\psi'_1(\mathbf{c}'_1)), \text{ for } (\mathbf{c}'_1, \mathbf{c}') \rightarrow (\mathbf{c}', \mathbf{c}'_1) \end{aligned}$$

These symmetry properties can be combined to give the following relationship:

$$4\mathcal{J}(\psi(\mathbf{c})) = \mathcal{J}(\psi(\mathbf{c})) + \mathcal{J}(\psi_1(\mathbf{c}_1)) - \mathcal{J}(\psi'(\mathbf{c}')) - \mathcal{J}(\psi'_1(\mathbf{c}'_1))$$

The linearity of the  $\mathcal{J}$  operator allows the latter result to be manipulated as:

$$\mathcal{J}(\psi(\mathbf{c})) = \frac{1}{4} \mathcal{J} [\psi(\mathbf{c}) + \psi_1(\mathbf{c}_1) - \psi'(\mathbf{c}') - \psi'_1(\mathbf{c}'_1)]$$

In conclusion, a function  $\psi(\mathbf{c})$  is a summation invariant if:

$$\Delta\psi(\mathbf{c}) = \psi'(\mathbf{c}') + \psi'_1(\mathbf{c}'_1) - \psi(\mathbf{c}) - \psi_1(\mathbf{c}_1) = 0 \quad (2.212)$$

That is,  $\psi(\mathbf{c})$  is a property of a molecule that is preserved in a collision. Hence, for the conserved quantities mass, momentum and energy yield:

$$\mathcal{J}(m) = \mathcal{J}(m\mathbf{c}) = \mathcal{J}(mc^2) = 0 \quad (2.213)$$

Thus, a general collision invariant relationship can be expressed as:

$$\mathcal{J}(\Delta\psi = 0) = 0 \quad (2.214)$$

By substitution of the relations (2.208) and (2.210) into (2.201), the *Enskog's equation of change* is obtained:

$$\frac{\partial}{\partial t}(n\langle\psi\rangle_M) = n\langle\frac{\mathcal{D}\psi}{Dt}\rangle_M - \nabla_{\mathbf{r}} \cdot (n\langle\mathbf{c}\psi\rangle_M) + \mathcal{J}(\psi) \quad (2.215)$$

where  $\mathcal{J}(\psi)$  denotes the rate of change of  $\psi$  per unit volume due to collisions.

### 2.6.1 The Governing Equations of Gas Dynamics

In this section the conservation equations of gas dynamics are derived from the Boltzmann equation.

The equation of change, (2.215), becomes particularly simple if  $\psi$  refers to a quantity which is conserved in collisions between molecules in accordance with (2.214). Therefore, for conservative quantities (2.215) reduces to:

$$\frac{\partial}{\partial t}(n\langle\psi\rangle_M) + \nabla_{\mathbf{r}} \cdot (n\langle\mathbf{c}\psi\rangle_M) = n\langle\frac{\mathcal{D}\psi}{Dt}\rangle_M \quad (2.216)$$

By letting  $\psi$  in (2.216) be  $m$ ,  $m\mathbf{c}$ , and  $\frac{1}{2}mc^2$ , respectively, the three fundamental conservation equations that are all satisfied by the gas are established.

#### 2.6.1.1 Conservation of Mass

Let  $\psi = m$ , thus the Enskog equation of change (2.216) reduces to:

$$\frac{\partial}{\partial t}(nm) + \nabla_{\mathbf{r}} \cdot (nm\langle\mathbf{c}\rangle_M) = 0 \quad (2.217)$$

By averaging the molecular velocity  $\mathbf{c}$  yields  $\mathbf{v} = \langle\mathbf{c}\rangle_M$  which is the mean velocity of the gas (2.64) as defined in Sect. 2.3.2. Furthermore, the mass density of the gas,



given by (2.58), is defined by  $\rho(\mathbf{r}, t) = mn(\mathbf{r}, t)$ . Equation (2.217) thus becomes:

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial \mathbf{r}} \cdot (\rho \mathbf{v}) = 0 \quad (2.218)$$

This is the *equation of continuity* of gas dynamics.

### 2.6.1.2 Conservation of Momentum

Let  $\psi = m\mathbf{c}$ , thus the Enskog equation of change (2.216) reduces to:

$$\frac{\partial}{\partial t}(nm\langle \mathbf{c} \rangle_M) + \nabla_{\mathbf{r}} \cdot (nm\langle \mathbf{c}\mathbf{c} \rangle_M) = nm\langle \frac{D\mathbf{c}}{Dt} \rangle_M \quad (2.219)$$

The last term in (2.219) is defined by (2.209), and can be reduced to:

$$\frac{D\mathbf{c}}{Dt} = \mathbf{F} \cdot \frac{\partial \mathbf{c}}{\partial \mathbf{c}} = \mathbf{F} \quad (2.220)$$

because  $\mathbf{c}$  is independent of  $\mathbf{r}$  and  $t$ , and  $\frac{\partial \mathbf{c}}{\partial \mathbf{c}}$  denotes a unit tensor.

By inserting (2.220), the mean velocity (2.64), and the mass density (2.58), the momentum equation (2.219) yields:

$$\frac{\partial}{\partial t}(\rho \mathbf{v}) + \nabla_{\mathbf{r}} \cdot (\rho \langle \mathbf{c}\mathbf{c} \rangle_M) = \rho \mathbf{F} \quad (2.221)$$

The second term on the LHS of (2.221) constitutes the sum of the pressure tensor (2.189) and the convective term. By use of (2.65), the molecular velocity can be eliminated as  $\mathbf{c} = \mathbf{v} + \mathbf{C}$ , and after some manipulation the dyad  $\langle \mathbf{c}\mathbf{c} \rangle_M$  can be expressed as:

$$\begin{aligned} \langle \mathbf{c}\mathbf{c} \rangle_M &= \langle (\mathbf{v} + \mathbf{C})(\mathbf{v} + \mathbf{C}) \rangle_M = \langle \mathbf{v}\mathbf{v} + \mathbf{C}\mathbf{C} + \mathbf{v}\mathbf{C} + \mathbf{v}\mathbf{C} \rangle_M \\ &= \mathbf{v}\mathbf{v} + \langle \mathbf{C}\mathbf{C} \rangle_M \end{aligned} \quad (2.222)$$

because the average of the peculiar velocity is zero, i.e.,  $\langle \mathbf{v}\mathbf{C} \rangle_M = \mathbf{v}\langle \mathbf{C} \rangle_M = 0$ .

By use of the dyad relation (2.222) and the pressure tensor definition (2.189), the momentum equation (2.221) can be written as:

$$\frac{\partial}{\partial t}(\rho \mathbf{v}) + \nabla_{\mathbf{r}} \cdot (\rho \mathbf{v}\mathbf{v}) = -\nabla_{\mathbf{r}} \cdot \mathbf{p} + \rho \mathbf{F} \quad (2.223)$$

This equation corresponds to the *Cauchy equation of motion in gas dynamics*.

### 2.6.1.3 Conservation of Energy

Let  $\psi = \frac{1}{2}mc^2$ , thus the Enskog equation of change (2.216) reduces to:

$$\frac{\partial}{\partial t} \left( \frac{1}{2} nm \langle c^2 \rangle_M \right) + \frac{1}{2} \frac{\partial}{\partial \mathbf{r}} \cdot (nm \langle \mathbf{c} c^2 \rangle_M) = \frac{1}{2} nm \left\langle \frac{\mathcal{D}c^2}{\mathcal{D}t} \right\rangle_M \quad (2.224)$$

The last term in (2.224) is defined by (2.209), and can be reduced to:

$$\frac{\mathcal{D}(\mathbf{c} \cdot \mathbf{c})}{\mathcal{D}t} = 2\mathbf{F} \cdot \left( \frac{\partial \mathbf{c}}{\partial \mathbf{c}} \cdot \mathbf{c} \right) = 2\mathbf{F} \cdot \mathbf{c} \quad (2.225)$$

because  $\mathbf{c}$  is independent of  $\mathbf{r}$  and  $t$ , and  $\frac{\partial \mathbf{c}}{\partial \mathbf{c}}$  denotes a unit tensor.

By inserting (2.225), the mean velocity (2.64), and the mass density (2.58), the total energy equation (2.224) can be written as:

$$\frac{\partial}{\partial t} \left( \frac{1}{2} \rho \langle c^2 \rangle_M \right) + \frac{1}{2} \frac{\partial}{\partial \mathbf{r}} \cdot (\rho \langle \mathbf{c} c^2 \rangle_M) = \rho \mathbf{F} \cdot \mathbf{v} \quad (2.226)$$

Equation (2.226) may be manipulated, using the same procedure as in the treatment of the equation of motion (2.223). The first term on the LHS of (2.226) can be manipulated by use of (2.65), eliminating the molecular velocity by  $\mathbf{c} = \mathbf{v} + \mathbf{C}$ , and after some further manipulation the covariance  $\frac{1}{2} \langle c^2 \rangle_M$  can be expressed as:

$$\frac{1}{2} \langle c^2 \rangle_M = \frac{1}{2} \langle C^2 \rangle_M + \frac{1}{2} \langle v^2 \rangle_M = e + \frac{1}{2} v^2 \quad (2.227)$$

where  $e$  is defined in accordance with (2.199), p. 246.

The second term on the LHS of (2.226) also needs further manipulation. By use of (2.65) in a similar manner, the covariance  $\frac{1}{2} \rho \langle \mathbf{c} c^2 \rangle_M$  can be expressed as:

$$\begin{aligned} \frac{1}{2} \rho \langle \mathbf{c} c^2 \rangle_M &= \frac{1}{2} \rho \langle \mathbf{c} (\mathbf{c} \cdot \mathbf{c}) \rangle_M = \frac{1}{2} \rho \langle (\mathbf{C} + \mathbf{v}) (C^2 + 2\mathbf{v} \cdot \mathbf{C} + v^2) \rangle_M \\ &= \frac{1}{2} \rho \left\{ \langle \mathbf{C} C^2 \rangle_M + \langle (2\mathbf{v} \cdot \mathbf{C}) \mathbf{C} \rangle_M + \langle \mathbf{C} v^2 \rangle_M + \langle \mathbf{v} C^2 \rangle_M \right. \\ &\quad \left. + \langle \mathbf{v} (2\mathbf{v} \cdot \mathbf{C}) \rangle_M + \langle \mathbf{v} v^2 \rangle_M \right\} \\ &= \frac{1}{2} \rho \langle \mathbf{C} C^2 \rangle_M + \rho \mathbf{v} \cdot \langle \mathbf{C} \mathbf{C} \rangle_M + \frac{1}{2} \rho \mathbf{v} \langle C^2 \rangle_M + \frac{1}{2} \rho \mathbf{v} v^2 \\ &= \mathbf{q} + \mathbf{p} \cdot \mathbf{v} + \rho \mathbf{v} e + \frac{1}{2} \rho \mathbf{v} v^2 \end{aligned} \quad (2.228)$$

Examining the peculiar velocity definition (2.65), it is seen that the average peculiar velocity equals zero, thus  $\langle \mathbf{C} v^2 \rangle_M = \mathbf{v} (2\mathbf{v} \cdot \langle \mathbf{C} \rangle_M) = 0$ . Furthermore, the last line on

the RHS is obtained introducing the heat flux  $\mathbf{q}$  as defined by (2.197), the pressure tensor  $\mathbf{p}$  as defined by (2.189), and the internal energy variable  $e$  as defined by (2.199).

By use of (2.227) and (2.228), the total energy equation (2.226) can be expressed as:

$$\frac{\partial}{\partial t}(\rho[e + \frac{1}{2}v^2]) + \frac{\partial}{\partial \mathbf{r}} \cdot (\rho \mathbf{v}[e + \frac{1}{2}v^2]) = -\frac{\partial}{\partial \mathbf{r}} \cdot \mathbf{q} - \frac{\partial}{\partial \mathbf{r}} \cdot (\mathbf{p} \cdot \mathbf{v}) + \rho \mathbf{F} \cdot \mathbf{v} \quad (2.229)$$

This relation corresponds to the *total energy equation*, for which the potential energy term is expressed in terms of the external force  $\mathbf{F}$ . By use of the momentum equation (2.219) a transport equation for the mean kinetic energy can be derived. Thereafter, the mean kinetic energy part is extracted from the total energy equation (2.229) (i.e., employing a similar procedure as was used manipulating the continuum model counterpart in Chap. 1, Sect. 1.2.4). The resulting internal energy equation yields:

$$\frac{\partial}{\partial t}(\rho e) + \nabla_{\mathbf{r}} \cdot (\rho \mathbf{v} e) = -\nabla_{\mathbf{r}} \cdot \mathbf{q} - \mathbf{p} : \nabla_{\mathbf{r}} \mathbf{v} \quad (2.230)$$

This Eq. (2.230) may be manipulated and expressed in terms of temperature by use of the continuity equation (2.218) and the definitions of  $e$  (2.199) and  $T$  (2.200):

$$\rho \frac{De}{Dt} = C_v \rho \left[ \frac{\partial T}{\partial t} + \mathbf{v} \cdot \nabla_{\mathbf{r}} T \right] = -\nabla_{\mathbf{r}} \cdot \mathbf{q} - \mathbf{p} : \nabla_{\mathbf{r}} \mathbf{v} \quad (2.231)$$

For dilute mono-atomic gases, for which the thermal energy consists of translational energy only, the specific heat at constant volume is given by (see e.g., Chapman and Cowling [20], Eq. (4.43, 2)):

$$C_v = \frac{3k}{2m} \quad (2.232)$$

The corresponding specific heat at constant pressure is given by:

$$C_p = C_v + R \quad (2.233)$$

The conservation equations (2.218), (2.223) and (2.229) are rigorous (i.e., for mono-atomic gases) consequences of the Boltzmann equation (2.184). It is important to note that the governing conservation equations are derived without the exact form of the collision term, the only requirement is that only summation invariant properties of mono-atomic gases are considered. That is, only properties that are conserved in molecular collisions are considered.

Nevertheless, it is clear that, in order to obtain practically useful gas dynamic equations from the general formulations derived above, suitable closures determining explicit expressions for the unknown quantities, i.e., the pressure tensor  $\mathbf{p}$  and the heat flux  $\mathbf{q}$ , in terms of the known variables are required. Of course, (2.189) and (2.197) provide prescriptions for calculating these quantities in terms of molecular quantities, but these relations require that the actual distribution function  $f$  which is a

solution of the Boltzmann equation (2.184) is known. Moreover, the pressure tensor is generally split into the pressure and the deviatoric or viscous stresses according to (2.194). In this case, the problem is reformulated and an expression for the viscous stresses are required instead. Anyhow, using the Chapman-Enskog series approximation of the distribution function, two well known forms of the gas dynamic equations are obtained adopting the zero and first order perturbation approximations of the distribution function as will be outlined in Sects. 2.8.1 and 2.8.2, respectively.

## 2.7 The Boltzmann H-Theorem

In this section the elementary definitions and results deduced from the H-theorem are given [10]. In summary, the statistical  $H$ -theorem of kinetic theory relates to the Maxwellian velocity distribution function and thermodynamics. Most important, the Boltzmann's  $H$ -theorem provides a mechanistic or probabilistic prove for the second law of thermodynamics. In this manner, the  $H$ -theorem also relates the thermodynamic entropy quantity to probability concepts. Further details can be found in the standard references [20, 39, 55, 68, 90, 117, 150, 157]. In practice, during the process of developing novel models for the collision term, the  $H$ -theorem merely serves as a requirement for the constitutive relations in order to fulfill the second law of thermodynamics (in a similar manner as for the continuum models).

### 2.7.1 The $H$ -Theorem Formulation

Formulating the H-theorem Boltzmann considered a simple gas consisting of spherical molecules, possessing only translational energy, and are subject to no external forces. If the gas state is uniform in space, so that the velocity distribution function  $f$  is independent of  $\mathbf{r}$ , the Boltzmann equation (2.184) reduces to:

$$\frac{\partial f}{\partial t} = \int \int (f' f'_1 - f f_1) g \sigma_A(\boldsymbol{\Omega}') d\boldsymbol{\Omega}' d\mathbf{c}_1 \quad (2.234)$$

in which the notation (index 1 or no index) is employed to indicate the two sets of identical molecules having the same mass but possibly different velocities.

Moreover, Boltzmann introduced a novel function  $H(t)$ , defined in terms of a complete integral over all values of the molecular velocities:

$$H = \int f \ln f d\mathbf{c} = n \langle \ln f \rangle_M \quad (2.235)$$

The function  $H(t)$  thus depends on the mode of distribution of the molecular velocities only [20].

Multiplying the reduced form of Boltzmann equation (2.184) by  $(1 + \ln f)$  and integrating over the phase space, the results is:

$$\int (1 + \ln f) \frac{\partial f}{\partial t} d\mathbf{c} = \int \int \int (1 + \ln f) (f' f'_1 - f f_1) g \sigma_A(\mathbf{\Omega}') d\mathbf{\Omega}' d\mathbf{c} d\mathbf{c}_1 \quad (2.236)$$

By use of (2.235), Boltzmann recognized that the term on the LHS of (2.236) can be manipulated as:

$$\frac{\partial H}{\partial t} = \int \frac{\partial}{\partial t} (f \ln f) d\mathbf{c} = \int (1 + \ln f) \frac{\partial f}{\partial t} d\mathbf{c} \quad (2.237)$$

Substitution of the expression on the LHS of (2.236) by use of (2.237), and with some further manipulation of the collision term, the reduced Boltzmann equation (2.236) becomes:

$$\frac{\partial H}{\partial t} = \frac{1}{4} \int \int \int \ln(f f_1 / f' f'_1) (f' f'_1 - f f_1) g \sigma_A(\mathbf{\Omega}, g) d\mathbf{\Omega}_{g'} d\mathbf{c} d\mathbf{c}_1 \quad (2.238)$$

To reach the form of (2.238), the collision term in (2.236) was manipulated as:

$$\begin{aligned} 4\psi(1 + \ln f) &= \psi([1 + \ln f] + [1 + \ln f_1] - [1 + \ln f'] - [1 + \ln f'_1]) \\ &= \psi(\ln f + \ln f_1 - \ln f' - \ln f'_1) = \psi(\ln f f_1 - \ln f' f'_1) \quad (2.239) \\ &= \psi(\ln \frac{f f_1}{f' f'_1}) = -\psi(\ln \frac{f' f'_1}{f f_1}) \end{aligned}$$

Setting  $\mathcal{E} = f f_1$  and  $\Upsilon = f' f'_1$ , (2.238) can be rewritten as:

$$\frac{\partial H}{\partial t} = \frac{1}{4} \int \int \int (\Upsilon - \mathcal{E}) \ln(\mathcal{E}/\Upsilon) g \sigma_A(\mathbf{\Omega}, g) d\mathbf{\Omega}_{g'} d\mathbf{c} d\mathbf{c}_1 \quad (2.240)$$

with  $\mathcal{E}$  and  $\Upsilon$  positive. Examining the three cases  $\mathcal{E} = \Upsilon$ ,  $\mathcal{E} > \Upsilon$ , and  $\mathcal{E} < \Upsilon$ , it is seen that  $(\Upsilon - \mathcal{E}) \ln(\mathcal{E}/\Upsilon) \leq 0$  for all three cases.

Moreover, since  $g \sigma_A(\mathbf{\Omega}, g) d\mathbf{\Omega}_{g'} d\mathbf{c} d\mathbf{c}_1$  is a positive measure, the integral on the right hand side of (2.238) is either negative or zero, so  $H$  can never increase. The resulting relation is known as Boltzmann's *H-theorem*:

$$\frac{\partial H}{\partial t} \leq 0 \quad (2.241)$$

This theorem states that, for any initial  $f$ ,  $H$  approaches a finite minimum limit, corresponding to a state of gas in which  $\partial H / \partial t = 0$  (steady state), and this can according to (2.238) occur, only if:

$$f' f'_1 = f f_1$$

$$\ln f' + \ln f'_1 = \ln f + \ln f_1 \quad (2.242)$$

The  $H$ -theorem is thus equivalent to the second law of thermodynamics which states that the entropy cannot decrease. A formal relationship between the  $H$  quantity and the entropy  $S$  is discussed in Sect. 2.7.3. Equation (2.242) also relates  $H$  to the theory of *irreversible thermodynamics*, as it is a probabilistic confirmation of the irreversibility of physical processes.

### 2.7.2 The Maxwellian Velocity Distribution

To find the exact equilibrium distribution that is a solution to (2.242), it can be shown that the resulting equilibrium distribution is given by (see e.g., [20], p. 69; [90], p. 162; [109]):

$$f^0(\mathbf{c}) = n \left( \frac{m}{2\pi kT} \right)^{\frac{3}{2}} e^{-\frac{m\mathbf{c}^2}{2kT}} \quad (2.243)$$

where  $k$  is the Boltzmann constant. In the Maxwellian distribution the parameters  $n$ ,  $\mathbf{c}$  and  $T$  are constants in  $\mathbf{r}$  and  $t$ . This distribution formula is often referred to as the *absolute Maxwellian*.

For the imaginary equilibrium flows we assume that in the neighborhood of any point in the gas, the distribution function is locally Maxwellian, and  $\rho$ ,  $T$ , and  $\mathbf{v}$  vary slowly in space and time. It can be shown that the approximation  $f(\mathbf{r}, \mathbf{c}, t) \approx f^0(\mathbf{r}, \mathbf{c}, t)$  is also a solution to (2.242), when  $f^0(\mathbf{r}, \mathbf{c}, t)$  is defined by:

$$f^0(\mathbf{r}, \mathbf{c}, t) = n(\mathbf{r}, t) \left( \frac{m}{2\pi kT(\mathbf{r}, t)} \right)^{\frac{3}{2}} e^{-\frac{m\mathbf{c}^2(\mathbf{r}, t)}{2kT(\mathbf{r}, t)}}$$

$$= n(\mathbf{r}, t) \left( \frac{m}{2\pi kT(\mathbf{r}, t)} \right)^{\frac{3}{2}} e^{-\frac{m(\mathbf{c}-\mathbf{v}(\mathbf{r}, t))^2}{2kT(\mathbf{r}, t)}}$$
(2.244)

It is important to note that this distribution function (2.244), defined so that it resembles (2.243) but with the constant values of  $n$ ,  $\mathbf{v}$  and  $T$  in (2.243) replaced by the corresponding functions of  $\mathbf{r}$  and  $t$ , remains a solution to (2.242). This distribution function, which is called the *local Maxwellian*, makes the kinetic theory much more general and practically relevant. Both the absolute- and local Maxwellians are termed equilibrium distributions. This result relates to the local and instantaneous equilibrium assumption in continuum mechanics as discussed in Chap. 1, showing that the assumption has a probabilistic fundament. It also follows directly from the local equilibrium assumption that the pressure tensor is related to the thermodynamic pressure, as mentioned in Sect. 2.5.

### 2.7.3 The H-Theorem and Entropy

In this section a relationship between the equilibrium value of  $H$  and entropy,  $S$ , is derived [20] (p. 78). For a gas at uniform steady state, the  $H(t)$  quantity defined by (2.235) can be expressed in terms of  $n$  and  $T$ . By use of the absolute Maxwellian distribution (2.243) and the energy equipartition theorem yields:

$$\begin{aligned} \langle \ln f \rangle_M &= \left\langle \left\{ \ln n + \frac{3}{2} \ln \left( \frac{m}{2\pi kT} \right) - \frac{\frac{1}{2}mC^2}{2kT} \right\} \right\rangle_M \\ &= \left\langle \left\{ \ln n + \frac{3}{2} \ln \left( \frac{m}{2\pi kT} \right) - \frac{3}{2} \right\} \right\rangle_M \end{aligned} \quad (2.245)$$

Thus, the  $H(t)$  quantity can be expressed as:

$$H = n \left\langle \left\{ \ln n + \frac{3}{2} \ln \left( \frac{m}{2\pi kT} \right) - \frac{3}{2} \right\} \right\rangle_M \quad (2.246)$$

Considering a gas with total mass,  $M$ , the volume occupied by the gas is  $V = \frac{M}{\rho} = \frac{M}{mn}$ . Integrating  $H(t)$  over the gas volume, it follows that:

$$H_0 = \int_V H d\mathbf{r} = \frac{M}{m} \left[ \ln n + \frac{3}{2} \ln \left( \frac{m}{2\pi kT} \right) - \frac{3}{2} \right] \quad (2.247)$$

Assuming that the kinetic theory definition of temperature and the thermodynamic counterpart are consistent, the entropy variable may be considered a function of  $V$  and  $T$  as obtained combining the first and second law of thermodynamics [45]. Moreover, Boltzmann let the gas of mass  $M$  undergo a small change of state, such that the temperature increases by  $\delta T$  and the volume increases by  $\delta V$ . Furthermore, considering that the total number of molecules is constant  $\delta(nV)$ , the volume change can be expressed in terms of a change in the number concentration of molecules  $\delta V/V = -\delta n/n$ .

Hence, the small change in entropy caused by the change of state can be expressed as [20] (see p. 41 and p. 81):

$$\delta S = M \left( C_V \frac{\delta T}{T} + \frac{k}{m} \frac{\delta V}{V} \right) = \frac{Mk}{m} \left( \frac{3}{2} \frac{\delta T}{T} - \frac{\delta n}{n} \right) \quad (2.248)$$

After integration the relation can be written as:

$$S = \frac{Mk}{m} \ln \left( \frac{T^{3/2}}{n} \right) + \text{constant} = -kH_0 - \frac{3M}{2m} \left( \ln \left( \frac{2\pi k}{m} \right) + 1 \right) + \text{constant} \quad (2.249)$$

where  $\ln T$  has been eliminated using (2.247).

This relation connects  $H_0$  with the entropy when the gas is at an uniform steady state:

$$S = -kH_0 + \text{Constant}' \quad (2.250)$$

It is commonly argued that the constant reflects the arbitrariness of the zero point of entropy. Due to the statistical relationship between  $H_0$  and  $S$  expressed through (2.250), the Boltzmann's  $H$ -theorem shows that for a gas that is not in a steady state  $H_0$  must decrease and the entropy  $S$  will increase accordingly. In accordance with (2.241) the following relationship holds:

$$\frac{dH_0}{dt} = -\frac{1}{k} \frac{dS}{dt} \leq 0 \quad (2.251)$$

or

$$\frac{dS}{dt} \geq 0 \quad (2.252)$$

The  $H$ -theorem is apparently a probability theory confirmation of the 2nd law of thermodynamics stating that the entropy cannot decrease in a physical process.

## 2.8 Solving the Boltzmann Equation

Various attempts have been made to obtain approximate solutions to the Boltzmann equation. Two of these methods were suggested independently by Chapman [18, 19] and by Enskog [35] giving identical results. In this book emphasis is placed on the Enskog method, rather than the Chapman one, as most modern work follows the Enskog approach since it is more intuitive and systematic, although still very demanding mathematically.

The Enskog [35] expansion method for the solution of the Boltzmann equation provides a series approximation to the distribution function. In the zero order approximation the distribution function is locally Maxwellian giving rise to the Euler equations of change. The first order perturbation results in the Navier-Stokes equations, while the second order expansion gives the so-called Burnett equations. The higher order approximations provide corrections for the larger gradients in the physical properties like  $\rho$ ,  $T$  and  $\mathbf{v}$ . The zero order approximation to  $f$  is valid when the system is at equilibrium and the gas properties contain no or very small macroscopic gradients. In particular, when the system is at equilibrium the heat fluxes and the viscous stresses vanish. The Navier-Stokes equations are valid whenever the relative changes in  $\rho$ ,  $T$  and  $\mathbf{v}$  in the distance of the mean free path are small compared to unity. Inasmuch as the Enskog theory is rather long and involved, this book only provide a brief outline of the problem and the method of attack, and then rather discuss the important results. When the second order approximations to the pressure tensor and the heat flux vector are inserted into the general conservation equation, one obtains the set of PDEs for the density, velocity and temperature which are called



the Burnett equations. In principle, these equations are regarded as valid for non-equilibrium flows. However, the use of these equations never led to any noticeable success (e.g., [39], pp. 150–151; [55], p. 464), merely due to the severe problem of providing additional boundary conditions for the higher order derivatives of the gas properties. Thus, the second order approximation will not be considered in further details in this book. Further details of the Enskog method are given by Enskog [35] and in the standard references like Hirschfelder et al. [55], Ferziger and Kaper [39], Vincenti and Kruger [157], Chapman and Cowling [20] and Liboff [90].

### 2.8.1 Equilibrium Flow: The Euler Equations

Applying the local Maxwellian distribution function (2.244), explicit expressions can be obtained for the heat flux,  $\mathbf{q}$  and the pressure tensor  $\mathbf{p}$ . Substituting  $f^0$  into the two flux formulas (2.189) and (2.197), give:

$$\mathbf{p} = m \int f^0 \mathbf{C} \mathbf{C} d\mathbf{c} = p \mathbf{e} \quad (2.253)$$

and

$$\mathbf{q} = \frac{1}{2} m \int f^0 \mathbf{C} C^2 d\mathbf{c} = 0 \quad (2.254)$$

In the zero order solution, there is no heat flow and the pressure tensor is diagonal. The diagonal elements in the pressure tensor denote the normal stresses that are identical to the thermodynamic pressure, as defined by (2.193). These conclusions are not obvious at first sight, so a brief mathematical verification is provided. In Cartesian tensor notation, the pressure tensor (2.189) is given by:

$$P_{ij} = \rho \left( \frac{m}{2\pi kT} \right)^{3/2} \int C_i C_j \exp \left( -\frac{mC^2}{2kT} \right) dC = p \delta_{ij} \quad (2.255)$$

where  $dC = d\mathbf{c}$ , since  $\mathbf{v}$  is not a function of  $\mathbf{c}$ .

Furthermore, as the integration is over the whole velocity space, it can be proved that any integral vanishes when the integrand is odd. Inspection of the pressure tensor shows that, since  $C_i$  and  $C_j$  themselves are odd functions of  $C_i$  and  $C_j$  respectively, whereas the exponential is an even function, the integrand as a whole is odd when  $i \neq j$  and even when  $i = j$ .

The derivation of the shear and normal stress terms is examined for two representative cases, which are the odd term ( $i = 1, j = 2$ ) and the even term ( $i = j = 1$ ). The two analytical integral solutions required are taken from the literature.<sup>31</sup>

For the particular odd term ( $i = 1, j = 2$ ) yields:

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<sup>31</sup> In the following mathematical manipulation we are solving even integrals on the form:

$$\begin{aligned}
\frac{P_{12}}{nm} &= \left(\frac{m}{2\pi kT}\right)^{3/2} \\
&\times \int_{-\infty}^{\infty} C_1 \exp\left(-\frac{mC_1^2}{2kT}\right) dC_1 \int_{-\infty}^{\infty} C_2 \exp\left(-\frac{mC_2^2}{2kT}\right) dC_2 \int_{-\infty}^{\infty} \exp\left(-\frac{mC_3^2}{2kT}\right) dC \\
&= \left(\frac{m}{2\pi kT}\right)^{3/2} \times 0 \times 0 \times 2 \left[ \frac{1}{2} \sqrt{\pi} \left(\frac{m}{2kT}\right)^{-1/2} \right] = 0,
\end{aligned} \tag{2.256}$$

and so on for the other shear stresses  $P_{13}$  and  $P_{23}$ . It is thus verified that for equilibrium flows all the viscous stresses vanish,  $\sigma = 0$ .

For the particular even term ( $i = j = 1$ ) yields:

$$\begin{aligned}
\frac{P_{11}}{nm} &= \left(\frac{m}{2\pi kT}\right)^{3/2} \\
&\times \int_{-\infty}^{\infty} C_1^2 \exp\left(-\frac{mC_1^2}{2kT}\right) dC_1 \int_{-\infty}^{\infty} \exp\left(-\frac{mC_2^2}{2kT}\right) dC_2 \int_{-\infty}^{\infty} \exp\left(-\frac{mC_3^2}{2kT}\right) dC \\
&= \left(\frac{m}{2\pi kT}\right)^{3/2} \times 2 \left[ \frac{\sqrt{\pi}}{4} \left(\frac{m}{2kT}\right)^{-3/2} \right] \times 2^2 \left[ \frac{\sqrt{\pi}}{2} \left(\frac{m}{2kT}\right)^{-1/2} \right]^2 \\
&= p \left(\frac{1}{nkT}\right) \left(\frac{m}{2\pi kT}\right)^{3/2} (2\pi)^{3/2} \left(\frac{m}{kT}\right)^{-5/2} = \frac{p}{nm},
\end{aligned} \tag{2.257}$$

and so on for  $P_{22}$  and  $P_{33}$ . The pressure tensor becomes,  $\mathbf{p} = p\mathbf{e}$ .

The heat flux is treated in a similar manner. By substituting  $f^0$  from (2.244) into the definition of  $\mathbf{q}$  (2.197), it is seen that this expression constitutes an odd integral, hence  $\mathbf{q} = 0$  (e.g., [157], Sect. 5). Since it has been verified that both the viscous stresses and the heat conduction terms vanish for equilibrium flows, no further constitutive stress tensor or heat flux relations are required to close the governing equations. The set of equilibrium flow equations is obtained by substituting (2.253) and (2.254) into the conservation equations (2.218), (2.223) and (2.229).

The system of equations are called the *Euler* equations for isentropic flow:

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(Footnote 31 continued)

$$\int_{-\infty}^{\infty} x^n \exp(-ax^2) dx = 2 \int_0^{\infty} x^n \exp(-ax^2) dx$$

Two even integral solutions are employed in this reformulation in which  $n = 0$  and  $n = 2$ , respectively, as listed below:

$$\int_0^{\infty} \exp(-ax^2) dx = \frac{\sqrt{\pi}}{2} a^{-1/2} \quad \text{and} \quad \int_0^{\infty} x^2 \exp(-ax^2) dx = \frac{\sqrt{\pi}}{4} a^{-3/2}$$

Further details can, for example, be found in Liboff [90] (pp. 526–527) and Chapman and Cowling [20] (Sect. 1.4).

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0 \quad (2.258)$$

$$\frac{\partial}{\partial t}(\rho \mathbf{v}) + \nabla \cdot (\rho \mathbf{v} \mathbf{v}) = -\nabla p + \rho \mathbf{F} \quad (2.259)$$

$$\frac{\partial}{\partial t}(\rho[e + \frac{1}{2}v^2]) + \nabla \cdot (\rho \mathbf{v}[e + \frac{1}{2}v^2]) = -\nabla \cdot (p \mathbf{v}) + \rho \mathbf{F} \cdot \mathbf{v} \quad (2.260)$$

### 2.8.2 Gradient Perturbations: Navier Stokes Equations

Applying the Enskog perturbation method, the properties of dilute gases which are only slightly deviating from equilibrium can be approximated. Only under these conditions will the flux vectors be about linear in the derivatives so that the formal definitions of the transport coefficients apply. In this limit the distribution function is still nearly Maxwellian, and the Boltzmann equation can be solved by a perturbation method. The resulting solutions are then used to obtain approximate expressions for the heat and momentum fluxes and for the corresponding transport coefficients.

The first step in the Enskog expansion is to introduce a perturbation parameter  $\varepsilon$  into the Boltzmann equation to enforce a state of equilibrium flow as the gas is dominated by a large collision term:

$$\begin{aligned} \frac{\mathcal{D}f}{Dt} &= \frac{1}{\varepsilon} \int_1 [f'(\mathbf{r}, \mathbf{c}', t) f'_1(\mathbf{r}, \mathbf{c}'_1, t) - f(\mathbf{r}, \mathbf{c}, t) f_1(\mathbf{r}, \mathbf{c}_1, t)] g \sigma_A(\boldsymbol{\Omega}') d\boldsymbol{\Omega}' d\mathbf{c}_1 \\ &= \frac{1}{\varepsilon} J(ff) \end{aligned} \quad (2.261)$$

where the perturbation parameter factor  $\varepsilon^{-1}$  measures the frequency of collisions. It is assumed that if  $\varepsilon \ll 1$ , the collisions are so frequent that the gas behaves like a continuum being in local equilibrium at every point.

Thereafter, the distribution function is expanded in a series in  $\varepsilon$ :

$$f = f^0 + \varepsilon f^1 + \varepsilon^2 f^2 + \dots \quad (2.262)$$

In a similar manner the time derivative is expanded as:

$$\frac{\partial}{\partial t} = \frac{\partial_0}{\partial t} + \varepsilon \frac{\partial_1}{\partial t} + \varepsilon^2 \frac{\partial_2}{\partial t} + \dots \quad (2.263)$$

stipulating that the time dependence of  $f$  is solely dependent on the gas dynamic variables  $\rho$ ,  $T$ , and  $\mathbf{v}$ , and expressed in terms of an exact differential.

The physical meaning of the expansion in time is that the lowest order terms vary most rapidly, whereas higher order terms are more slowly varying. If these series expansions are introduced into the modified Boltzmann equation (2.261), and the coefficients of equal powers of  $\varepsilon$  equated, the distribution function can be uniquely

determined to a specified order provided that  $f$  still satisfies the moment relations defining the physical properties like density, gas velocity and temperature.

Following this procedure, the result is:

$$0 = J(f^0 f^0) \quad (2.264)$$

$$\frac{D_{c,0} f^0}{D_c t} = J(f^0 f^1) \quad (2.265)$$

The solution of (2.264) gives rise to the absolute Maxwellian,  $f^0$ , as discussed in Sect. 2.7.2. Considering the first order approximation, (2.265) is supposedly solved for  $f^1$ . It is then required that the physical properties ( $\rho, \mathbf{v}, T$ ) are determined by the zero order approximation,  $f^0$ , whereas the higher order terms in the expansion contribute to  $\mathbf{q}$  and  $\sigma$  only.

Next, in the first order perturbation solution  $f^1$  is written in terms of the perturbation function  $\Phi$ . Hence,

$$f \approx f^0 + f^1 \approx f^0 + \Phi f^0 = f^0(1 + \Phi) \quad (2.266)$$

where  $\varepsilon$  is set to unity.

After (2.265) has been solved for  $\Phi$  (i.e., instead of  $f^1$ ),  $f$  is known to second order  $f = f^0(1 + \Phi)$ . Note that when the perturbation function  $\Phi \neq 0$  but still  $\Phi \ll 1$ , the system is only slightly different from equilibrium as prerequisites. When the first order approximation is introduced through (2.266), (2.265) is said to be an inhomogeneous linear integral equation for  $\Phi$ . The form of  $\Phi$  is then established without actually obtaining a complete solution. Instead, by functional analysis a partial solution is written in the form (e.g., Chapman and Cowling [20], Sect. 7.3; Hirschfelder et al. [55], Chap. 7, Sect. 3):

$$\Phi = -\frac{1}{n} \left[ \sqrt{\frac{2kT}{m}} \mathbf{A} \cdot \frac{\partial}{\partial \mathbf{r}} (\ln T) + 2\mathbf{B} : \frac{\partial}{\partial \mathbf{r}} \mathbf{v} \right] \quad (2.267)$$

where  $\mathbf{A}$  is a vector function of  $\mathcal{C} = \sqrt{\frac{m}{2kT}} \mathbf{C}$ ,  $n$  and  $T$ , whereas  $\mathbf{B}$  is a tensor function of  $\mathcal{C}$ ,  $n$  and  $T$ .

To determine the form of the two functions  $\mathbf{A}$  and  $\mathbf{B}$  the solution for  $\Phi$  (2.267) is substituted into the linearized Boltzmann equation (2.265), and thereafter the coefficients of the different components of  $\nabla T$  and  $\nabla \mathbf{v}$  in the resulting relation are equated. The only vectors that can be formed from these quantities are products of  $\mathcal{C}$  itself and scalar functions  $A(\mathcal{C}, n, T)$ , expressed as:

$$\mathbf{A} = A(\mathcal{C}, n, T) \mathcal{C} \quad (2.268)$$

$\mathbf{B}$  can be shown to be a symmetrical, traceless and non-divergent tensor [20, 39, 90]. The only second order symmetrical traceless tensors that can be formed from  $\mathcal{C}$ ,  $n$  and  $T$  are products of  $\overline{\mathcal{C}\mathcal{C}}$ <sup>32</sup> and scalar functions  $B(\mathcal{C}, n, T)$ .

Hence, it follows that:

$$\mathbf{B} = \overline{\mathcal{C}\mathcal{C}} B(\mathcal{C}, n, T) \quad (2.269)$$

Finally, solutions to the integral flux equations like (2.189) and (2.197) are then obtained by expressing the scalar functions  $A(\mathcal{C}, n, T)$  and  $B(\mathcal{C}, n, T)$  in terms of certain polynomials<sup>33</sup> (i.e., Sonine polynomials). However, without showing all the lengthy details of the method by which the two scalar functions are determined, we briefly sketch the problem definition in which the partial solution (2.267) is used to determine expressions for the viscous-stress tensor  $\sigma$  and the heat flux vector  $\mathbf{q}$ .

Introducing the expressions for the first order approximation of the distribution function (2.266) and thereafter the partial solution for  $\Phi$  (2.267) into the pressure tensor definition (2.189), the pressure tensor approximation is given by [55]:

$$\begin{aligned} p &= m \int f \mathbf{C} \mathbf{C} d\mathbf{c} = m \int f^0 (1 + \Phi) \mathbf{C} \mathbf{C} d\mathbf{c} \\ &= \underbrace{m \int f^0 \mathbf{C} \mathbf{C} d\mathbf{c}}_1 + \underbrace{m \int f^0 \Phi \mathbf{C} \mathbf{C} d\mathbf{c}}_2 \end{aligned} \quad (2.270)$$

where the parameter  $\varepsilon$  has been set equal to one.

From the previous section, it is recognized that term 1 on the RHS of (2.270) equals the pressure term,  $p\mathbf{e}$ , as for equilibrium systems. It can be shown by kinetic theory that term 2 on the RHS corresponds to the viscous stress tensor  $\sigma$  as defined by the pressure tensor (2.194). In order to determine the stress tensor term 2 in (2.270), the perturbation function  $\Phi$  in the integrand is substituted by the partial solution (2.267). Omitting integrals of odd functions of the components of  $\mathcal{C}$  or  $\mathbf{C}$ , only the term containing the  $\mathbf{B}$  remains. After some lengthy manipulations, the result is:

$$\sigma = -\mu \left( \nabla \mathbf{v} + (\nabla \mathbf{v})^T - \frac{2}{3} (\nabla \cdot \mathbf{v}) \mathbf{e} \right) \quad (2.271)$$

Note that the viscosity parameter  $\mu$  has been introduced as a pre-factor in front of the tensor functions by substitution of the kinetic theory transport coefficient expression after comparing the kinetic theory result with the definition of the viscous stress tensor  $\sigma$ , (2.194). In other words, this model inter-comparison defines the viscosity parameter in accordance with the Enskog theory.

<sup>32</sup> This notation is used denoting a symmetrical, traceless and non-divergent tensor [20, 39, 90].

<sup>33</sup> The detailed mathematical analysis needed determining these integrals are omitted in this book as it is rather lengthy and involved, instead the reader being interested in these pure mathematics are referred to the formal mathematical procedures given in the standard references (e.g., Enskog [35]; Hirschfelder et al. [55]; Chapman and Cowling [20], p. 126; Liboff [90], p. 187).

An analytical expression for the heat flux vector can be derived in a similar manner using the Enskog approach. That is, introducing the first order approximation of the distribution function from (2.266) into the heat flux definition (2.197) and thereafter substitute the partial solution for  $\Phi$ , as defined by (2.267), into the resulting flux vector integrand as follows [55]:

$$\mathbf{q} = \frac{1}{2}m \int f^0(1 + \Phi)C^2 \mathbf{C} d\mathbf{C} = -k\nabla T \quad (2.272)$$

Hence, the conductivity  $k$  in (2.272) is determined by model inter-comparison in accordance with the Enskog method. In general, it is important to recognize that both the Newton viscosity law and Fourier's law of heat conduction are automatically generated from the approximate kinetic theory solution of Enskog.

In conclusion, when these first order expressions for the pressure tensor and the heat flow vector are substituted into the general conservation equations (2.218), (2.223) and (2.229), the following set of partial differential equations are obtained:

$$\frac{1}{\rho} \frac{D\rho}{Dt} = -\nabla \cdot \mathbf{v} \quad (2.273)$$

$$\rho \frac{D\mathbf{v}}{Dt} = -\nabla p - \nabla \cdot \boldsymbol{\sigma} + \rho \mathbf{F} \quad (2.274)$$

$$\rho \frac{D}{Dt} \left( e + \frac{1}{2} v^2 \right) = -\nabla \cdot \mathbf{q} - \nabla \cdot (p\mathbf{v}) - \nabla \cdot (\boldsymbol{\sigma} \cdot \mathbf{v}) + \rho \mathbf{F} \cdot \mathbf{v} \quad (2.275)$$

where  $\boldsymbol{\sigma}$  and  $\mathbf{q}$  are given by (2.271) and (2.272), respectively.

The resulting set of conservation equations derived by kinetic theory corresponds to the governing equations of gas dynamics (sometimes referred to as the Navier-Stokes equations).

## 2.9 Multicomponent Mixtures

In this section we briefly discuss some of the important issues that arise when the kinetic gas theory is extended to gas mixtures. For a more detailed study of kinetic theory of mixtures the reader is referred to Hirschfelder et al. [55], Williams [162] (app D) and Ferziger and Kaper [39].

### 2.9.1 The Boltzmann Equations for a Mixture of Chemical Species

It is first necessary to generalize the definitions of the important functions. If we denote the chemical species in a gas mixture by  $s$ , then  $n_s$ ,  $m_s$ ,  $f_s$ ,  $\mathbf{c}_s$ ,  $\mathbf{C}_s$ ,  $\mathbf{F}_s$ , etc. will in general be different for each species.

The starting point for the kinetic theory of low density, non-reacting mixtures of mono-atomic gases is the knowledge of the distribution function  $f_s(\mathbf{r}, \mathbf{c}_s, t)$ .  $f_s(\mathbf{r}, \mathbf{c}_s, t)$  is defined in such a way that the quantity  $f_s(\mathbf{r}, \mathbf{c}_s, t)d\mathbf{c}_s d\mathbf{r}$  represents the probable number of molecules of the  $s$ -th species which at the time  $t$  lie in a unit volume element  $d\mathbf{r}$  about the point  $\mathbf{r}$  and which have velocities within the range  $d\mathbf{c}_s$  about  $\mathbf{c}_s$ . It is emphasized that  $\mathbf{c}_s$  denotes the molecular velocity of a species  $s$  with respect to a coordinate system fixed in space.

The total number of molecules of species  $s$  per unit spatial volume yields:

$$n_s(\mathbf{r}, t) = \int f_s(\mathbf{r}, \mathbf{c}_s, t)d\mathbf{c}_s \quad (2.276)$$

For the mixture as a whole we have:

$$n(\mathbf{r}, t) = \sum_s \int f_s(\mathbf{r}, \mathbf{c}_s, t)d\mathbf{c}_s = \sum_s n_s \quad (2.277)$$

and

$$\rho(\mathbf{r}, t) = \sum_s m_s \int f_s(\mathbf{r}, \mathbf{c}_s, t)d\mathbf{c}_s = \sum_s m_s n_s = \sum_s \rho_s \quad (2.278)$$

The mean (number average) values of any function  $\psi_s(\mathbf{c}_s)$  over all the molecules of a particular species,  $s$ , yield:

$$\langle \psi \rangle_{M,s} = \frac{1}{n_s} \int \psi_s(\mathbf{c}_s) f_s(\mathbf{r}, \mathbf{c}_s, t)d\mathbf{c}_s \quad (2.279)$$

The corresponding mean (number average) values of any function  $\psi_s(\mathbf{c}_s)$  over all the species  $n$  in the mixture are:

$$\langle \psi \rangle_{M,n} = \frac{1}{n} \sum_s \int \psi_s(\mathbf{c}_s) f_s(\mathbf{r}, \mathbf{c}_s, t)d\mathbf{c}_s = \frac{1}{n} \sum_s n_s \langle \psi \rangle_{M,s} \quad (2.280)$$

The corresponding mixture mass average value of any function  $\psi_s(\mathbf{c}_s)$  is defined by:

$$\langle \psi \rangle_{M,m} = \frac{1}{\rho} \sum_s m_s \int \psi_s(\mathbf{c}_s) f_s(\mathbf{r}, \mathbf{c}_s, t)d\mathbf{c}_s = \frac{1}{\rho} \sum_s n_s m_s \langle \psi \rangle_{M,s} \quad (2.281)$$

In particular, the mass average velocity  $\mathbf{v}_m$  of the mixture is given by:

$$\mathbf{v}_m = \langle \mathbf{c}_s \rangle_{M,m} = \frac{1}{\rho} \sum_s \rho_s \langle \mathbf{c}_s \rangle_{M,s} \quad (2.282)$$

It is recognized that the mass average velocity for a mixture,  $\mathbf{v}_m$ , is not equal to the number or molar average velocity  $\langle \mathbf{c}_s \rangle_{M,n}$ .

The number average velocity for a particular species,  $s$ , is defined by:

$$\begin{aligned}\langle \mathbf{c}_s \rangle_{M,s} &= \frac{1}{n_s} \int \mathbf{c}_s f_s(\mathbf{r}, \mathbf{c}_s, t) d\mathbf{c}_s \\ &= \frac{1}{n_s m_s} \int m_s \mathbf{c}_s f_s(\mathbf{r}, \mathbf{c}_s, t) d\mathbf{c}_s = \mathbf{v}_s(\mathbf{r}, t)\end{aligned}\quad (2.283)$$

Note that for each species the molecular number and mass average velocities are equal, as all the molecules have the same mass.

The peculiar velocity of a molecule of species  $s$  is defined in terms of the mass average velocity:

$$\mathbf{C}_s(\mathbf{r}, \mathbf{c}_s, t) = \mathbf{c}_s - \mathbf{v}_m(\mathbf{r}, t) \quad (2.284)$$

The species  $s$  diffusion velocity denotes the average velocity of the particular type of species with respect to a reference frame moving with the mass average velocity of the gas mixture:

$$\mathbf{v}_{d,s} = \langle \mathbf{C}_s \rangle_{M,s} - \mathbf{v}_m = \mathbf{v}_s - \mathbf{v}_m \quad (2.285)$$

Thus, the diffusion velocity for a given species equals the average of the corresponding peculiar velocity and can be written in the form:

$$\mathbf{v}_{d,s} = \frac{1}{n_s} \int (\mathbf{c}_s - \mathbf{v}_m) f_s(\mathbf{r}, t) d\mathbf{c}_s \quad (2.286)$$

Hence, from the definitions of the diffusion and mass average velocities it follows that:

$$\begin{aligned}\sum_s n_s m_s \mathbf{v}_{d,s} &= \sum_s m_s \int (\mathbf{c}_s - \mathbf{v}_m) f_s(\mathbf{r}, t) d\mathbf{c}_s \\ &= \sum_s m_s n_s (\langle \mathbf{c}_s \rangle_{M,s} - \mathbf{v}_m) = 0\end{aligned}\quad (2.287)$$

The kinetic theory temperature is defined in terms of the mean (number average) peculiar kinetic energy:

$$\begin{aligned}\frac{1}{2} \sum_s m_s \int (\mathbf{c}_s - \mathbf{v}_m)^2 f_s d\mathbf{c}_s &= \frac{1}{2} \sum_s m_s n_s \langle (\mathbf{c}_s - \mathbf{v}_m)^2 \rangle_M \\ &= \frac{1}{2} \sum_s m_s n_s \langle C_s^2 \rangle_M = \frac{3}{2} n k T\end{aligned}\quad (2.288)$$

The rigorous development of the kinetic theory of gases is based upon the Boltzmann equation for the velocity distribution function  $f_s$ . An extended Boltzmann equation, similar to (2.184), describes how  $f_s$  evolves in time and space:



$$\frac{\partial f_s}{\partial t} + \mathbf{c}_s \cdot \nabla f_s + \mathbf{F}_s \cdot \frac{\partial f_s}{\partial \mathbf{c}_s} = \sum_{r=1}^q \left( \frac{\partial f_s}{\partial t} \right)_{\text{Collision}} (f_s | f_r) \quad (2.289)$$

where the generalized multicomponent form of the collision term is approximated as:

$$\left( \frac{\partial f_s}{\partial t} \right)_{\text{Collision}} (f_s | f_r) = \int \int (f'_s f'_r - f_s f_r) g_{sr} \sigma_{A_{sr}}(\Omega', g_{sr}) d\Omega'_{g',sr} d\mathbf{c}_s \quad (2.290)$$

in which  $f'_s = f'_s(\mathbf{r}, \mathbf{c}'_s, t)$ , the magnitude of the relative velocities is  $g_{sr} = |\mathbf{c}_s - \mathbf{c}_r| = |\mathbf{c}'_s - \mathbf{c}'_r|$ , and  $\sigma_{A_{sr}}(\Omega', g_{sr})$  is the differential cross section between particles  $s$  and  $r$ . The external force per unit mass acting on a molecules of species  $s$  is denoted by  $\mathbf{F}_s$ .

The set of  $q$  coupled equations on the form (2.289), with the generalized collision term defined by (2.290), comprises the generalization of the Boltzmann equation for mono-atomic molecules to  $q$  species. In each of these equations, the distribution functions for all the species appear on the RHS of the equation under the integration sign. Moreover, the sum of integrals describes the entry and exit of particles of  $s$  in or out of the phase element.

### 2.9.2 The Diffusive Flux Vectors for a Mixture of Chemical Species

The collective flux vector associated with the property  $\psi_s(\mathbf{c}_s)$  is given by:

$$\Phi_s = \int \psi_s f_s \mathbf{C}_s d\mathbf{c}_s = \int \psi_s f_s \mathbf{C}_s d\mathbf{C}_s \quad (2.291)$$

It is noted that, as for simple systems computing average quantities, integration over  $\mathbf{C}_s$  is equivalent to integration over  $\mathbf{c}_s$  since the two velocities differ by a constant, and the integration is over the entire range of velocities.

The specific species mass, heat and momentum fluxes can now be expressed by substituting the individual conservative properties for the function  $\psi_s$ .

The diffusive mass flux vector is obtained if  $\psi_s = m_s$ :

$$\mathbf{j}_s = m_s \int (\mathbf{c}_s - \mathbf{v}_m) f_s d\mathbf{c}_s = m_s \int \mathbf{C}_s f_s d\mathbf{C}_s = n_s m_s \langle \mathbf{C}_s \rangle_{M,s} = n_s m_s \mathbf{v}_{d,s}, \quad (2.292)$$

As shown earlier by (2.287), the sum of all the species mass flux vectors equals zero:

$$\sum_s \mathbf{j}_s = 0 \quad (2.293)$$

The three flux vectors associated with the species momentum transport in the  $x$ ,  $y$  and  $z$ -directions are obtained from (2.291) when  $\psi_s = m_s C_{s,x}$ ,  $\psi_s = m_s C_{s,y}$  and  $\psi_s = m_s C_{s,z}$ , respectively.

The nine components of these three vectors form a symmetric pressure tensor,  $\mathbf{p}_s$ , hence the mixture pressure yields:

$$\begin{aligned} \mathbf{p} &= \sum_s \mathbf{p}_s = \sum_s m_s \int (\mathbf{c}_s - \mathbf{v}_m)(\mathbf{c}_s - \mathbf{v}_m) f_s d\mathbf{c}_s = \sum_s m_s \int \mathbf{C}_s \mathbf{C}_s f_s d\mathbf{C}_s \\ &= \sum_s m_s n_s \langle \mathbf{C}_s \mathbf{C}_s \rangle_{M,s} \end{aligned} \quad (2.294)$$

where the thermodynamic pressure is given by  $p = \frac{1}{3} \text{tr}(\mathbf{p}) = \frac{1}{3} \mathbf{p} : \mathbf{e} = \sum_s p_s = nkT$ , and the viscous stresses yield:  $\boldsymbol{\sigma} = \mathbf{p} - p\mathbf{e}$ .

The species  $s$  heat flux vector associated with the transport of kinetic energy is obtained if we let  $\psi_s = \frac{1}{2} m_s C_s^2$ , hence the mixture heat flux vector is determined by the sum over all the components:

$$\begin{aligned} \mathbf{q} &= \sum_s \mathbf{q}_s = \frac{1}{2} \sum_s m_s \int (\mathbf{c}_s - \mathbf{v}_m)^2 (\mathbf{c}_s - \mathbf{v}_m) f_s d\mathbf{c}_s = \frac{1}{2} \sum_s m_s \int C_s^2 \mathbf{C}_s f_s d\mathbf{C}_s \\ &= \frac{1}{2} \sum_s m_s n_s \langle C_s^2 \mathbf{C}_s \rangle_M \end{aligned} \quad (2.295)$$

Analytical expressions for the multicomponent flux vectors can be derived using the Enskog [35] perturbation method as sketched for one component mono-atomic gases in Sect. 2.8.

### 2.9.3 The Enskog's Equation for a Mixture of Chemical Species

If the species  $s$  Boltzmann equation (2.289) is multiplied by the molecular property  $\psi_s(\mathbf{c}_s)$  and thereafter integrated over all molecular velocities, the general Enskog's equation of change is achieved:

$$\frac{\partial}{\partial t} \int \psi_s f_s d\mathbf{c}_s + \nabla \cdot \int \mathbf{c}_s \psi_s f_s d\mathbf{c}_s + \int \mathbf{F}_s \cdot \frac{\partial \psi_s}{\partial \mathbf{c}_s} f_s d\mathbf{c}_s = \int \psi_s \left( \frac{\partial f_s}{\partial t} \right)_{\text{Collision}} d\mathbf{c}_s \quad (2.296)$$

### 2.9.4 The Equation of Change for a Mixture of Chemical Species

To derive the species equations of change we let  $\psi_s$  denote successively the mass  $m_s$ , the momentum  $m_s \mathbf{c}_s$ , and the energy  $\frac{1}{2} m_s (\mathbf{C}_s \cdot \mathbf{C}_s)$ . Thereafter, the corresponding

mixture equations are obtained simply by adding all the specific species  $s$  equations. The governing equations are given by [55] (Sect. 7-2):

$$\frac{\partial \rho_s}{\partial t} + \nabla \cdot (\rho_s \mathbf{v}_m) + \nabla \cdot \mathbf{j}_s = 0, \quad (2.297)$$

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}_m) = 0, \quad (2.298)$$

$$\frac{\partial}{\partial t}(\rho \mathbf{v}_m) + \nabla \cdot (\rho \mathbf{v}_m \mathbf{v}_m) = -\nabla p - \nabla \cdot \boldsymbol{\sigma}_m + \sum_s \rho_s \mathbf{F}_s \quad (2.299)$$

$$\frac{\partial}{\partial t}(\rho[e + \frac{1}{2}v_m^2]) + \nabla \cdot (\rho \mathbf{v}_m[e + \frac{1}{2}v_m^2]) = -\nabla \cdot \mathbf{q} - \nabla \cdot (\mathbf{p} \cdot \mathbf{v}_m) + \rho \mathbf{F} \cdot \mathbf{v}_m \quad (2.300)$$

where the internal energy per unit volume is defined by  $\rho e = \frac{3}{2}nkT = \frac{1}{2} \sum_s m_s \int (\mathbf{c}_s - \mathbf{v}_m)^2 f_s d\mathbf{c}_s$ .

### 2.9.5 Mass Diffusion Fluxes for Mixtures of Chemical Species

It is possible to justify several alternative definitions of the multicomponent diffusivities. The multicomponent mass flux vectors themselves are expressed in either of two mathematical forms or frameworks referred to as the generalized Fick's- and Maxwell-Stefan equations. In this subsection, the mass diffusion flux models for mixtures of chemical species are examined. The bulk diffusion flux models considered are the Fick's first law for binary mixtures, the approximate Fickian Wilke model, the generalized Fick's first law, and the rigorous Maxwell-Stefan model. For the combined bulk and Knudsen diffusion fluxes, the Fickian Wilke-Bosanquet and dusty gas models are considered. The dusty gas model designate an extended Maxwell-Stefan model. In this survey of the mass diffusion flux models, emphasis is placed on the first principles derivation of the governing flux equations, the physical interpretations of the terms in the resulting models, the consistency with Fick's first law for binary systems, and the relationships between the molar and mass based fluxes. The conventional modeling practice considers the mass average mixture velocity as a primitive variable instead of the number or molar averaged mixture velocity. The mass averaged velocity is the natural and most convenient basis for the laws of conservation of mixture mass, momentum and energy. It is noticed that the total number of moles of the molecules in a mixture is not necessarily conserved in reactive systems, whereas the elements and the mixture mass are preserved quantities. Separate equations of motion and energy for each species  $s$  can be derived by continuum arguments [9]. However, for mixtures containing a large number of different species the resulting sets of separate species mole, momentum and energy equations are neither feasible nor needed for solving transport problems. Besides, the species

momentum and energy fluxes are not measurable quantities. Therefore, for the calculation of multicomponent problems containing convective transport phenomena the mass average velocity based description of the diffusion has an essential advantage. If this description is chosen, then all the conservation equations contain only mass average velocities, while in the molar description of the diffusion the equations of motion and energy contain mass average velocities whereas the species mass balance equations contain number or mole average velocities. The two velocities are equal only when all the components of the system have the same molar mass, hence the mass average velocity based diffusion flux formulation is recommended for reactor simulations.

### 2.9.5.1 The Fick's First Law for Binary Mixtures

The Fick's first law of binary diffusion [40], proposed by Fick in 1855, expresses the mass flux as a negative function of the driving force, is defined by:

$$\mathbf{j}_s = -\rho D_{sr} \nabla \omega_s, \quad \text{where } s, r = 1, 2. \quad (2.301)$$

This mass diffusion flux relation serves as basis for the generalized Fickian multi-component formulations.

### 2.9.5.2 Generalized Fick's First Law Based on Kinetic Theory

Numerous generalized Fickian mass diffusion flux models have been proposed based on the concept of kinetic theory. Four such models are outlined in this subsection.

The Enskog series solution to the species  $s$  Boltzmann equation can be obtained in the same manner as sketched for the simple systems in Sect. 2.8. Near equilibrium the perturbation function  $\Phi_s$  can be expressed as a linear function of the various gradients (Curtiss and Hirschfelder [24], p. 551; Hirschfelder et al. [55], p. 469; Curtiss [25], p. 2918):

$$\Phi_s = -(\mathbf{A}_s \cdot \frac{\nabla T}{T}) - (\mathbf{B}_s : \nabla \mathbf{v}_m) + n \sum_{r=1}^N (\mathcal{C}_{s,r} \cdot \mathbf{d}_r) \quad (2.302)$$

where  $s = 1, 2, 3, \dots, N$ . The vector  $\mathbf{A}_s$ , the tensor  $\mathbf{B}_s$ , and the vectors  $\mathcal{C}_{s,r}$  are functions of  $\mathbf{c}_s$ ,  $\mathbf{r}$ , and  $t$ .

By inserting this expression for  $\Phi_s$  into the integrals for the flux vectors, Hirschfelder et al. [55] obtained expressions for the mass diffusion vector, the pressure tensor, and the heat flux vector. In particular, the integral for the diffusion flux vector can be expressed in terms of  $\Phi_s$ .

Hence, for a  $N$  component gas mixture the multicomponent mass flux vector was expressed as (Hirschfelder et al. [55], p. 478, p. 516):

$$\begin{aligned}
\mathbf{j}_s &= n_s m_s \mathbf{v}_{d,s} = m_s \int \mathbf{C}_s f_s d\mathbf{C}_s \approx m_s \int \mathbf{C}_s f_s^0 \Phi_s d\mathbf{C}_s \\
&= m_s \int \left[ -(\mathbf{A}_s \cdot \frac{\nabla T}{T}) + n \sum_r \mathbf{C}_{s,r} \cdot \mathbf{d}_r \right] \mathbf{C}_s f_s^0 d\mathbf{C}_s \quad (2.303) \\
&\approx \frac{n^2}{\rho} \sum_{r=1}^N m_s m_r \mathcal{D}_{sr} \mathbf{d}_r - D_s^T \frac{\nabla T}{T}
\end{aligned}$$

where the  $\mathcal{D}_{sr}$  are the generalized multicomponent diffusion coefficients, and the  $D_s^T$  are the generalized multicomponent thermal diffusion coefficients, respectively. It is noted that the term involving  $\mathbf{B}_s$  vanishes on integration (see Hirschfelder et al. [55], p. 478). The given relations correspond to Eqs. (7.4-1)–(7.4-3) in the book of Hirschfelder et al. [55], pp. 478–479.

The multicomponent thermal diffusion coefficients  $D_s^T$ , have the property:

$$\sum_{s=1}^N D_s^T = 0. \quad (2.304)$$

The multicomponent thermal diffusion coefficients serve as reminders that the kinetic theory predicts the cross effects like the transport of mass resulting from a temperature gradient (thermal diffusion). It can also be shown that the theory predicts transport of energy resulting from a concentration gradient (the diffusion-thermo effects). These second-order effects are often referred to as the Soret—and Dufour effects. It is noted that these terms do not appear when applying simple kinetic theory, only the more rigorous solution methods resolve these properties.

For dilute mono-atomic gases the generalized diffusional driving force vector,  $\mathbf{d}_s$ , that includes the composition gradients, the pressure gradient, and the external force differences, is defined<sup>34</sup> by (Curtiss and Hirschfelder [24], p. 551; Bird et al. [9]):

$$\begin{aligned}
\mathbf{d}_s &= \nabla x_s + (x_s - \omega_s) \frac{\nabla p}{p} - \frac{\rho_s}{p} \left[ \mathbf{g}_s - \sum_{r=1}^N \omega_r \mathbf{g}_r \right] \\
&= \frac{1}{cRT} \left[ (\nabla p_s - \rho_s \mathbf{g}_s) - \omega_s \left( \nabla p - \sum_{r=1}^N \rho_r \mathbf{g}_r \right) \right] \quad (2.305)
\end{aligned}$$

where  $x_s$  and  $\omega_s$  are the mole fraction and mass fraction, respectively.

It can be shown that  $\sum_s \mathbf{d}_s = 0$  by simple summation. This diffusional driving force vector, valid for a mixture of dilute mono-atomic gases, can be generalized for other gases using principles of irreversible thermodynamics. The generalized diffusional driving force vector is given in (2.382), p. 282.

<sup>34</sup> It is noted that the external force difference driving force defined in Hirschfelder et al. [55] at p 516, contains a couple of misprints.

By analysis of the model equations, i.e., (2.303) and (2.305), Hirschfelder et al. [55] concluded that these diffusion coefficients  $\mathcal{D}_{sr}$  are not uniquely defined. In the development of the kinetic theory of multicomponent mixtures, Hirschfelder et al. [55] resolved this lack of uniqueness by arbitrarily taking the diagonal coefficient  $\mathcal{D}_{ii}$  to be zero. However, this convention did lead to coefficients which are not symmetric. Moreover, Hirschfelder et al. [55] did relate the diffusion transport coefficients occurring in the mass diffusion flux model resulting from kinetic theory (2.303) with a corresponding set of phenomenological coefficients occurring in an alternative mass diffusion flux model derived from the principles of irreversible thermodynamics (2.313). The irreversible thermodynamics relation is examined at page 304. By comparison of the two model formulations, the generalized thermal diffusion coefficients were related to the phenomenological coefficients by:  $D_s^T = \alpha_{s0}$ . The diffusion coefficients,  $\mathcal{D}_{sr}$ , were related to the phenomenological coefficients,  $\alpha_{sr}$ , in the following manner (Curtiss and Hirschfelder [24], p. 552; Hirschfelder et al. [55], p. 479 and p. 715):

$$\mathcal{D}_{sr} = -\frac{\rho p}{n^2 m_s m_r} \left( \frac{\alpha_{sr}}{n_r m_r} + \frac{1}{n_s m_s} \sum_{\substack{k=1 \\ k \neq s}}^N \alpha_{sk} \right) \quad (2.306)$$

Fifty years later, Curtiss and Bird [26] proposed that the multicomponent diffusion coefficient relations can be written in simpler form by using the quantities  $\check{D}_{sr} = (\omega_i \omega_j / x_i x_j) \mathcal{D}_{sr}$ , rather than  $\mathcal{D}_{sr}$  from (2.305). The modified diffusion coefficients  $\check{D}_{sr}$  are thus related to  $\alpha_{sr}$  by:

$$\check{D}_{sr} = -\frac{cRT}{\rho} \left( \frac{\alpha_{sr}}{n_r m_r} + \frac{1}{n_s m_s} \sum_{\substack{k=1 \\ k \neq s}}^N \alpha_{sk} \right) \quad (2.307)$$

The  $\check{D}_{sr}$  have the properties  $\check{D}_{ss} = \sum_{k=1}^N (\check{D}_{ks} - \check{D}_{rk}) = 0$ , for  $s, r = 1, 2, 3, \dots, N$ . For this choice of multicomponent diffusivities, the mass diffusion flux vectors can be expressed as:

$$\mathbf{j}_s = -\rho \sum_{r=1}^N \check{D}_{sr} \mathbf{d}_r - D_s^T \frac{\nabla T}{T} \quad (2.308)$$

It is noted that neither of these two sets of generalized Fickian diffusivities are symmetric, i.e.,  $\mathcal{D}_{sr} \neq \mathcal{D}_{rs}$  and  $\check{D}_{sr} \neq \check{D}_{rs}$ . These diffusion coefficients are thus not practical because the number of parameters to fit is very large requiring numerous costly experimentally determined data sets.

In response to the disadvantageous lack of symmetry argument, Curtiss [25] made an alternative generalized Fickian diffusion coefficient definition proposal in 1968:

$$\hat{D}_{sr} = \frac{cRT\alpha_{sr}}{\rho_s\rho_r} \quad (2.309)$$

These multicomponent Fickian diffusivities,  $\hat{D}_{sr}$ , are symmetric [25], i.e.,  $\hat{D}_{sr} = \hat{D}_{rs}$ , and they obey the relations  $\sum_{s=1}^N \omega_s \hat{D}_{sr} = 0$  for  $s, r = 1, 2, 3, \dots, N$ . In terms of these symmetric diffusivity coefficients, the species mass flux was expressed as [26]:

$$\mathbf{j}_s = \rho_s \mathbf{v}_{d,s} = -\rho_s \sum_{r=1}^N \hat{D}_{sr} \mathbf{d}_r - D_s^T \frac{\nabla T}{T} \quad (2.310)$$

Comparing the generalized Fickian flux formulations of Curtiss and Bird [26] and Curtiss [25], it is noted that in (2.308) there is a  $\rho$  in front of the summation sign, whereas in (2.310) there is a  $\rho_s$ .

In the second edition of the textbook by Bird et al. [9] from 2002, a third alternative definition of the Fickian multicomponent mass diffusion coefficients was proposed, deviating from relation (2.309) by the sign convention only. These diffusion coefficients were thus defined by:

$$\mathbb{D}_{sr} = -\frac{cRT\alpha_{sr}}{\rho_s\rho_r} \quad (2.311)$$

These diffusivities are also symmetric ( $\mathbb{D}_{sr} = \mathbb{D}_{rs}$ ) and they obey the relations  $\sum_{s=1}^N \omega_s \mathbb{D}_{sr} = 0$  for  $s, r = 1, 2, 3, \dots, N$ . In terms of these symmetric diffusivity coefficients, the species mass flux was expressed as [26]:

$$\mathbf{j}_s = \rho_s \sum_{r=1}^N \mathbb{D}_{sr} \mathbf{d}_r - D_s^T \frac{\nabla T}{T} \quad (2.312)$$

Comparing the latter two symmetric Fickian flux formulations, it is noted that in (2.310) there is a minus sign in front of the summation sign, whereas in (2.312) there is a plus sign.

It is remarked that even though the latter two Fickian diffusivity proposals, i.e., (2.309) and (2.311), are symmetric, the multicomponent Fickian diffusivities  $\hat{D}_{sr}$  and  $\mathbb{D}_{sr}$  do not correspond to the approximately concentration independent binary diffusivities, i.e.,  $D_{sr}$ , which are available from binary diffusion experiments or kinetic theory determined by the inter-molecular forces between  $s - r$  pair of gases. Instead, these generalized multicomponent Fickian diffusion coefficients are strongly composition dependent. For these reasons, the generalized Fickian diffusivities are hardly used in practice because of the large number of costly experimental data sets that are required for parameter fitting.

### 2.9.5.3 Generalized Fick's First Law and Generalized Driving Forces Based on Irreversible Thermodynamics Principles

The principles of irreversible thermodynamics may be used to study the species mass and heat conduction transport. In this approach, the diffusion coefficients are defined in terms of the Onsager [102, 103] phenomenological coefficients. For a  $q$  component gas mixture, the linearity postulate in irreversible thermodynamics can be employed to obtain the multicomponent mass flux vectors (Hirschfelder et al. [55], p. 714; Curtiss and Bird [26, 27]):

$$\mathbf{j}_s = n_s m_s \mathbf{v}_{d,s} = -p \sum_{r=1}^N \frac{\alpha_{sr}}{n_r m_r} \mathbf{d}_r - \alpha_{s0} \frac{\nabla T}{T} \quad (2.313)$$

where  $s = 1, 2, 3, \dots, N$ . The coefficients,  $\alpha_{sr}$ , correspond to the phenomenological coefficients of Onsager which satisfy the reciprocal relations considering the processes of diffusion and thermal conduction. One of the phenomenological coefficient indices refers to the temperature variable, whereas the other indices refer to the species in the mixture. The flux equations in irreversible thermodynamics describe the coupling among the fluxes of the various system properties. The linearity postulate states that the fluxes are linear functions of all the driving forces [9, 26, 32, 55, 91].

In the derivation of (2.313) the original Onsager phenomenological coefficients were redefined as:

$$\alpha_{kr} - \sum_{\substack{k=1 \\ k \neq s}}^N \alpha_{sk} = 0 \quad \text{and} \quad \alpha_{rk} = \alpha_{kr} = - \sum_{\substack{s=1 \\ s \neq k}}^N \alpha_{rs} = 0 \quad (2.314)$$

for  $r = 1, 2, 3, \dots, N$ . That is, the new  $\alpha_{sr}$  are symmetric and also satisfy the relations  $\sum_{s=1}^N \alpha_{sr} = \sum_{s=1}^N \alpha_{rs} = 0$ .

A comparison with the results of the kinetic theory of dilute gases with those from the irreversible thermodynamics also shows that  $D_s^T = \alpha_{s0}$ . By use of (2.314) it is concluded that the generalized thermal diffusion coefficients  $D_s^T$ , have the property (2.304). Moreover, it was shown in the previous subsection that the various generalized Fickian diffusivities  $\mathcal{D}_{sr}$ ,  $\check{D}_{sr}$ ,  $\hat{D}_{sr}$  and  $\mathbb{D}_{sr}$  derived from kinetic theory can be related to the phenomenological coefficients by the following relations (2.306), (2.307), (2.309) and (2.311).

The *multicomponent generalization of Fick's first law of binary diffusion* is a second mass flux formulation on the Fickian form derived based on irreversible thermodynamics principles. This empirical formulation was first proposed by Onsager [104]. The generalized Fick's first law is defined by<sup>35</sup> [28, 32, 91, 104, 148]:

<sup>35</sup> In the chemical engineering literature the generalized or multicomponent form of Fick's first law of binary diffusion is normally written on a molar basis.



$$\mathbf{j}_s = -\rho \sum_{r=1}^{N-1} \dot{D}_{sr} \nabla \omega_r \quad s = 1, 2, 3, \dots, N-1 \quad (2.315)$$

This law is restricted to multicomponent systems, i.e.,  $N > 2$ . The diffusivities,  $\dot{D}_{sr}$ , defined by this relation may take negative values and are not, in general, symmetric ( $\dot{D}_{sr} \neq \dot{D}_{rs}$ ). The vector form of this mass flux is given by (2.316):

$$\mathbf{j} = -\rho[\text{diag}(\dot{\mathbf{D}})]\nabla(\boldsymbol{\omega}) \quad (2.316)$$

A multicomponent Fickian diffusion flux on this form was first suggested in irreversible thermodynamics and has no origin in kinetic theory of dilute gases. Hence, basically, these multicomponent flux equations represent a purely empirical generalization of Fick's first law and define a set of empirical multicomponent diffusion coefficients.

In retrospect the irreversible thermodynamics community did somewhat rationalize the origin of these equations and buttress this rationale with more fundamental principles [28]. Three basic postulates were required in order to derive the generalized Fick's law equations (2.316). The first postulate states that the thermodynamic properties such as entropy, chemical potential, and temperature can be correctly defined in a differential volume of a system that is not at equilibrium. The second postulate states that a linear relation exists between the forces and fluxes. The third postulate is that the Onsager phenomenological coefficients are symmetric. With these three postulates, it was possible to relate the generalized Fick's first law multicomponent diffusivities in (2.316) to the original Onsager phenomenological coefficients determining the basis for (2.313). That is, in the literature surveys by de Groot and Mazur [32] (Chap. 11), Taylor and Krishna [148] and Cussler [28] it was concluded that not all of the generalized Fick's law multicomponent diffusion coefficients are independent but are subject to certain constraints. However, these theoretical constraints are not very useful in practice, since they require detailed thermodynamic information that is rarely available. Anyhow, the thermodynamic theory does not provide any values for (quantification of) the multicomponent diffusion coefficients,  $\dot{D}_{sr}$ , so in practice all of them have to be determined from experiments. Hence, these coefficients cannot be interpreted simply, and there is therefore no fundamental theory predicting any formal relationships between the multicomponent—and the Fick first law binary diffusivities even for dilute gases in this particular diffusion model formulation.

An extension of the generalized diffusional driving force flux vector derived for dilute gases in kinetic theory (2.305) has been deduced based on principles of irreversible thermodynamics (e.g., Bird et al. [9], p. 766):

$$cRT\mathbf{d}_s = c_s \nabla \bar{g}_s + c_s \bar{s}_s \nabla T - \omega_s \nabla p - \rho_s \mathbf{g}_s - \omega_s \sum_{r=1}^N \rho_r \mathbf{g}_r \quad (2.317)$$

This extended form of the generalized diffusional driving force flux vector is valid for dilute gases, as well as dense gases and liquids. Moreover, it can be shown that  $\sum_s \mathbf{d}_s = 0$  by making use of the properties of partial molal quantities and the Gibbs-Duhem relation. In order to develop a more rigorous expression for the *driving forces in mass transfer* valid also for dense gases and liquids, use is normally made of physical laws and postulates taken from irreversible thermodynamics. For multicomponent systems it is advantageous to relate the diffusion fluxes to the activity rather than number—or mass fractions, since the activity formulation is valid for ideal as well as non-ideal systems. Notwithstanding, the binary diffusivities,  $D_{sr}$ , and the Maxwell-Stefan diffusivities,  $\tilde{D}_{sr}$ , are almost identical for ideal gas mixtures solely. For non-ideal gas mixtures and liquids the multi-component diffusivities are empirical parameters only. However, the generalized driving force formulation is claimed to be more useful in describing the inter-diffusion in dense gases and liquids (e.g., Curtiss and Bird [26, 27]; Taylor and Krishna [148]).

The Gibbs-Duhem equation is derived from the Euler and Gibbs equations (e.g., Prausnitz et al. [108], app D; Slattery [132], p. 443). The mass based form of the Gibbs-Duhem equation is outlined next. The total differential of the Gibbs free energy  $\hat{G}$  in terms of the natural variables (i.e.,  $T$ ,  $p$ ,  $m_s$ ) is:

$$d\hat{G} = \left( \frac{\partial \hat{G}}{\partial p} \right)_{T,m} dp + \left( \frac{\partial \hat{G}}{\partial T} \right)_{p,m} dT + \sum_{r=1}^N \left( \frac{\partial \hat{G}}{\partial m_r} \right)_{T,p,m_{r \neq s}} dm_r \quad (2.318)$$

With the substitution of the Maxwell relations and the definition of chemical potential, the total derivative expression is transformed into:

$$d\hat{G} = V dp - \hat{S} dT + \sum_{r=1}^N \mu_r dm_r \quad (2.319)$$

The partial mass chemical potential of the  $s$ -th species is defined as:

$$\mu_s = \check{G}_s = \left( \frac{\partial \hat{G}}{\partial m_s} \right)_{T,p,m_{r \neq s}} \quad (2.320)$$

The Gibbs free energy can also be computed from:

$$\hat{G} = \sum_{r=1}^N \mu_r m_r \quad (2.321)$$

The total differential of this expression is:

$$d\hat{G} = \sum_{r=1}^N \mu_r dm_r + \sum_{r=1}^N m_r d\mu_r \quad (2.322)$$

Considering that  $d\hat{G} = 0$  at thermodynamic equilibrium, and by combining the two relations for the total differential of the Gibbs free energy gives the Gibbs-Duhem equation:

$$\hat{S}dT - Vdp + \sum_{r=1}^N m_r d\mu_r = 0 \quad (2.323)$$

This relation implies that changes in the intensive quantities are not independent.

In fluid mechanics it might be natural to employ mass based thermodynamic properties whereas the classical thermodynamics convention is to use mole based variables. It follows that the extensive thermodynamic functions (e.g., internal energy, Gibbs free energy, Helmholtz energy, enthalpy, entropy, and specific volume) can be expressed in both ways, either in terms of mass or mole. The two forms of the Gibbs-Duhem equation are:

$$mSdT - Vdp + \sum_{s=1}^N m\omega_s d\mu_s = 0 \quad (2.324)$$

using specific variables, and

$$n\hat{S}dT - Vdp + \sum_{s=1}^N nx_s d\bar{G}_s = 0 \quad (2.325)$$

in terms of specific molar variables.

The thermodynamic notation is defined using one thermodynamic property as an example. It is postulated that the Gibbs free energy is a function of pressure, temperature and composition, hence we can write:

$$\hat{G} = \hat{G}(T, p, m_1, m_2, m_3, \dots, m_N) \quad (2.326)$$

in terms of mass, and

$$\hat{G} = \hat{G}(T, p, n_1, n_2, n_3, \dots, n_N) \quad (2.327)$$

in terms of mole.

In irreversible thermodynamics it is more convenient to use intensive or specific variables instead. Again we have two possible ways of defining the specific functions, either using molar specific variables which are given per mole or specific variables which are given per unit mass. Hence,

$$G = \frac{\hat{G}}{m} = G(T, p, \omega_1, \omega_2, \omega_3, \dots, \omega_{N-1}) \quad (2.328)$$

and

$$\underline{G} = \frac{\hat{\diamond} G}{n} = \underline{G}(T, p, x_1, x_2, x_3, \dots, x_{N-1}) \quad (2.329)$$

In thermodynamics partial variables are also used intensively. Accordingly, two sets of partial variables can be defined. The *partial mass variable* yields<sup>36</sup>:

$$\mu_s = \check{G}_s = \left( \frac{\partial \hat{G}}{\partial m_s} \right)_{T, p, m_r \neq s}, \quad s, r = 1, 2, \dots, N. \quad (2.330)$$

This quantity is related to the corresponding intensive variables in the following way (Slattery [132], Sect. 8.4):

$$\left( \frac{\partial \hat{G}}{\partial m_s} \right)_{T, p, m_r \neq s} - \left( \frac{\partial \hat{G}}{\partial m_q} \right)_{T, p, m_r \neq q} = \left( \frac{\partial G}{\partial \omega_s} \right)_{T, p, \omega_r \neq q, s} \quad (2.331)$$

The corresponding *partial molar variable* is written as:

$$\bar{G}_s = \left( \frac{\partial \hat{\diamond} G}{\partial n_s} \right)_{T, p, n_r \neq s}, \quad s, r = 1, 2, \dots, N. \quad (2.332)$$

which is related to the corresponding intensive variables:

$$\left( \frac{\partial \hat{\diamond} G}{\partial n_s} \right)_{T, p, n_r \neq s} - \left( \frac{\partial \hat{\diamond} G}{\partial n_q} \right)_{T, p, n_r \neq q} = \left( \frac{\partial G}{\partial x_s} \right)_{T, p, x_r \neq q, s} \quad (2.333)$$

The partial mass and the partial molar variables are simply related by:

$$\bar{G}_s = M_{w_s} \mu_s \quad (2.334)$$

Finally, we relate the intensive variables to the partial variables in the following manner:

$$G(T, p, \omega_1, \omega_2, \omega_3, \dots, \omega_{N-1}) = \sum_{s=1}^N \left( \frac{\partial \hat{G}}{\partial m_s} \right)_{T, p, m_r \neq s} \omega_s \quad (2.335)$$

and

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<sup>36</sup> In this book the partial mass and molar variables are defined employing the same notation as used by Slattery [132]

$$\underline{G}(T, p, x_1, x_2, x_3, \dots, x_{N-1}) = \sum_{s=1}^N \left( \frac{\partial \hat{G}}{\partial n_s} \right)_{T, p, n_{r \neq s}} x_s \quad (2.336)$$

The starting point for the rigorous derivation of the diffusive fluxes in terms of the activity is the entropy equation as given by (1.174), wherein the entropy flux vector is defined by (1.175) and the rate of entropy production per unit volume is written (1.176) as discussed in Sect. 1.2.4. To eliminate  $S$  from the Gibbs-Duhem relation formulated in terms of specific quantities (2.324) we need the definitions of  $\hat{H} = mH$  and  $\hat{G} = mG$ :

$$mG = mH - TmS = \sum_{s=1}^N m\omega_s \mu_s \quad (2.337)$$

$$mH = mE + pV = \sum_{s=1}^N m\omega_s \check{H}_s \quad (2.338)$$

where  $\check{H}_s = \left( \frac{\partial \hat{H}}{\partial m_s} \right)_{T, p, m_{r \neq s}}$ , and  $H(T, p, \omega_1, \omega_2, \dots, \omega_{N-1})$  denotes the intensive or specific enthalpy.

By use of (2.337) and (2.338), an expression for  $MS$  can be obtained:

$$mS = \frac{mH - mG}{T} = \frac{mE + pV - \sum_{s=1}^N m\omega_s \mu_s}{T} \quad (2.339)$$

Hence, by substitution of the given expressions for  $MS$  (2.339) into the mass form of the Gibbs-Duhem equation (2.324) yields:

$$\left( \frac{mH - mG}{T} \right) dT - Vdp + \sum_{s=1}^N m\omega_s d\mu_s = 0 \quad (2.340)$$

After division by the volume and the temperature, this equation can be put in a form useful to manipulate the entropy production term. Thus, introducing the partial mass quantities from (2.337) and (2.338) into (2.339), the result is:

$$\frac{1}{T^2} \left( \sum_{s=1}^N \rho_s \check{H}_s dT - \sum_{s=1}^N \rho_s \mu_s dT \right) - \frac{1}{T} dp + \frac{1}{T} \sum_{s=1}^N \rho_s d\mu_s = 0 \quad (2.341)$$

By minor manipulation of the terms:

$$\frac{1}{T^2} \sum_{s=1}^N \rho_s \check{H}_s dT + \sum_{s=1}^N \rho_s d \left( \frac{\mu_s}{T} \right) - \frac{1}{T} dp = 0 \quad (2.342)$$

Assuming that this relation is valid at the state of local equilibrium, the differentiation can be exchanged by the  $\nabla$ -operator (Curtiss and Bird [26, 27]):

$$\frac{1}{T^2} \sum_{s=1}^N \rho_s \check{h}_s \nabla T + \sum_{s=1}^N \rho_s \nabla \left( \frac{\mu_c}{T} \right) - \frac{1}{T} \nabla p = 0 \quad (2.343)$$

With the aim of expressing the rate of entropy production  $\Phi_{\text{total}}$  due to mass diffusion in terms of a convenient driving force,  $\frac{cRT}{\rho_s} \mathbf{d}_s$ , we add some extra terms in the third term on the RHS of (1.176) in such a way that the entropy production term remains unaltered utilizing the property that  $\sum_s \mathbf{j}_s = 0$ . The form of the terms that are added is guided by the terms in the Gibbs-Duhem equation (2.343).

The modified entropy production rate (1.176) is commonly written as [26, 27]:

$$\begin{aligned} \Phi_{\text{total}} = & -\frac{1}{T^2} (\mathbf{q} \cdot \nabla T) - \frac{1}{T} (\boldsymbol{\sigma} : \nabla \mathbf{v}) - \frac{1}{T} \sum_{r=1}^N A_r r_r \\ & - \sum_{s=1}^N \left( \frac{\mathbf{j}_s}{\rho_s} \cdot \left[ \rho_s \nabla \left( \frac{\mu_s}{T} \right) - \frac{\rho_s}{\rho T} \nabla p + \frac{\rho_s \check{h}_s}{T^2} \nabla T - \frac{\rho_s \check{h}_s}{T^2} \nabla T - \frac{\rho_s \mathbf{g}_s}{T} + \frac{\rho_s}{\rho T} \sum_{r=1}^N \rho_r \mathbf{g}_r \right] \right) \end{aligned} \quad (2.344)$$

The entropy production term has been written as a sum of products of fluxes and forces. However, there are only  $N - 1$  independent mass fluxes  $\mathbf{j}_s$ , and the Gibbs-Duhem equation (2.343) tells us that there are only  $N - 1$  independent forces as well [9].

Furthermore, it is noted that the first three terms in the brackets on the RHS of (2.344) are similar to the terms in the Gibbs-Duhem relation (2.343). However, two of these three terms do not contribute to the sum. The pressure term vanishes because  $\sum_s \mathbf{j}_s = 0$ . The two enthalpy terms obviously cancel because they are identical with opposite signs. Moreover, the last term in the brackets on the RHS of (2.344), involving the sum of external forces, is zero as  $\sum_s \mathbf{j}_s = 0$ . One of the two remaining terms, i.e., the one containing the enthalpy, we combine with the  $\mathbf{q}$  term. Hence, the modified entropy flux vector (1.175) and production terms (1.176) become:

$$\mathbf{J}_s = \frac{1}{T} \left( \mathbf{q} - \sum_{r=1}^N \mathbf{j}_r \check{h}_r \right) + \sum_{r=1}^N \check{s}_r \mathbf{j}_r \quad (2.345)$$

and

$$T \Phi_{\text{total}} = -\frac{1}{T} \left[ \mathbf{q} - \sum_{r=1}^N \mathbf{j}_r \check{h}_r \right] \cdot \nabla T - \sum_{r=1}^N \mathbf{j}_r \cdot \frac{cRT}{\rho_r} \mathbf{d}_r - \boldsymbol{\sigma} : \nabla \mathbf{v} - \sum_{r=1}^N A_r r_r \quad (2.346)$$

where

$$\frac{cRT}{\rho_s} \mathbf{d}_s = T \nabla \left( \frac{\mu_s}{T} \right) + \frac{\check{h}_s}{T} \nabla T - \frac{1}{\rho} \nabla p - \mathbf{g}_s + \frac{1}{\rho} \sum_{r=1}^N \rho_r \mathbf{g}_r \quad (2.347)$$

Due to the linearity postulate in irreversible thermodynamics, each vector flux must depend linearly on all the vector forces in the system. We may thus rewrite the fluxes as [26, 27]:

$$\mathbf{q} - \sum_{r=1}^N \mathbf{j}_r \check{h}_r = -\frac{1}{T} \alpha_{00} \nabla T - \sum_{r=1}^N \left( \frac{cRT \alpha_{0r}}{\rho_r} \right) \mathbf{d}_r \quad (2.348)$$

$$\mathbf{j}_s = -\frac{1}{T} \alpha_{s0} \nabla T - \rho_s \sum_{r=1}^N \left( \frac{cRT \alpha_{sr}}{\rho_s \rho_r} \right) \mathbf{d}_r \quad (2.349)$$

where  $s = 1, 2, \dots, N$ . The  $\alpha_{sr}$  are the symmetric phenomenological coefficients according to the Onsager reciprocal relations. Henceforth, the thermal diffusion coefficients are denoted by  $D_s^T = \alpha_{s0} = \alpha_{0s}$  and the Fickian diffusivities are given by  $\hat{D}_{sr} = \frac{cRT \alpha_{sr}}{\rho_s \rho_r}$  as foreseen in the preceding paragraphs.

The generalized diffusional driving forces  $\mathbf{d}_s$  either in terms of mass or molar functions, can be extended to a more rigorous form valid for dense gases and liquids using the partial mass Gibbs free energy definition,  $\check{G}_s = \check{h}_s - T \check{s}_s$ , and the chain rule of partial differentiation assuming that the chemical potential (i.e.,  $\mu_s = \check{G}_s$ ) is a function of temperature, pressure and concentration (Slattery [132], Sect. 8.4).  $\mathbf{d}_s$  can then be expressed in several useful forms as listed below. Expressing the thermodynamic functions on a mass basis yields:

$$\begin{aligned} \mathbf{d}_s &= \frac{\rho_s}{cRT} \left( \check{s}_s \nabla T + \nabla \mu_s - \frac{1}{\rho} \nabla p - \mathbf{g}_s + \frac{1}{\rho} \sum_{r=1}^N \rho_r \mathbf{g}_r \right) \\ &= \frac{\rho_s}{cRT} \left[ \sum_{\substack{r=1 \\ r \neq s}}^N \left( \frac{\partial \mu_s}{\partial \omega_r} \right)_{T, p, \omega_k \neq r, s} \nabla \omega_r + \left( \check{V}_s - \frac{1}{\rho} \right) \nabla p - \mathbf{g}_s + \frac{1}{\rho} \sum_{r=1}^N \rho_r \mathbf{g}_r \right] \\ &= \frac{\rho_s}{cRT} \left[ \nabla_{T, p} \mu_s + \left( \check{V}_s - \frac{1}{\rho} \right) \nabla p - \mathbf{g}_s + \frac{1}{\rho} \sum_{r=1}^N \rho_r \mathbf{g}_r \right] \end{aligned} \quad (2.350)$$

These relations may also be reformulated on a mole basis:

$$\begin{aligned}
\mathbf{d}_s &= \frac{c_s M_{w_s}}{c R T} \left( \frac{\bar{s}_s}{M_{w_s}} \nabla T + \nabla \left( \frac{\bar{g}_s}{M_{w_s}} \right) - \frac{1}{\rho} \nabla p - \mathbf{g}_s + \frac{1}{\rho} \sum_{r=1}^N \rho_r \mathbf{g}_r \right) \\
&= \frac{x_s}{R T} \left[ \sum_{\substack{r=1 \\ r \neq s}}^N \left( \frac{\partial \bar{g}_s}{\partial x_r} \right)_{T, p, x_{k \neq r, s}} \nabla x_r + \bar{V}_s \nabla p \right] \\
&\quad + \frac{x_s M_{w_s}}{R T} \left( -\frac{1}{\rho} \nabla p - \mathbf{g}_s + \frac{1}{\rho} \sum_{r=1}^N \rho_r \mathbf{g}_r \right) \\
&= \frac{x_s}{R T} \nabla_{T, p} \bar{g}_s + \frac{x_s M_{w_s}}{R T} \left[ \left( \check{V}_s - \frac{1}{\rho} \right) \nabla p - \mathbf{g}_s + \frac{1}{\rho} \sum_{r=1}^N \rho_r \mathbf{g}_r \right]
\end{aligned} \tag{2.351}$$

The transformations of the thermodynamic quantities like the partial mass Gibbs free energy might need further explanation. By use of the chain rule of partial differentiation the chemical potential on a mass basis is expanded considering that the chemical potential,  $\mu_s$ , is a function of  $T$ ,  $p$  and  $\omega_s$ :

$$d\mu_s = \left( \frac{\partial \mu_s}{\partial T} \right)_{p, \omega} dT + \left( \frac{\partial \mu_s}{\partial p} \right)_{T, \omega} dp + \sum_{\substack{r=1 \\ r \neq s}}^N \left( \frac{\partial \mu_s}{\partial \omega_r} \right)_{T, p, \omega_{k \neq r, s}} d\omega_r \tag{2.352}$$

where the partial derivatives with respect to  $T$  and  $p$  are eliminated by the thermodynamic relations,

$$\left( \frac{\partial \mu_s}{\partial T} \right)_{p, x} = -\check{S}_s \tag{2.353}$$

and

$$\left( \frac{\partial \mu_s}{\partial p} \right)_{T, \omega} = \check{V}_s \tag{2.354}$$

where  $\check{V}_s$  is the partial mass volume.

Alternatively, expressing the chemical potential on a molar basis we get:

$$d\bar{G}_s = \left( \frac{\partial \bar{G}_s}{\partial T} \right)_{p, x} dT + \left( \frac{\partial \bar{G}_s}{\partial p} \right)_{T, x} dp + \sum_{\substack{r=1 \\ r \neq s}}^N \left( \frac{\partial \bar{G}_s}{\partial x_r} \right)_{T, p, x_{k \neq r, s}} dx_r \tag{2.355}$$

where the partial derivatives with respect to  $T$  and  $p$  are substituted by the thermodynamic relations,

$$\left( \frac{\partial \bar{G}_s}{\partial T} \right)_{p, x} = -\bar{S}_s \tag{2.356}$$



and

$$\left(\frac{\partial \bar{G}_s}{\partial p}\right)_{T,x} = \bar{V}_s \quad (2.357)$$

where  $\bar{V}_s$  is the partial molar volume.

Hence, from (2.352) and (2.355) we may define the following short notations:

$$d_{T,p}\mu_s = \sum_{\substack{r=1 \\ r \neq s}}^N \left(\frac{\partial \mu_s}{\partial \omega_r}\right)_{T,p,\omega_k \neq r,s} d\omega_r = RT \sum_{\substack{r=1 \\ r \neq s}}^N \left(\frac{\partial \ln a_s}{\partial \omega_r}\right)_{T,p,\omega_k \neq r,s} d\omega_r \quad (2.358)$$

and

$$d_{T,p}\bar{G}_s = \sum_{\substack{r=1 \\ r \neq s}}^N \left(\frac{\partial \bar{G}_s}{\partial x_r}\right)_{T,p,x_k \neq r,s} dx_r = RT \sum_{\substack{r=1 \\ r \neq s}}^N \left(\frac{\partial \ln a_s^m}{\partial x_r}\right)_{T,p,x_k \neq r,s} dx_r \quad (2.359)$$

in which we are keeping the temperature  $T$  and pressure  $p$  constant.

It is postulated that the given relations are valid for a system at local equilibrium, the differential 'd' may thus be substituted by the  $\nabla$ -operator in the forthcoming derivations.

For the description of inter-diffusion in dense gases and liquids the expression for  $\mathbf{d}_s$  is further modified introducing a fugacity (i.e., a corrected pressure) or an activity (i.e., a corrected mole fraction) function [108]. The activity  $a_s(T, \omega_1, \omega_2, \omega_3, \omega_{N-1})$  for species  $s$  is defined by:

$$\mu_s = \mu_s^0 + RT \ln \frac{\hat{f}_s}{f_s^0} = \mu_s^0 + RT \ln a_s \quad (2.360)$$

where the auxiliary fugacity and activity functions are related by  $a_s = \hat{f}_s / f_s^0$ .  $\mu_s^0$  denotes the chemical potential at some reference state. While either  $\mu_s^0$  or  $f_s^0$  is arbitrary, both may not be chosen independently, since when one is chosen the other is fixed.

For liquids it is convenient to choose a particular reference state, a *standard state*, that can be defined by the Gibbs free energy of 1 mole of pure  $s$  at the mixture temperature,  $T$ , and a specified pressure, say 1 bar. Hence, in this case  $\mu_s^0$  is a function of temperature only,  $\mu_s^0 = \mu_s^0(T, p = 1\text{ bar}, \omega \rightarrow 1)$ . Alternatively,  $\mu_s^0$  may be chosen as the chemical potential for pure species  $s$  at the system temperature and pressure in which  $\mu_s^0 = \mu_s^0(T, p)$ . That is, numerous reference states are possible, which one to be chosen matters little provided that the model formulation is consistent. Henceforth, we are using the given standard state as defined above.

For dense gases it is often more convenient to use the fugacity,  $\hat{f}_s$ , defined by:

$$\mu_s = \mu_s^* + RT \ln \frac{\hat{f}_s}{f_s^*} \quad (2.361)$$

where  $\mu_s^*$  denotes a reference state being an ideal gas state at the system temperature and a standard pressure state (e.g.,  $p^* = 1$  bar). However, in either case using fugacities or activities the model derivation is very similar so we proceed considering the activity formulation only.

Introducing the mass based activity variable, the first term on the RHS of (2.347) is rewritten by use of the chain rule of partial differentiation considering that the chemical potential is a function of temperature, pressure and composition. The mass based chain rule of partial differentiation of the chemical potential function is given by (2.352).

It follows that the first term on the RHS of the mass based expression (2.347) can be written as:

$$\begin{aligned} \rho_s T \nabla \left( \frac{\mu_s}{T} \right) &= \rho_s T \nabla \left( \frac{\mu_s^0}{T} \right) + \rho_s RT \nabla \ln a_s = \rho_s \nabla \mu_s^0 - \rho_s \mu_s^0 \nabla \ln T + \rho_s RT \nabla \ln a_s \\ &= -\rho_s \check{s}_s^0 \nabla T - \rho_s \mu_s^0 \nabla \ln T + \rho_s RT \nabla \ln a_s \\ &= -\rho_s (T \check{s}_s^0 + \mu_s^0) \nabla \ln T + \rho_s RT \nabla \ln a_s \\ &= -\rho_s \check{h}_s^0 \nabla \ln T + \rho_s RT \nabla \ln a_s \end{aligned} \quad (2.362)$$

In (2.362) the relation:

$$\nabla \mu_s^0 = \left( \frac{d\mu_s^0}{dT} \right) \nabla T = -\check{s}_s^0 \nabla T \quad (2.363)$$

holds because  $\mu_s^0(T)$  is a function of temperature only.

The Gibbs free energy definition is employed in order to express the standard state chemical potential  $\mu_s^0$  and entropy  $\check{s}_s^0$  potentials and introduce the entropy potential  $\check{h}_s^0$ :

$$\mu_s = \check{g}_s = \check{h}_s - T \check{s}_s \quad (2.364)$$

Substitution of (2.362) into (2.347), the extended generalized diffusional driving force vector relation can be manipulated as:

$$\frac{cRT}{\rho_s} \mathbf{d}_s = RT \nabla \ln a_s + (\check{h}_s - \check{h}_s^0) \nabla \ln T - \frac{1}{\rho} \nabla p - \mathbf{g}_s + \frac{1}{\rho} \sum_{r=1}^N \rho_r \mathbf{g}_r \quad (2.365)$$

The chain rule of partial differentiation of  $\mu_s$  (2.352), in which the partial derivatives therein are eliminated by (2.353) and (2.354), is employed in order to rewrite the first term on the RHS of (2.365):

$$RT \nabla \ln a_s = RT \sum_{\substack{r=1 \\ r \neq s}}^N \left( \frac{\partial \ln a_s}{\partial \omega_r} \right)_{T,p,\omega_{k \neq r,s}} \nabla \omega_r + \check{V}_s \nabla p - (\check{h}_s - \check{h}_s^0) \nabla \ln T \quad (2.366)$$

in which  $\check{V}_s$  denotes the partial mass volume which can be related to the volume fraction of species  $s$  by:  $\phi_s = \rho_s \check{V}_s = c_s \bar{V}_s$ .

Inserting (2.366) into (2.365), gives:

$$\begin{aligned} cRT \mathbf{d}_s &= \rho_s RT \sum_{\substack{r=1 \\ r \neq s}}^N \left( \frac{\partial \ln a_s}{\partial \omega_r} \right)_{T,p,\omega_{k \neq r,s}} \nabla \omega_r + \rho_s \left( \check{V}_s - \frac{1}{\rho} \right) \nabla p - \rho_s \mathbf{g}_s + \omega_s \sum_{r=1}^N \rho_r \mathbf{g}_r \\ &= \rho_s RT \nabla_{T,p} \ln a_s + \rho_s \left( \check{V}_s - \frac{1}{\rho} \right) \nabla p - \rho_s \mathbf{g}_s + \omega_s \sum_{r=1}^N \rho_r \mathbf{g}_r \end{aligned} \quad (2.367)$$

A problem related to the use of thermodynamic quantities on a mass basis instead of molar basis is that all the existing thermodynamic models naturally are expressed in terms of molar quantities. For example, in the case of concentrated non-ideal liquid mixtures the thermodynamic quantities can be calculated from the existing models of the excess Gibbs energy  $G^E$  which are normally expressed in terms of specific molar functions. There are numerous models for  $G^E$  available, e.g., NRTL, UNIQUAC and UNIFAC, all providing thermodynamic properties on the molar basis [108].

The modeling problems related to the mass based formulation of the thermodynamic relations are illustrated next considering a binary mixture. For flowing systems it is natural to seek an expression for the driving force in terms of mass fractions using (2.350) and (2.360). For a binary mixture the result is:

$$\begin{aligned} \mathbf{d}_1 &= \frac{\rho_1}{cRT} \left[ \left( \frac{\partial \mu_1}{\partial \omega_2} \right)_{T,p} \nabla \omega_2 + \left( \check{V} - \frac{1}{\rho} \right) \nabla p - \omega_2 (\mathbf{g}_1 - \mathbf{g}_2) \right] \\ &= \frac{\rho}{c} \left( \frac{\partial \ln a_1}{\partial \ln \omega_1} \right)_{T,p} \nabla \omega_1 + \frac{\rho_1}{cRT} \left[ \left( \check{V} - \frac{1}{\rho} \right) \nabla p - \omega_2 (\mathbf{g}_1 - \mathbf{g}_2) \right] \end{aligned} \quad (2.368)$$

where we have introduced an activity on a mass basis.

However, this mass based activity property is an unconventional variable and there exists no model for it yet. In addition, a principal disadvantage of working in terms of mass based activities like  $a_1$  is that for ideal solutions  $M_w \left( \frac{\partial \ln a_1}{\partial \ln \omega_1} \right)_{T,p} \neq 1$  in general. Instead, the driving force is usually rewritten on a molar basis using (2.350), (2.351) and (2.370). Hence, we obtain:

$$\begin{aligned} \mathbf{d}_1 &= \frac{\rho_1}{cRT} \left[ \left( \frac{\partial \mu_1}{\partial \omega_2} \right)_{T,p} \nabla \omega_2 + \left( \check{V} - \frac{1}{\rho} \right) \nabla p - \omega_2 (\mathbf{g}_1 - \mathbf{g}_2) \right] \\ &= \frac{x_1}{RT} \left( \frac{\partial \bar{G}_1}{\partial x_2} \right)_{T,p} \nabla x_2 + \frac{x_1 M_{w1}}{RT} \left[ \left( \check{V} - \frac{1}{\rho} \right) \nabla p - \omega_2 (\mathbf{g}_1 - \mathbf{g}_2) \right] \\ &= \left( \frac{\partial \ln a_1^m}{\partial \ln x_1} \right)_{T,p} \nabla x_1 + \frac{x_1 M_{w1}}{RT} \left[ \left( \check{V} - \frac{1}{\rho} \right) \nabla p - \omega_2 (\mathbf{g}_1 - \mathbf{g}_2) \right] \end{aligned} \quad (2.369)$$

The principal advantages of working in terms of  $a_1^m$  is that there exist thermodynamics models for this property and for ideal solutions  $(\frac{\partial \ln a_1^m}{\partial \ln x_1})_{T,p} = 1$ .

The important partial mass properties in (2.365) are easily transformed into molar basis as the partial mass and partial molar variables of species  $s$  are related by the molecular weight. The activity for species  $s$  is redefined by:

$$\bar{G}_s = \bar{G}_s^0 + RT \ln a_s^m \quad (2.370)$$

where  $a_s^m = a_s^m(T, x_1, x_2, x_3, \dots, x_{N-1})$ . This mole based activity variable  $a_s^m$  (2.370) is introduced into the first term on the RHS of (2.347).

The standard state Gibbs free energy potential is eliminated by use of the following relation:

$$\nabla \bar{g}_s^0 = (\frac{d\bar{g}_s^0}{dT}) \nabla T = -\bar{s}_s^0 \nabla T \quad (2.371)$$

This relationship holds because  $\bar{G}_s^0(T)$  is a function of temperature only.

The Gibbs free energy definition is employed in order to express the standard state chemical potential  $\bar{g}_s^0$  and entropy  $\bar{s}_s^0$  potentials and introduce the entropy potential  $\bar{h}_s^0$ .

$$\bar{g}_s = \bar{h}_s - T \bar{s}_s \quad (2.372)$$

Substitution of (2.370), (2.371) and (2.372) into (2.347), the first term on the RHS of the expression (2.347) can be written as:

$$\begin{aligned} c_s T \nabla \left( \frac{\bar{g}_s}{T} \right) &= c_s T \nabla \left( \frac{\bar{g}_s^0}{T} \right) + c_s RT \nabla \ln a_s^m = c_s \nabla \bar{g}_s^0 - c_s \bar{g}_s^0 \nabla \ln T + \rho_s RT \nabla \ln a_s^m \\ &= -c_s \bar{s}_s^0 \nabla T - c_s \bar{g}_s^0 \nabla \ln T + c_s RT \nabla \ln a_s^m \\ &= -c_s (T \bar{s}_s^0 + \bar{g}_s^0) \nabla \ln T + c_s RT \nabla \ln a_s^m \\ &= -c_s \bar{h}_s^0 \nabla \ln T + c_s RT \nabla \ln a_s^m \end{aligned} \quad (2.373)$$

Substitution of (2.373) into the expression (2.347), the extended diffusional driving force vector can be manipulated as:

$$cRT \mathbf{d}_s = c_s RT \nabla \ln a_s^m + (\bar{h}_s - \bar{h}_s^0) \nabla \ln T - \omega_s \nabla p - \rho_s \mathbf{g}_s + \omega_s \sum_{r=1}^N \rho_r \mathbf{g}_r \quad (2.374)$$

The chain rule of partial differentiation of  $\bar{G}_s$ , in which the partial derivatives therein are eliminated by use of (2.356) and (2.357), is employed in order to rewrite the first term on the RHS of (2.374):

$$\nabla \bar{g}_s = -\bar{s}_s \nabla T + \bar{V}_s \nabla p + \nabla_{T,p} \bar{g}_s \quad (2.375)$$

where the last term is written in the compact form (2.359).

By substitution of (2.370), (2.371) and (2.372), the LHS and RHS of (2.375) become:

$$\nabla \bar{g}_s^0 + R \ln a_s^m \nabla T + RT \nabla \ln a_s^m = -\bar{s}_s^0 \nabla T + R \ln a_s^m \nabla T + RT \nabla \ln a_s^m \quad (2.376)$$

$$\begin{aligned} \frac{(\bar{g}_s^0 + RT \ln a_s^m - \bar{h}_s)}{T} \nabla T + \bar{V}_s \nabla p + \nabla_{T,p} \bar{g}_s &= R \ln a_s^m \nabla T \\ &+ (\bar{g}_s^0 - \bar{h}_s) \nabla \ln T \\ &+ \bar{V}_s \nabla p + \nabla_{T,p} \bar{g}_s \end{aligned} \quad (2.377)$$

Substitution of these two relations into (2.375) gives an expression for the first term on the RHS of (2.374):

$$c_s RT \nabla \ln a_s^m = -c_s (\bar{h}_s - \bar{h}_s^0) \nabla \ln T + c_s \bar{V}_s \nabla p + c_s \nabla_{T,p} \bar{g}_s \quad (2.378)$$

The molar form of the driving force (2.374) becomes:

$$\begin{aligned} c RT \mathbf{d}_s &= c_s RT \nabla_{T,p} \ln a_s^m + (c_s \bar{V}_s - \omega_s) \nabla p - \rho_s \mathbf{g}_s + \omega_s \sum_{r=1}^N \rho_r \mathbf{g}_r \\ &= c_s RT \sum_{\substack{r=1 \\ r \neq s}}^N \left( \frac{\partial \ln a_s^m}{\partial x_r} \right)_{T,p,x_{k \neq s,r}} \nabla x_r + (c_s \bar{V}_s - \omega_s) \nabla p \\ &\quad - \rho_s \mathbf{g}_s + \omega_s \sum_{r=1}^N \rho_r \mathbf{g}_r \end{aligned} \quad (2.379)$$

This is the most frequently used mole based form of the extended generalized diffusional driving force vector formulation, that can be employed for dilute gases as well as dense gases and liquids.

For ideal solutions:

$$\sum_{\substack{r=1 \\ r \neq s}}^N \left( \frac{\partial \ln a_s^m}{\partial \ln x_r} \right)_{T,p,x_{k \neq s,r}} = 1 \quad (2.380)$$

The ratio of activity and mole fraction defines the activity coefficient,  $a_s^m = x_s \gamma_s$  [108]. For an ideal mixture, the activity is equal to the mole fraction since the activity coefficient equals unity. That is, we may expand the first term on the RHS in a convenient manner, excluding  $x_N$  (i.e., for a solvent containing several solutes it might be convenient to label the solvent as species  $N$ ):

$$\begin{aligned}
x_s \sum_{r=1}^{N-1} \left( \frac{\partial \ln a_s^m}{\partial x_r} \right)_{T,p,x} \nabla x_r &= x_s \sum_{r=1}^{N-1} \left( \frac{\partial \ln(\gamma_s^m x_s)}{\partial x_r} \right)_{T,p,x} \nabla x_r \\
&= x_s \sum_{r=1}^{N-1} \left( \frac{1}{\gamma_s^m x_s} \frac{\partial \gamma_s^m x_s}{\partial x_r} \right)_{T,p,x} \nabla x_r \\
&= x_s \sum_{r=1}^{N-1} \left( \frac{\partial \ln x_s}{\partial x_r} + \frac{\partial \ln \gamma_s^m}{\partial x_r} \right)_{T,p,x} \nabla x_r \quad (2.381) \\
&= \sum_{r=1}^{N-1} \left( \delta_{sr} + x_s \frac{\partial \ln \gamma_s^m}{\partial x_r} \right)_{T,p,x} \nabla x_r
\end{aligned}$$

For ideal solutions  $\gamma_s^m = 1$ , hence the  $N - 1$  independent driving forces yield:

$$\mathbf{d}_s = \nabla x_s + \frac{1}{cRT} (c_s \bar{V}_s - \omega_s) \nabla p - \frac{\rho_s}{cRT} \mathbf{g}_s + \frac{\omega_s}{cRT} \sum_{r=1}^N \rho_r \mathbf{g}_r \quad (2.382)$$

This reduced form of the extended generalized diffusional driving force vector corresponds to (2.305) which was derived from the kinetic theory of dilute gases.

#### 2.9.5.4 The Maxwell-Stefan Multicomponent Diffusion Flux Model

For dilute gases, the generalized multicomponent Fickian diffusion coefficients are strongly composition dependent. It follows that these diffusion coefficients do not correspond to the approximately concentration independent binary diffusivities,  $D_{sr}$ , which are available from binary diffusion experiments or kinetic theory since  $\tilde{D}_{sr} \approx D_{sr}$ . In response to this Fickian model limitation it has been proposed to transform the Fickian diffusion flux model, in which the mass-flux vector,  $\mathbf{j}_s$ , is expressed in terms of the driving force,  $\mathbf{d}_s$ , into the corresponding Maxwell-Stefan form [95, 97, 142, 143] where  $\mathbf{d}_s$  is given as a linear function of  $\mathbf{j}_s$ . The key idea is to rewrite the Fickian diffusion flux in terms of an alternative set of diffusivities (i.e., preferably the known binary diffusivities) which are less concentration dependent than the Fickian diffusivities.

The proposed transformation can be done using the method suggested by Curtiss and Bird [26, 27] which is in accordance with the work of Merk [101]. To shorten the notation they temporary define a modified diffusion velocity,  $\mathbf{v}'_{d,s}$ , by:

$$\rho_s \mathbf{v}'_{d,s} = \mathbf{j}_s + D_s^T \nabla \ln T \quad (2.383)$$

Thereafter, the modified diffusion velocity is expressed in terms of the driving forces using (2.310). For species  $s$  and  $k$  the resulting relationships are given by:

$$\mathbf{v}'_{d,s} = - \sum_{r=1}^N \hat{D}_{sr} \mathbf{d}_r \quad (2.384)$$

$$\mathbf{v}'_{d,k} = - \sum_{r=1}^N \hat{D}_{kr} \mathbf{d}_r \quad (2.385)$$

Next, each of the two relations is multiplied by the multicomponent inverse diffusivities,  $\hat{C}_{sk}$  with  $k \neq s$ , and if the first equation is subtracted from the second one, the result is:

$$\hat{C}_{sk}(\mathbf{v}'_{d,k} - \mathbf{v}'_{d,s}) = - \sum_{r=1}^N \hat{C}_{sk}(\hat{D}_{kr} - \hat{D}_{sr}) \mathbf{d}_r \quad (2.386)$$

Then, the sum on  $k$  is performed:

$$\sum_{\substack{k=1 \\ k \neq s}}^N \hat{C}_{sk}(\mathbf{v}'_{d,k} - \mathbf{v}'_{d,s}) = - \sum_{r=1}^N \left[ \sum_{\substack{k=1 \\ k \neq s}}^N \hat{C}_{sk}(\hat{D}_{kr} - \hat{D}_{sr}) \right] \mathbf{d}_r \quad (2.387)$$

where  $s = 1, 2, 3, \dots, N$ .

Curtiss and Bird [26, 27] and Slattery [132] (Sect. 8.4.4) state that from kinetic theory of dilute gas mixtures, it appears that the coefficients  $\hat{C}_{sk}$  are determined in such a way that the following relations are satisfied:

$$\sum_{\substack{k=1 \\ k \neq s}}^N \hat{C}_{sk}(\hat{D}_{kr} - \hat{D}_{sr}) = -\delta_{sr} + \omega_s \quad (2.388)$$

Accordingly, by use of the property  $\sum_{s=1}^q \omega_s \hat{D}_{sr} = 0$ , the RHS of (2.387) reduces to  $+\mathbf{d}_s$ . The modified diffusion velocity (2.383) can thus be related to the standard diffusion velocity (2.310), and expressed by:

$$\mathbf{v}'_{d,s} = \frac{\mathbf{j}_s}{\rho_s} + \frac{D_s^T}{\rho_s} \nabla \ln T = \mathbf{v}_{d,s} + \frac{D_s^T}{\rho_s} \nabla \ln T \quad (2.389)$$

Hence, the diffusion problem (2.387) can be expressed in terms of the actual diffusion velocities:

$$\sum_{\substack{k=1 \\ k \neq s}}^N \hat{C}_{sk}(\mathbf{v}_{d,k} - \mathbf{v}_{d,s}) = \mathbf{d}_s - \sum_{\substack{k=1 \\ k \neq s}}^N \hat{C}_{sk} \left( \frac{D_k^T}{\rho_k} - \frac{D_s^T}{\rho_s} \right) \nabla \ln T \quad (2.390)$$

where  $s = 1, 2, 3, \dots, N$ .

These relations are called *the generalized Maxwell-Stefan equations* and are the inverted counterparts of the Fick diffusion equations (2.310). These two descriptions contain the same information and are interrelated as proven by Curtiss and Bird [26, 27] for dilute mono-atomic gas mixtures. Finally, the Maxwell-Stefan diffusivities are defined by:

$$\hat{C}_{sk} = \frac{x_s x_k}{\tilde{D}_{sk}} \quad (2.391)$$

Thereby, the generalized Maxwell-Stefan equations can be expressed several ways:

$$\begin{aligned} \mathbf{d}_s - \sum_{\substack{k=1 \\ k \neq s}}^N \frac{x_s x_k}{\tilde{D}_{sk}} \left( \frac{D_k^T}{\rho_k} - \frac{D_s^T}{\rho_s} \right) \frac{\nabla T}{T} &= \sum_{\substack{k=1 \\ k \neq s}}^N \frac{x_s x_k}{\tilde{D}_{sk}} (\mathbf{v}_{d,k} - \mathbf{v}_{d,s}) \\ &= \sum_{\substack{k=1 \\ k \neq s}}^N \frac{x_s x_k}{\tilde{D}_{sk}} (\{\mathbf{v}_k - \mathbf{v}_m\} - \{\mathbf{v}_s - \mathbf{v}_m\}) = \sum_{\substack{k=1 \\ k \neq s}}^N \frac{x_s x_k}{\tilde{D}_{sk}} (\mathbf{v}_k - \mathbf{v}_s) \\ &= \sum_{\substack{k=1 \\ k \neq s}}^N \frac{x_s x_k}{\tilde{D}_{sk}} \left( \frac{\mathbf{n}_k}{\rho_k} - \frac{\mathbf{n}_s}{\rho_s} \right) = \sum_{\substack{k=1 \\ k \neq s}}^N \frac{x_s x_k}{\tilde{D}_{sk}} \left( \frac{\mathbf{j}_k}{\rho_k} - \frac{\mathbf{j}_s}{\rho_s} \right) \\ &= \sum_{\substack{k=1 \\ k \neq s}}^N \frac{1}{c \tilde{D}_{sk}} (x_s \mathbf{N}_k - x_k \mathbf{N}_s) = \sum_{\substack{k=1 \\ k \neq s}}^N \frac{1}{c \tilde{D}_{sk}} (x_s \mathbf{J}_k^* - x_k \mathbf{J}_s^*) \end{aligned} \quad (2.392)$$

where  $s = 1, 2, 3, \dots, N$ .

The combined molar flux with respect to stationary axes is defined by:

$$\mathbf{N}_s = c_s \mathbf{v}_s = c x_s \mathbf{v}_s = c_s \mathbf{v}_m^* + \mathbf{J}_s^*, \quad (2.393)$$

The corresponding combined mass flux is defined by:

$$\mathbf{n}_s = \rho_s \mathbf{v}_s = \rho \omega_s \mathbf{v}_s = \rho_s \mathbf{v}_m + \mathbf{j}_s \quad (2.394)$$

For multicomponent diffusion in gases and liquids, the generalized Maxwell-Stefan forms (2.392) and the extended generalized diffusional driving force vector (2.379) gives:



$$\begin{aligned}
\sum_{s=1}^N \frac{x_s x_r}{\tilde{D}_{sr}} (\mathbf{v}_s - \mathbf{v}_r) = & -x_s \nabla_{T,p} \ln a_s^m \\
& - \frac{1}{cRT} \left[ (c_s \bar{V}_s - \omega_s) \nabla p - \rho_s \mathbf{g}_s + \omega_s \sum_{r=1}^N \rho_r \mathbf{g}_r \right] \\
& + \sum_{\substack{k=1 \\ k \neq s}}^N \frac{x_s x_k}{\tilde{D}_{sk}} \left( \frac{D_k^T}{\rho_k} - \frac{D_s^T}{\rho_s} \right) \frac{\nabla T}{T}
\end{aligned} \tag{2.395}$$

where  $s = 1, 2, \dots, N$ . This equation has been written in terms of the difference of molecular velocities,  $\mathbf{v}_s - \mathbf{v}_r$ . Equations (2.392) may then be used to write this equation in terms of any desired mass or molar fluxes. In the case of employing the mass based model form, it might be convenient to convert the mole fractions to mass fractions by use of (2.519).

It is seen from (2.397), or maybe easier from the Fickian formulation (2.310), that when the driving force (2.305) is approximated by the mole fraction gradients, there is an important difference between binary diffusion and multicomponent diffusion fluxes (e.g., Toor [152]; Taylor and Krishna [148]). In binary systems the movement of species  $s$  is always proportional to the negative of the concentration gradient of species  $s$ . In multicomponent diffusion, however, we may also experience *reverse diffusion* in which a species moves against its own concentration gradient, *osmotic diffusion* in which a species diffuses even though its concentration gradient is zero, and *diffusion barrier* when a species does not diffuse even though its concentration gradient is nonzero.

#### Mole based Maxwell-Stefan model forms

For dilute gas mixtures, a set of simplifying assumptions is normally considered very good approximations for ordinary mass transport problems. That is, the thermal diffusion mechanism is assumed negligible compared to the other mass transport phenomena for ordinary temperature gradients, the body force per unit mass is the same on each species when gravity is the only body force acting on the gas mixture, and either the pressure is constant or the molecular weights of all the species in the mixture are about the same. For such system operating conditions, the driving force (2.305) reduces to:

$$\mathbf{d}_s \approx \nabla x_s \tag{2.396}$$

The resulting set of Maxwell-Stefan equations, i.e., using the first expression in last line on the RHS of (2.392), is given by:

$$\nabla x_s = \sum_{r=1}^N \frac{x_i x_j}{\tilde{D}_{sr}} (\mathbf{v}_r - \mathbf{v}_s) = - \sum_{r=1}^N \frac{1}{c \tilde{D}_{sr}} (x_r \mathbf{N}_s - x_s \mathbf{N}_r) \tag{2.397}$$

where  $s = 1, 2, 3, \dots, N$ .

This relation is referred to as the original Maxwell-Stefan model equations, since Maxwell [95, 97] was the first to derive diffusion equations in a form analogous to (2.397) for dilute binary gas mixtures using kinetic theory arguments (i.e., Maxwell's seminal idea was that concentration gradients result from the friction between the molecules of different species, hence the proportionality coefficients,  $\hat{C}_{sk}$ , were interpreted as inverse friction or drag coefficients), and Stefan [142, 143] extended the approach to ternary dilute gas systems. It is emphasized that the original model equations were valid for ordinary diffusion only and did not include thermal, pressure, and forced diffusion. It is sometimes convenient to cast the governing set of equations into a  $N - 1$  dimensional matrix form.

Starting out from the diffusive molar fluxes, as given by the last term on the RHS of (2.392), yield:

$$\mathbf{d}_s = - \sum_{r=1}^N \frac{x_r \mathbf{J}_s^* - x_s \mathbf{J}_r^*}{c \tilde{D}_{sr}} \quad (2.398)$$

where  $s = 1, 2, 3, \dots, N$ .

However, only  $N - 1$  of the diffusion fluxes are independent, hence:

$$\mathbf{J}_N^* = - \sum_{r=1}^{N-1} \mathbf{J}_r^* \quad (2.399)$$

Using the latter relation, (2.398) may be rewritten as:

$$\begin{aligned} \mathbf{d}_s &= - \sum_{r=1}^N \frac{x_r \mathbf{J}_s^* - x_s \mathbf{J}_r^*}{c \tilde{D}_{sr}} = - \sum_{r=1}^{N-1} \frac{x_r \mathbf{J}_s^* - x_s \mathbf{J}_r^*}{c \tilde{D}_{sr}} - \left( \frac{x_N \mathbf{J}_s^* - x_s \mathbf{J}_N^*}{c \tilde{D}_{sN}} \right) \\ &= - \sum_{r=1}^{N-1} \frac{x_r \mathbf{J}_s^* - x_s \mathbf{J}_r^*}{c \tilde{D}_{sr}} - \left( \frac{x_N \mathbf{J}_s^* - x_s \left( - \sum_{r=1}^{N-1} \mathbf{J}_r^* \right)}{c \tilde{D}_{sN}} \right) \\ &= - \sum_{r=1}^{N-1} \left( - \frac{x_s \mathbf{J}_r^*}{c \tilde{D}_{sr}} + \frac{x_s \mathbf{J}_r^*}{c \tilde{D}_{sN}} \right) - \sum_{r=1}^{N-1} \frac{x_r \mathbf{J}_s^*}{c \tilde{D}_{sr}} - \frac{x_N \mathbf{J}_s^*}{c \tilde{D}_{sN}} \\ &= - \sum_{r=1}^{N-1} \left( - \frac{x_s \mathbf{J}_r^*}{c \tilde{D}_{sr}} + \frac{x_s \mathbf{J}_r^*}{c \tilde{D}_{sN}} \right) - \sum_{r=1}^N \frac{x_r \mathbf{J}_s^*}{c \tilde{D}_{sr}} \quad (2.400) \\ &= - \sum_{\substack{r=1 \\ r \neq s}}^{N-1} \left( - \frac{x_s}{c \tilde{D}_{sr}} + \frac{x_s}{c \tilde{D}_{sN}} \right) \mathbf{J}_r^* - \sum_{\substack{k=1 \\ k \neq s}}^N \frac{x_k}{c \tilde{D}_{sk}} \mathbf{J}_s^* - \frac{x_s}{c \tilde{D}_{sN}} \mathbf{J}_s^* \\ &= \frac{1}{c} \left\{ - \sum_{\substack{r=1 \\ r \neq s}}^{N-1} B_{sr} \mathbf{J}_r^* - B_{ss} \mathbf{J}_s^* \right\} \end{aligned}$$

where the coefficients  $B_{ss}$  and  $B_{sr}$  are defined by:

$$B_{sr} = -x_s \left( \frac{1}{\tilde{D}_{sr}} - \frac{1}{\tilde{D}_{sN}} \right) \quad (2.401)$$

and

$$B_{ss} = \frac{x_s}{\tilde{D}_{sN}} + \sum_{\substack{k=1 \\ k \neq s}}^N \frac{x_k}{\tilde{D}_{sk}} \quad (2.402)$$

Let  $\mathbf{d}$  and  $\mathbf{J}^*$  denote, respectively, the vectors of independent driving forces  $\mathbf{d}_1, \mathbf{d}_2, \mathbf{d}_3, \dots, \mathbf{d}_{N-1}$  and independent diffusion fluxes  $\mathbf{J}_1^*, \mathbf{J}_2^*, \mathbf{J}_3^*, \dots, \mathbf{J}_{N-1}^*$ , thus the  $N - 1$  equations can be written in the  $N - 1$  dimensional matrix form as:

$$c\mathbf{d} = -[B]\mathbf{J}^* \quad (2.403)$$

where  $[B]$  is a square matrix of order  $N - 1$ .

Then, to find an explicit expression for  $\mathbf{J}^*$  the previous relation is pre-multiplied by the inverse of  $[B]$ . The result is:

$$c[B]^{-1}\mathbf{d} = -[B]^{-1}[B]\mathbf{J}^* = -\mathbf{J}^* \quad (2.404)$$

or, more conveniently, the diffusive flux vector can be defined in terms of the driving force vector:

$$\mathbf{J}^* = -c[B]^{-1}\mathbf{d} \quad (2.405)$$

In particular cases it is desired to work with an explicit expression for the mole flux of a single species type  $s$ ,  $\mathbf{J}_s^*$ , avoiding the matrix form given above. Such an explicit model can be derived manipulating the original Maxwell-Stefan model (2.398), with the approximate driving force (2.396), assuming that the mass fluxes for all the other species are known:

$$\begin{aligned} \mathbf{J}_s^* &= \frac{-c\nabla x_s + \sum_{\substack{r=1 \\ r \neq s}}^N \frac{\mathbf{J}_r^* x_s}{\tilde{D}_{sr}}}{\sum_{\substack{r=1 \\ r \neq s}}^N \frac{x_r}{\tilde{D}_{sr}}} \\ &= D_s \left( -c\nabla x_s + \sum_{\substack{r=1 \\ r \neq s}}^N \left( \frac{\mathbf{J}_r^* x_s}{\tilde{D}_{sr}} \right) \right) \end{aligned} \quad (2.406)$$

in which  $D_s$  is given by:

$$D_s = \left( \sum_{\substack{r=1 \\ r \neq s}}^N \frac{x_r}{\tilde{D}_{sr}} \right)^{-1} \quad (2.407)$$

where  $s = 1, 2, 3, \dots, N$ . It is noted that Datta and Vilekar [30] outlined a more rigorous procedure deriving an explicit expression for the Maxwell-Stefan diffusion fluxes into the Fickian form.

A rigorous derivation of these relations were given by Curtiss and Hirschfelder [24] extending the Enskog theory to multicomponent systems. One important result of the Curtiss and Hirschfelder [24] theory of dilute mono-atomic gas mixtures is that it did show that the Maxwell-Stefan diffusivities are to a very good approximation equal to the binary diffusivities,  $\tilde{D}_{sr} \approx D_{sr}$ . On the other hand, Curtiss and Bird [26, 27] did show that for dense gases and liquids the Maxwell-Stefan equations are still valid, but the strongly concentration dependent diffusivities appearing therein are not the binary diffusivities but merely empirical parameters. It is thus noted that for these two types of systems (i.e., dense gases and liquids), the practical application of the generalized Fick's first law diffusivities and the Maxwell-Stefan diffusivities are equivalent in that both sets of coefficients require numerous costly experimentally determined data sets to enable proper parameter fitting.

#### *Mass based Maxwell-Stefan model forms*

The corresponding combined mass flux form of the Maxwell-Stefan relation can be expressed as:

$$\mathbf{d}_s = - \sum_{r=1}^N \frac{x_s x_r (\mathbf{v}_s - \mathbf{v}_r)}{\tilde{D}_{sr}} = - \sum_{r=1}^N \frac{x_s x_r \left( \frac{\mathbf{n}_s}{\omega_s} - \frac{\mathbf{n}_r}{\omega_r} \right)}{\rho \tilde{D}_{sr}} \quad (2.408)$$

The combined flux variable in the Maxwell-Stefan equation given above is then eliminated using the definition (2.394), thus:

$$\mathbf{d}_s = - \sum_{r=1}^N \frac{x_s x_r \left( \frac{\mathbf{j}_s + \rho \omega_s \mathbf{v}_m}{\omega_s} - \frac{\mathbf{j}_r + \rho \omega_r \mathbf{v}_m}{\omega_r} \right)}{\rho \tilde{D}_{sr}} = - \sum_{r=1}^N \frac{x_s x_r \left( \frac{\mathbf{j}_s}{\omega_s} - \frac{\mathbf{j}_r}{\omega_r} \right)}{\rho \tilde{D}_{sr}} \quad (2.409)$$

By use of (2.519), the Maxwell-Stefan equation can be manipulated as:

$$\begin{aligned}
\mathbf{d}_s &= - \sum_{r=1}^N \left( \frac{x_s x_r \frac{\mathbf{j}_s}{\omega_s} - x_s x_r \frac{\mathbf{j}_r}{\omega_r}}{\rho \tilde{D}_{sr}} \right) \\
&= - \sum_{r=1}^N \frac{\left( \frac{\omega_s M_w}{M_{w_s}} \right) \left( \frac{\omega_r M_w}{M_{w_r}} \right) \frac{\mathbf{j}_s}{\omega_s} - \left( \frac{\omega_s M_w}{M_{w_s}} \right) \left( \frac{\omega_r M_w}{M_{w_r}} \right) \frac{\mathbf{j}_r}{\omega_r}}{\rho \tilde{D}_{sr}} \\
&= - \frac{M_w^2}{\rho M_{w_s}} \sum_{r=1}^N \frac{\omega_r \mathbf{j}_s - \omega_s \mathbf{j}_r}{M_{w_r} \tilde{D}_{sr}}
\end{aligned} \tag{2.410}$$

However, only  $N - 1$  of the diffusion fluxes are independent, hence:

$$\mathbf{j}_N = - \sum_{r=1}^{N-1} \mathbf{j}_r \tag{2.411}$$

Eliminating the diffusive flux  $\mathbf{j}_N$  from (2.410), by use of (2.411), yields:

$$\begin{aligned}
\mathbf{d}_s \frac{\rho M_{w_s}}{M_w^2} &= - \sum_{r=1}^{N-1} \frac{\omega_r \mathbf{j}_s - \omega_s \mathbf{j}_r}{M_{w_r} \tilde{D}_{sr}} - \left( \frac{\omega_N \mathbf{j}_s - \omega_s \mathbf{j}_N}{M_{w_N} \tilde{D}_{sN}} \right) \\
&= - \sum_{r=1}^{N-1} \frac{\omega_r \mathbf{j}_s - \omega_s \mathbf{j}_r}{M_{w_r} \tilde{D}_{sr}} - \left( \frac{\omega_N \mathbf{j}_s - \omega_s \left( - \sum_{r=1}^{N-1} \mathbf{j}_r \right)}{M_{w_N} \tilde{D}_{sN}} \right) \\
&= - \sum_{r=1}^{N-1} \left( - \frac{\omega_s \mathbf{j}_r}{M_{w_r} \tilde{D}_{sr}} + \frac{\omega_s \mathbf{j}_r}{M_{w_N} \tilde{D}_{sN}} \right) - \sum_{r=1}^{N-1} \left( \frac{\omega_r \mathbf{j}_s}{M_{w_r} \tilde{D}_{sr}} \right) - \left( \frac{\omega_N \mathbf{j}_s}{M_{w_N} \tilde{D}_{sN}} \right) \\
&= - \sum_{r=1}^{N-1} \left( - \frac{\omega_s \mathbf{j}_r}{M_{w_r} \tilde{D}_{sr}} + \frac{\omega_s \mathbf{j}_r}{M_{w_N} \tilde{D}_{sN}} \right) - \sum_{r=1}^N \left( \frac{\omega_r \mathbf{j}_s}{M_{w_r} \tilde{D}_{sr}} \right) \\
&= - \sum_{\substack{r=1 \\ r \neq s}}^{N-1} \left( - \frac{\omega_s \mathbf{j}_r}{M_{w_r} \tilde{D}_{sr}} + \frac{\omega_s \mathbf{j}_r}{M_{w_N} \tilde{D}_{sN}} \right) - \left( - \frac{\omega_s \mathbf{j}_s}{M_{w_s} \tilde{D}_{ss}} + \frac{\omega_s \mathbf{j}_s}{M_{w_N} \tilde{D}_{sN}} \right) \\
&\quad - \sum_{\substack{r=1 \\ r \neq s}}^N \left( \frac{\omega_r \mathbf{j}_s}{M_{w_r} \tilde{D}_{sr}} \right) - \left( \frac{\omega_s \mathbf{j}_s}{M_{w_s} \tilde{D}_{ss}} \right) \\
&= - \sum_{\substack{r=1 \\ r \neq s}}^{N-1} \left( - \frac{\omega_s}{M_{w_r} \tilde{D}_{sr}} + \frac{\omega_s}{M_{w_N} \tilde{D}_{sN}} \right) \mathbf{j}_r - \left( \frac{\omega_s}{M_{w_N} \tilde{D}_{sN}} + \sum_{\substack{k=1 \\ k \neq s}}^N \left( \frac{\omega_k}{M_{w_k} \tilde{D}_{sk}} \right) \right) \mathbf{j}_s
\end{aligned} \tag{2.412}$$

A more compact notation is achieved introducing two coefficient matrices:

$$\mathbf{d}_s = -\frac{M_w^2}{\rho M_{w_s}} \left( \sum_{\substack{r=1 \\ r \neq s}}^{N-1} B'_{sr} \mathbf{j}_r + B'_{ss} \mathbf{j}_s \right) \quad (2.413)$$

where the coefficient matrices  $B_{sr}$  and  $B_{ss}$  are defined by:

$$B'_{sr} = -\omega_s \left( \frac{1}{M_{w_r} \tilde{D}_{sr}} - \frac{1}{M_{w_N} \tilde{D}_{sN}} \right) \quad (2.414)$$

and

$$B'_{ss} = \frac{\omega_s}{M_{w_N} \tilde{D}_{sN}} + \sum_{\substack{k=1 \\ k \neq s}}^N \frac{\omega_k}{M_{w_k} \tilde{D}_{sk}} \quad (2.415)$$

The diffusion flux can then be written on the vector form:

$$\mathbf{j} = -\frac{\rho(\mathbf{M}_w)}{M_w^2} [B']^{-1} \mathbf{d} \quad (2.416)$$

For the particular cases in which the model for the driving force reduces to the mole fraction gradient, an explicit relation for  $\mathbf{j}_s$  can be expressed in terms of the other unknown fluxes  $\mathbf{j}_r$ . This nonlinear model must thus be solved by an iteration procedure. Besides, when the mass based formulation is used, it is convenient to rewrite the driving force in terms of the corresponding mass fraction gradient:

$$\mathbf{d}_s \approx \nabla x_s = \nabla \left( \frac{\omega_s M_w}{M_{w_s}} \right) = \frac{1}{M_{w_s}} \nabla (\omega_s M_w) = \frac{1}{M_{w_s}} (\omega_s \nabla M_w + M_w \nabla \omega_s) \quad (2.417)$$

By inserting (2.417) into (2.410), gives:

$$\frac{1}{M_{w_s}} (\omega_s \nabla M_w + M_w \nabla \omega_s) = -\frac{M_w^2}{\rho M_{w_s}} \sum_{r=1}^N \frac{\omega_r \mathbf{j}_s - \omega_s \mathbf{j}_r}{M_{w_r} \tilde{D}_{sr}} \quad (2.418)$$

After multiplication by  $M_{w_s}/M_w$ , this expression can be manipulated as:

$$\omega_s \nabla \ln(M_w) + \nabla \omega_s = \frac{M_w}{\rho} \sum_{r=1}^N \frac{\omega_s \mathbf{j}_r - \omega_r \mathbf{j}_s}{M_{w_r} \tilde{D}_{sr}} \quad (2.419)$$

The RHS of the relation can be further manipulated, as the terms for  $r = s$  cancel out. The result is given by:

$$\omega_s \nabla \ln(M_w) + \nabla \omega_s = \frac{M_w}{\rho} \left( \sum_{\substack{r=1 \\ r \neq s}}^N \frac{\omega_s \mathbf{j}_r}{M_{w_r} \tilde{D}_{sr}} - \mathbf{j}_s \sum_{\substack{r=1 \\ r \neq s}}^N \frac{\omega_r}{M_{w_r} \tilde{D}_{sr}} \right) \quad (2.420)$$

An explicit relation for the diffusive flux of species  $s$ ,  $\mathbf{j}_s$ , can be obtained with minor manipulation:

$$\mathbf{j}_s = D'_s \left( -\rho \omega_s \nabla \ln(M_w) - \rho \nabla \omega_s + M_w \omega_s \sum_{\substack{r=1 \\ r \neq s}}^N \frac{\mathbf{j}_r}{M_{w_r} \tilde{D}_{sr}} \right) \quad (2.421)$$

where the effective mass based diffusion coefficient is defined by:

$$D'_s = \left( M_w \sum_{\substack{r=1 \\ r \neq s}}^N \frac{\omega_r}{M_{w_r} \tilde{D}_{sr}} \right)^{-1} \quad (2.422)$$

The relation (2.421) can be used to solve the set of Maxwell-Stefan equations iteratively.

Kleijn [65] used this Maxwell-Stefan formulation simulating chemical vapor deposition reactors. One advantage of this explicit formula is that the multicomponent flux is relatively easy to implement as user defined functions in commercial flow codes. However, the conventional matrix form probably enables the design of more efficient solution strategies.

#### *Maxwell-Stefan model consistency with Fick's first law*

The consistency with Fick's first law for binary systems (2.301) is examined comparing the generalized Fickian mass flux vectors (2.310), including the Maxwell-Stefan diffusivity (2.391), the Bird et al. [9] generalized Fickian diffusivity (2.311), and the binary diffusivity. For binary systems, i.e.,  $s, r = 1, 2$ , the Fickian mass flux vector (2.310) reduces to:

$$\begin{aligned} \mathbf{j}_1 &= -D_1^T \nabla \ln T - \rho_1 (\hat{D}_{11} \mathbf{d}_1 + \hat{D}_{12} \mathbf{d}_2) = -D_1^T \nabla \ln T + \rho \hat{D}_{12} \mathbf{d}_1 \\ &= -D_1^T \nabla \ln T + \rho \left\{ -\tilde{D}_{12} \frac{\omega_1 \omega_2}{x_1 x_2} \right\} \mathbf{d}_1 \approx -D_1^T \nabla \ln T + \rho \left\{ -D_{12} \frac{\omega_1 \omega_2}{x_1 x_2} \right\} \mathbf{d}_1 \\ &= -D_1^T \nabla \ln T - \rho \mathbb{D}_{12} \mathbf{d}_1 = -D_1^T \nabla \ln T - \rho \left\{ \tilde{D}_{12} \frac{\omega_1 \omega_2}{x_1 x_2} \right\} \mathbf{d}_1 \end{aligned} \quad (2.423)$$

where we have used the additional requirements that  $\mathbf{j}_1 + \mathbf{j}_2 = 0$  in accordance with (2.293),  $\mathbf{d}_1 + \mathbf{d}_2 = 0$  due to the properties specified for the generalized driving force (2.305). For binary mixtures, the current diffusivities (2.310) have the following

properties  $\omega_1 \hat{D}_{11} + \omega_2 \hat{D}_{21} = \omega_1 \hat{D}_{12} + \omega_2 \hat{D}_{22} = 0$ , and  $\hat{D}_{12} = \hat{D}_{21}$ . For dilute gases the multicomponent Fickian diffusivities  $\tilde{D}_{12}$  are also related to the Maxwell-Stefan and Fick's first law diffusivities as shown by Curtiss [25] and tabulated by Curtiss and Bird [26, 27] and Bird et al. [9], i.e.,  $\hat{D}_{11} = -\frac{\omega_2 \omega_2}{x_1 x_2} \tilde{D}_{12}$  and  $\hat{D}_{12} = -\frac{\omega_1 \omega_2}{x_1 x_2} \tilde{D}_{12}$ . It is further noticed that for gases at low density the Maxwell-Stefan diffusivities are approximately equal to the Fick first law binary diffusivities, i.e.  $\tilde{D}_{12} \approx D_{12}$ .

Comparing the binary diffusivities  $\hat{D}_{12}$  and the Maxwell-Stefan diffusivity  $\tilde{D}_{12}$  and the Fick's first law diffusivity  $D_{12}$ , it is revealed that these coefficients differ by a factor that is a function of the composition. Moreover, these diffusivities do not even have the same sign. It is noted, however, that for binary mixtures the alternative Fickian binary diffusivity  $\mathbb{D}_{12}$  do have the same sign as the Maxwell-Stefan and thus the Fick's first law binary diffusivities. This explains why the plus sign was chosen in (2.311). The binary form of the generalized Maxwell-Stefan equation (2.423) might also be combined with the extended generalized diffusional driving force vector (2.369).

The result is:

$$\begin{aligned}
 \mathbf{j}_1 &= -D_1^T \nabla \ln T + \rho \left\{ -\tilde{D}_{12} \frac{\omega_1 \omega_2}{x_1 x_2} \right\} \mathbf{d}_1 = -D_1^T \nabla \ln T - \left( \frac{c^2}{\rho} \right) M_{\omega_1} M_{\omega_2} \tilde{D}_{12} \mathbf{d}_1 \\
 &= -D_1^T \nabla \ln T - \left( \frac{c^2}{\rho} \right) M_{\omega_1} M_{\omega_2} \tilde{D}_{12} \\
 &\quad \times \left[ \frac{x_1}{RT} \left( \frac{\partial \tilde{G}_1}{\partial x_2} \right)_{T,P} \nabla x_2 + \frac{x_1 M_{w_1}}{RT} \left[ \left( \check{V} - \frac{1}{\rho} \right) \nabla p - \omega_2 (\mathbf{g}_1 - \mathbf{g}_2) \right] \right] \\
 &= -D_1^T \nabla \ln T - \left( \frac{c^2}{\rho} \right) M_{\omega_1} M_{\omega_2} \tilde{D}_{12} \\
 &\quad \times \left[ \left( \frac{\partial \ln a_1^m}{\partial \ln x_1} \right)_{T,P} \nabla x_1 + \frac{x_1 M_{w_1}}{RT} \left[ \left( \check{V} - \frac{1}{\rho} \right) \nabla p - \omega_2 (\mathbf{g}_1 - \mathbf{g}_2) \right] \right] \quad (2.424)
 \end{aligned}$$

If the pressure-, thermal-, and forced-diffusion terms are dropped, the binary diffusivities can be expressed as:

$$\mathbf{j}_1 = -\frac{c^2}{\rho} M_{w_1} M_{w_2} \left\{ \tilde{D}_{12} \left( \frac{\partial \ln a_1^m}{\partial \ln x_1} \right)_{T,P} \right\} \nabla x_1 \quad (2.425)$$

The driving force can also be expressed in terms of the mass fraction gradient using (2.524):

$$\begin{aligned}
 \mathbf{j}_1 &= -\frac{c^2}{\rho} M_{\omega_1} M_{\omega_2} \left\{ \tilde{D}_{12} \left( \frac{\partial \ln a_1^m}{\partial \ln x_1} \right)_{T,P} \right\} \left[ \left( \frac{\rho}{c} \right)^2 \frac{1}{M_{\omega_1} M_{\omega_2}} \nabla \omega_1 \right] \\
 &= -\rho \left\{ \tilde{D}_{12} \left( \frac{\partial \ln a_1^m}{\partial \ln x_1} \right)_{T,P} \right\} \nabla \omega_1 = -\rho D_{12} \nabla \omega_1 \quad (2.426)
 \end{aligned}$$



where we have used the relation (2.524) between mole and mass fraction gradients;  $\nabla x_1 = M_\omega^2 \nabla \omega_1 / (M_{\omega_1} M_{\omega_2})$ . This result confirms that for binary systems the Maxwell-Stefan model reduces to the Fick's first law (2.301). Moreover, it follows that for dilute gas systems  $D_{12} \approx \tilde{D}_{12}$ . Similarly, it can be shown that the Fick's first law diffusivity is the same whether this law is formulated on a mass or molar basis.

It is informative to express the overall binary mass diffusion flux (2.424) as a linear sum of the four terms [7, 9, 55, 132] and examine the importance of each of the mass diffusion flux vector contributions in chemical reactor analysis:

$$\mathbf{j}_1 = \mathbf{j}_1^o + \mathbf{j}_1^p + \mathbf{j}_1^g + \mathbf{j}_1^T \quad (2.427)$$

The relative importance of the various contributions to the overall mass diffusion flux in chemical reactor analysis is discussed in Sect. 1.2.2.

The *ordinary diffusion flux*, which is normally significant in reactor analysis, is expressed as:

$$\mathbf{j}_1^o = -\rho \left\{ \tilde{D}_{12} \left( \frac{\partial \ln a_1^m}{\partial \ln x_1} \right)_{T,p} \right\} \nabla \omega_1 = -\rho D_{12} \nabla \omega_1 \quad (2.428)$$

where  $\nabla x_1 = M_\omega^2 \nabla \omega_1 / (M_{\omega_1} M_{\omega_2})$ .

For non-ideal mixtures, the Fick first law binary diffusivity,  $D_{12}$ , can thus be expressed in terms of the Maxwell-Stefan diffusivity,  $\tilde{D}_{12}$ , by:

$$D_{12} = \tilde{D}_{12} \left( \frac{\partial \ln a_1^m}{\partial \ln x_1} \right)_{T,p} \quad (2.429)$$

The *pressure diffusion* is given by:

$$\mathbf{j}_1^p = \frac{M_{w_1} x_1}{RT} \left( \check{V} - \frac{1}{\rho} \right) \nabla p \quad (2.430)$$

This term is significant in systems where there are very large pressure gradients [91]. However, the operating pressure gradients in chemical reactors are usually not large enough so this term is not significant in reactor models.

The *forced diffusion* is expressed as:

$$\mathbf{j}_1^g = -\frac{M_{w_1} x_1 \omega_2}{RT} (\mathbf{g}_1 - \mathbf{g}_2) \quad (2.431)$$

which may be of importance describing aqueous electrolytes [91]. If gravity is the only external force, as in most chemical reactors, then  $\mathbf{g}_1 = \mathbf{g}_2 = \mathbf{g}$  and  $\mathbf{j}_1^{(g)}$  vanishes.

The *thermal diffusion* term is written as:

$$\mathbf{j}_1^T = -D_1^T \nabla \ln T \quad (2.432)$$

This term is usually not important in reactor modeling, since sufficiently large temperature gradients are not common in chemical process plants.

*Application of the Maxwell-Stefan model to dense gases and liquids*

For non-ideal systems the Maxwell-Stefan diffusivities for multicomponent dense gases and liquids deviate from the Fick first law binary coefficients derived from kinetic theory and are thus merely empirical parameters [26]. Hence, for non-ideal systems either  $D_{12}$  or  $\tilde{D}_{12}$  must be fitted to experimental data. In the first approach the actual diffusivities  $D_{12}$  are measured directly, thus this procedure requires no additional activity data. In the second approach the non-ideal effects are divided from the Maxwell-Stefan diffusivities. These are the binary Maxwell-Stefan coefficients,  $\tilde{D}_{12}$ , that are fitted to experimental diffusivity data. The non-ideality corrections may be computed from a suitable thermodynamic model. These thermodynamic models generally contains numerous model parameters that have to be fitted to suitable thermodynamic data. This type of simulations were performed extensively by Taylor and Krishna [148]. The various forms of the multicomponent diffusion flux formulations are all of limited utility in describing multicomponent diffusion in non-ideal systems as they all contain a large number of empirical parameters that have to be determined experimentally.

### 2.9.5.5 The Approximate Wilke Multicomponent Diffusion Flux Model

Wilke [161] proposed a simpler model for calculating the effective diffusion coefficients for diffusion of a species  $s$  into a multicomponent mixture of stagnant gases. For dilute gases the Maxwell-Stefan diffusion equation is reduced to a multicomponent diffusion flux model on the binary Fick's law form in which the binary diffusivity is substituted by an effective multicomponent diffusivity. The Wilke model derivation is examined in the sequel.

*Approximate mole based Wilke diffusion model*

The combined molar flux of species  $s$  in a binary mixture is defined in accordance with (2.393), using Fick's law:

$$\mathbf{N}_s = c_s \mathbf{v}_m^* + \mathbf{J}_s^* = x_s c \mathbf{v}_m^* - c D_{sr} \nabla x_s = x_s (\mathbf{N}_s + \mathbf{N}_r) - c D_{sr} \nabla x_s \quad (2.433)$$

in which  $c \mathbf{v}_m^* = \mathbf{N}_s + \mathbf{N}_r$  for binary mixtures.

Wilke [161], among others, postulated that an analogous equation for the combined molar flux of species  $s$  in a multicomponent mixture can be written as [7] (p. 571):

$$\mathbf{N}_s = x_s \sum_{r=1}^N \mathbf{N}_r - c D_{sm} \nabla x_s \quad (2.434)$$

where  $D_{sm}$  represents the effective diffusion coefficient of component  $s$  with respect to the composition of the multicomponent gas mixture.

To express the effective diffusion coefficient in terms of the known binary diffusivities Wilke invoked the Maxwell-Stefan equation. From the last line on the RHS of (2.392) a particular form of the Maxwell-Stefan equation is given:

$$\nabla x_s = \sum_{\substack{r=1 \\ r \neq s}}^N \frac{1}{c \tilde{D}_{sr}} (x_s \mathbf{N}_r - x_r \mathbf{N}_s) \quad (2.435)$$

For dilute systems all gases except the species  $s$  molecules are being stagnant, hence all the fluxes denoted by  $\mathbf{N}_r$ , for  $r \neq s$ , are zero. Thus, the Wilke relation (2.434) reduces to:

$$\mathbf{N}_s = -\frac{c D_{sm}}{1 - x_s} \nabla x_s, \quad (2.436)$$

and the Maxwell-Stefan equation (2.435) yields:

$$\nabla x_s = -\sum_{\substack{r=1 \\ r \neq s}}^N \frac{1}{c \tilde{D}_{sr}} x_r \mathbf{N}_s \quad (2.437)$$

Then, by solving (2.436) for  $\nabla x_s$  and equating the result to the simplified driving force (2.396) in the Maxwell-Stefan equations (2.435), we get (see [7], p. 571 and [34]):

$$\frac{1}{D_{sm}} = \frac{1}{(1 - x_s)} \sum_{\substack{r=1 \\ r \neq s}}^N \frac{x_r}{\tilde{D}_{sr}} \quad (2.438)$$

The diffusion of species  $s$  in a multicomponent mixture can then be written in the form of Fick's law of binary diffusion, using the effective diffusion coefficient  $D_{sm}$  instead of the binary diffusivity. The Wilke equation is defined by:

$$\mathbf{J}_s^* = -c D_{sm} \nabla x_s \quad (2.439)$$

However, the Wilke equation does not in general satisfy the constraint that the species mole fractions must sum to 1 [22].

A similar model often used by reaction engineers is derived for the limiting case in which all the convective fluxes can be neglected. Consider a dilute component  $s$  that diffuses into a homogeneous mixture, then  $\mathbf{J}_r^* \approx 0$  for  $r \neq s$ . To describe this molecular transport the Maxwell-Stefan equations given by the last line in (2.392) are adopted. With the given restrictions, the model reduces to:

$$\nabla x_s = \sum_{\substack{r=1 \\ r \neq s}}^N \frac{1}{c \tilde{D}_{sr}} (x_s \mathbf{J}_r^* - x_r \mathbf{J}_s^*) \approx -\sum_{\substack{r=1 \\ r \neq s}}^N \frac{1}{c \tilde{D}_{sr}} x_r \mathbf{J}_s^* \quad (2.440)$$

By solving the effective multicomponent diffusion flux, as postulated by Wilke (2.439), for  $\nabla x_s$  and equating the result to the simplified driving force (2.396) in the Maxwell-Stefan equations (2.440), the result is:

$$\frac{1}{D_{sm}} = \sum_{\substack{r=1 \\ r \neq s}}^N \frac{x_r}{\tilde{D}_{sr}} \quad (2.441)$$

This simple relation provides fair approximations of the molecular fluxes for several multicomponent systems in which  $s$  is a trace component [114] (p. 597).

*Approximate mass based Wilke diffusion model*

The corresponding mass based Wilke approximate formulation [161] is outlined next. In this model the diffusion of species  $s$  in a multicomponent mixture is written in the form of Fick's law with an effective diffusion coefficient  $D'_{sm}$  instead of the conventional binary molecular diffusion coefficient. Following the ideas of Wilke [161] we postulate that an equation for the combined mass flux of species  $s$  in a multicomponent mixture can be written as:

$$\mathbf{n}_s = \omega_s \sum_{r=1}^N \mathbf{n}_r - \rho D'_{sm} \nabla \omega_s \quad (2.442)$$

where  $D'_{sm}$  represents the effective diffusion coefficient of component  $s$  with respect to the mass based composition of the multicomponent gas mixture.

From the second last line on the RHS of (2.392) a particular form of the Maxwell-Stefan equation is given:

$$\nabla x_s = \sum_{\substack{r=1 \\ r \neq s}}^N \frac{x_s x_r (\frac{\mathbf{n}_r}{\omega_r} - \frac{\mathbf{n}_s}{\omega_s})}{\rho \tilde{D}_{sr}} \quad (2.443)$$

For dilute systems all gases except the species  $s$  molecules are being stagnant, hence all the fluxes denoted by  $\mathbf{n}_r$ , for  $r \neq s$ , are zero. Hence, the Wilke relation (2.442) reduces to:

$$\mathbf{n}_s = - \frac{\rho D'_{sm}}{1 - \omega_s} \nabla \omega_s, \quad (2.444)$$

The Maxwell-Stefan equation (2.443) reduces to:

$$\nabla x_s \approx - \sum_{\substack{r=1 \\ r \neq s}}^N \frac{x_s x_r \frac{\mathbf{n}_s}{\omega_s}}{\rho \tilde{D}_{sr}} \quad (2.445)$$

Noting that the driving force can be expressed in terms of mass fractions instead of mole fractions in according to (2.417), and by transforming the mole fractions on the RHS into mass fractions, the relation above can be written as:

$$\omega_s \nabla M_w + M_w \nabla \omega_s \approx - \frac{M_w^2 \mathbf{n}_s}{\rho} \sum_{\substack{r=1 \\ r \neq s}}^N \frac{\omega_r}{M_{w_r} \tilde{D}_{sr}} \quad (2.446)$$

With minor manipulation this relation can be written as:

$$\nabla \omega_s \approx - \frac{M_w \mathbf{n}_s}{\rho} \sum_{\substack{r=1 \\ r \neq s}}^N \frac{\omega_r}{M_{w_r} \tilde{D}_{sr}} - \omega_s \frac{\nabla M_w}{M_w} \quad (2.447)$$

For dilute mixtures consisting of species having about the same molecular weight, the last term on the RHS of (2.447) might be neglected:

$$\nabla \omega_s \approx - \frac{M_w \mathbf{n}_s}{\rho} \sum_{\substack{r=1 \\ r \neq s}}^N \frac{\omega_r}{M_{w_r} \tilde{D}_{sr}} \quad (2.448)$$

By solving (2.444) for  $\nabla \omega_s$  and equating the result to the same gradient as derived from the simplified Maxwell-Stefan equations (2.448), we obtain an expression for the effective mass based diffusivity:

$$\frac{1}{D'_{sm}} \approx \frac{M_w}{1 - \omega_s} \sum_{\substack{r=1 \\ r \neq s}}^N \frac{\omega_r}{M_{w_r} \tilde{D}_{sr}} \quad (2.449)$$

This effective diffusivity expression is consistent with the multicomponent diffusive flux written on the Fick's law form:

$$\mathbf{j}_s = -\rho D'_{sm} \nabla \omega_s, \quad (2.450)$$

which might be applied when the given restrictions are fulfilled.

### 2.9.5.6 Combined Bulk and Knudsen Diffusion Fluxes: The Wilke-Bosanquet and Dusty Gas Models

To describe the combined bulk and Knudsen diffusion fluxes in the transition gas transport regime, the simple Wilke-Bosanquet model [11, 70, 151] and the more rigorous *dusty gas model* [62, 70, 71, 94] can be used either on the mass or molar forms. Knudsen diffusion refers to a gas transport regime where the mean free

path between particle-particle collisions is significantly larger than the characteristic spatial dimension of the system considered. The transition region between Knudsen and bulk diffusion is of considerable importance because many processes involving gas transport in restricted geometries lies in this region.

From the classic Knudsen formula the value of the Knudsen diffusion transport coefficient,  $D_{i,K}$ , can be computed [46, 66, 67]:

$$D_{s,K} = \frac{d_{\text{pore}}}{3} \sqrt{\frac{8RT}{\pi M_s}} = \frac{2}{3} \sqrt{\frac{8R}{\pi}} \frac{d_{\text{pore}}}{2} \sqrt{\frac{T}{M_s}} \approx 97.0 \frac{d_{\text{pore}}}{2} \left( \frac{T}{M_s} \right)^{1/2} \quad (2.451)$$

where  $R = 8.3143 \times 10^3$  [Nm/(kg mol K)].

The Knudsen formula (2.451) was originally verified [66, 67] in macro-pores, i.e. pore size in the range of 50 nm to 50  $\mu\text{m}$ , but is widely applied at the meso-pore scale with adsorption effects neglected [6]. Because of the assumption that every gas-wall collision is purely diffusive, the computed Knudsen diffusion coefficient by (2.451) is considered to be an ideal upper limit [61]. The adsorption effect (van der Waals interactions) lowers the Knudsen diffusivities because adsorption causes the molecules to “stick” to the wall, and perhaps hop to a neighboring adsorption site, rather than return to the bulk after collision. Hence, the trajectory of a weakly adsorbed gas molecule strikes the pore wall and return to the bulk largely in keeping with the diffusive reflection scenario prescribed by the Knudsen theory. On the other hand, the trajectory of strongly adsorbed species are largely influenced by the hopping of the molecules to neighboring positions along the surface, rather than being reflected into the “core” of the pore. The validity of the Knudsen formula (2.451) is thus based on the requirement that the time during which the molecules are in the free space (i.e., under the influence of the uniform potential of the gas phase) significantly exceeds the time during which the molecules experience the attractive forces of the surface. This is equivalent to the requirement that the number of molecules in “bulk” notably exceed the number of molecules closer to the surface [74]. Because equation (2.451) holds in the limiting case of purely diffusive collision, i.e. when the molecules does not adsorb at pore walls, the validity of the correlation is debated in the literature. The results of the studies of [6, 72–75] cast doubts on the validity of the Bosanquet—and dusty gas models when applied to mixtures in which at least one of the species has strong adsorption characteristics, because of the neglect of van der Waals interactions between the wall and the diffusing molecules in the purely hard sphere analysis of Knudsen.

#### *The Wilke-Bosanquet model*

As a first approach to calculate the combined bulk and Knudsen diffusive flux using a Fickian flux formulation, the *Bosanquet formula* [11] has been suggested in literature [11, 70, 151]. In this approach, the Fick form formulation uses a diffusivity computed as the reciprocal additivity of the diffusion coefficients in the ordinary and Knudsen diffusion regimes.

*Mole based Wilke-Bosanquet model*

Similar to (2.439) the diffusion flux is:

$$\mathbf{J}_s = -cD_{s,\text{eff}}\nabla x_s \quad (2.452)$$

The  $D_{s,\text{eff}}$  is given by the harmonic average relation of Bosanquet [11, 151]:

$$\frac{1}{D_{s,\text{eff}}} = \frac{1}{D_{sm}} + \frac{1}{D_{s,K}} \quad (2.453)$$

where  $D_{sm}$  is given by (2.438) and the Knudsen diffusivity  $D_{s,K}$  can be calculated from (2.451) which is derived based on the Kinetic theory principles [46].

*Mass based Wilke-Bosanquet model*

Similar to (2.450) the diffusion flux is:

$$\mathbf{j}_s = -\rho D'_{s,\text{eff}}\nabla \omega_s, \quad (2.454)$$

The  $D'_{s,\text{eff}}$  is given by the analogue harmonic average relation of Bosanquet [11, 151]:

$$\frac{1}{D'_{s,\text{eff}}} = \frac{1}{D'_{sm}} + \frac{1}{D_{s,K}} \quad (2.455)$$

where  $D'_{sm}$  is given by (2.449) and the Knudsen diffusivity  $D_{s,K}$  can be calculated from (2.451).

The effective Knudsen diffusion coefficients are proportional to the pore diameter and independent of pressure, while the bulk diffusivities are independent of pore diameter and inversely proportional to pressure [62]. However, both bulk diffusivities and Knudsen diffusivities are dependent on the temperature. Relations for the Knudsen transport coefficient and binary diffusivities are represented in Table 2.1.

*Mole based dusty-gas model*

The dusty gas model represents an extension of the Maxwell-Stefan bulk diffusion model where a description of the Knudsen diffusion mechanisms is included. In order to include the Knudsen molecule—wall collision mechanism in the Maxwell-Stefan model originally derived considering bulk gas molecule-molecule collisions only, the wall (medium) molecules are treated as an additional pseudo component in the gas mixture. The pore wall medium is approximated as consisting of giant molecules, called *dust*, which are uniformly distributed in space and held stationary by an external clamping force. This implies that both the diffusive flux and the concentration gradient with respect to the dust particles vanish.

For the  $N + 1$ -component pseudo-mixture we may modify the formulation of the Maxwell-Stefan equation given in the last line of (2.392) and the generalized diffusional driving force expression (2.305). The dusty gas model can be expressed as:

**Table 2.1** Relations for Knudsen and binary diffusion coefficients based on kinetic theory of gases

Knudsen diffusion coefficient [46, 66, 67]:

$$D_{s,K} = 97.0 \frac{d_{\text{pore}}}{2} \left( \frac{T}{M_s} \right)^{1/2} \quad (2.451)$$

Binary diffusion coefficients [114]:

$$D_{s,r} = \frac{0.00266 \cdot 101325 T^{3/2}}{0.01^2 p \Omega_{D,sr} \sigma_{sr}^2 M_{sr}^{1/2}} \quad (2.627)$$

where the property units are;  $D_{s,r}$  [ $\text{m}^2/\text{s}$ ],  $p$  [Pa], and  $T$  [K].

The property functions are:

The molecular weight factor [kg/kmol] is defined as:

$$M_{sr} = 2 \left( \frac{1}{M_s} + \frac{1}{M_r} \right)^{-1} \quad (2.456)$$

The  $\sigma_{sr}$  [ $\text{\AA}$ ] denotes the characteristic Lennard-Jones diameter:

$$\sigma_{sr} = \frac{\sigma_s + \sigma_r}{2} \quad (2.457)$$

The Lennard-Jones characteristic energy [J] is approximated as:

$$\epsilon_{sr} = (\epsilon_s \epsilon_r)^{1/2} \quad (2.458)$$

The dimensionless collision integral,  $\Omega_{D,sr}$ , is given as:

$$\Omega_{sr} = \frac{A}{(T_{sr}^{**})^B} + \frac{C}{\exp(DT_{sr}^{**})} + \frac{E}{\exp(FT_{sr}^{**})} + \frac{G}{\exp(HT_{sr}^{**})} \quad (2.459)$$

where

$$\begin{array}{lll} T_{sr}^{**} = kT/\epsilon_{sr} & A = 1.06036 & B = 0.15610 \\ C = 0.19300 & D = 0.47635 & E = 1.03587 \\ F = 1.52996 & G = 1.76474 & H = 3.89411 \end{array} \quad (2.460)$$

$$\begin{aligned} - \sum_{r=1}^N \frac{N'_s x'_r - N'_r x'_s}{c' \tilde{D}'_{sr}} - \frac{N'_s x'_{N+1} - N'_{N+1} x'_s}{c' \tilde{D}'_{s,N+1}} &= \nabla x'_s + \frac{(x'_s - \omega'_s) \nabla p'}{p'} \\ &\quad - \frac{c'_s \mathbf{g}'_s - \omega'_s \sum_{r=1}^{N+1} c'_r \mathbf{g}'_r}{p'} \end{aligned} \quad (2.461)$$

where  $s = 1, 2, \dots, N+1$ . However, only  $N$  of these equations are independent. It is thus required to solve  $(N-1)$  equations for the bulk species and 1 for the pseudo-component denoting the pore wall medium.

The quantities marked with a prime refer to the pseudo-mixture, that is the gas mixture with the dust molecules. This distinction will be maintained by writing  $p'$ ,  $c'$ ,  $x'_s$ ,  $\tilde{D}'_{sr}$  and  $\omega'_s$  for the quantities referred to the pseudo-mixture and  $p$ ,  $c$ ,  $x_s$ ,  $\tilde{D}_{sr}$  and  $\omega_s$  for the same quantities referred to the actual ideal gas. Note also that for the species concentrations  $c_s$ , partial pressures  $p_s$  and the molar flux vectors there are no distinction between the two quantities.

To ensure that the dust molecules are motionless,  $N'_{N+1} = 0$ , a net external force is used to prevent them from moving in response to any gas pressure gradients [71]:

$$\nabla p = c_{N+1} \mathbf{g}_{N+1} \quad (2.462)$$



Moreover, it is assumed that there are no external forces acting on the actual species,  $\mathbf{g}_s = 0$  for  $s = 1, \dots, N$ . The form of the  $q$  independent equations is thus given by:

$$-\sum_{r=1}^N \frac{\mathbf{N}'_s x'_r - \mathbf{N}'_r x'_s}{c' \tilde{D}'_{sr}} - \frac{\mathbf{N}'_s x'_{N+1}}{c' \tilde{D}'_{s,N+1}} = \nabla x'_s + \frac{(x'_s - \omega'_s) \nabla p'}{p'} + \frac{\omega'_s c_{N+1} \mathbf{g}_{N+1}}{p'} \quad (2.463)$$

To obtain a form of the dusty gas model that can be used in practice the primed variables associated with the pseudo-mixture have to be transformed to the un-primed variables associated with the gas.

The two first terms on the RHS can be formulated as:

$$\begin{aligned} \nabla x'_s + \frac{x'_s}{p'} \nabla p' &= \nabla \left( \frac{p'_s}{p'} \right) + \frac{x'_s}{p'} \nabla p' = p'_s \nabla \left( \frac{1}{p'} \right) + \frac{1}{p'} \nabla p'_s + \frac{x'_s}{p'} \nabla p' \\ &= -\frac{p'_s}{p'^2} \nabla p' + \frac{1}{p'} \nabla p'_s + \frac{x'_s}{p'} \nabla p' \\ &= -\frac{x'_s}{p'} \nabla p' + \frac{1}{p'} \nabla p'_s + \frac{x'_s}{p'} \nabla p' = \frac{1}{p'} \nabla p'_s \end{aligned} \quad (2.464)$$

From the equation of state for an ideal gas we observe:

$$p' = c' RT = (c + c_{N+1}) RT = p + c_{N+1} RT \quad (2.465)$$

Hence, applying the nabla operator yields:

$$\nabla p' = \nabla p + c_{N+1} R \nabla T \quad (2.466)$$

Inserting this result into (2.462), gives:

$$c_{N+1} \mathbf{g}_{N+1} = \nabla p' - c_{N+1} R \nabla T \quad (2.467)$$

By use of the ideal gas law, (2.464) can be rewritten as:

$$\frac{1}{p'} \nabla p'_s = \frac{1}{c' RT} \nabla (c'_s RT) = \frac{c'_s \nabla (\ln T)}{c'} + \frac{\nabla c'_s}{c'} \quad (2.468)$$

Then, employing these formulas, (2.463) can be rewritten as:

$$\begin{aligned}
-\sum_{r=1}^N \frac{\mathbf{N}'_s x'_r - \mathbf{N}'_r x'_s}{c' \tilde{D}'_{sr}} - \frac{\mathbf{N}'_s x'_{N+1}}{c' \tilde{D}'_{s,N+1}} &= \nabla x'_s + \frac{x'_s \nabla p'}{p'} - \frac{\omega'_s \nabla p'}{p'} + \frac{\omega'_s c_{N+1} \mathbf{g}_{N+1}}{p'} \\
&= \frac{1}{p'} \nabla p'_s - \frac{\omega'_s \nabla p'}{p'} + \frac{\omega'_s (\nabla p' - c_{N+1} R \nabla T)}{p'} \\
&= \frac{c'_s \nabla (\ln T)}{c'} + \frac{\nabla c'_s}{c'} + \frac{\omega'_s c_{N+1} R \nabla T}{p'} \quad (2.469)
\end{aligned}$$

To complete the transformation of the dusty gas model containing primed quantities into the un-primed variables associated with the actual gas, one must employ the following definitions:

$$x'_s = \frac{c'_s}{c'} \quad (2.470)$$

$$c'_s = c_s \quad (2.471)$$

$$\tilde{D}_{sr}^e = \frac{c' \tilde{D}'_{sr}}{c} \quad (2.472)$$

$$\tilde{D}_{sK}^e = \frac{\tilde{D}'_{s,N+1}}{x'_{N+1}} \quad (2.473)$$

$$x_s = \frac{c_s}{c} \quad (2.474)$$

$$\mathbf{N}'_s = \mathbf{N}_s \quad (2.475)$$

Multiplying the first term on the LHS of (2.469) by  $c'/c'$ , we obtain:

$$-\sum_{r=1}^N \frac{\mathbf{N}'_s x'_r c' - \mathbf{N}'_r x'_s c'}{c'^2 \tilde{D}'_{sr}} = -\sum_{r=1}^N \frac{\mathbf{N}_s c_r - \mathbf{N}_r c_s}{c'^2 \tilde{D}'_{sr}} = -\sum_{r=1}^N \frac{\mathbf{N}_s x_r - \mathbf{N}_r x_s}{c' \tilde{D}_{sr}^e} \quad (2.476)$$

The mass fraction of species  $s$  can be expressed as:

$$\begin{aligned}
\omega'_s &= \frac{m_s}{m_{total}} = \frac{\frac{m_s}{V}}{\frac{m_{total}}{V}} = \frac{\rho_s}{\rho_{total}} = \frac{\rho_s}{\sum_{r=1}^N \rho_r + \rho_{N+1}} = \frac{c_s M_{w_s}}{\sum_{r=1}^N (c_r M_{w_r}) + c_{N+1} M_{w_{N+1}}} \quad (2.477)
\end{aligned}$$

When  $M_{w_{N+1}} \rightarrow \infty$ ,  $\omega'_s \rightarrow 0$ , so the last term on the RHS of (2.469) vanishes. Hence, (2.469) becomes:

$$-\sum_{r=1}^N \frac{\mathbf{N}_s x_r - \mathbf{N}_r x_s}{\tilde{D}_{sr}^e} - \frac{\mathbf{N}'_s x'_{N+1}}{\tilde{D}'_{s,N+1}} \approx c_s \nabla (\ln T) + \nabla c_s \quad (2.478)$$

By employing the relations;  $\tilde{D}_{sK}^e = \frac{\tilde{D}'_{s,N+1}}{x'_{N+1}}$  and  $\mathbf{N}'_s = \mathbf{N}_s$ , we get:

$$-\sum_{r=1}^N \frac{\mathbf{N}_s x_r - \mathbf{N}_r x_s}{\tilde{D}_{sr}^e} - \frac{\mathbf{N}_s}{\tilde{D}_{sK}^e} = c_s \nabla(\ln T) + \nabla c_s \quad (2.479)$$

Moreover, by use of the ideal gas law;  $c_s = \frac{p_s}{RT}$ , the RHS can be manipulated like:

$$\begin{aligned} -\sum_{r=1}^N \frac{\mathbf{N}_s x_r - \mathbf{N}_r x_s}{\tilde{D}_{sr}^e} - \frac{\mathbf{N}_s}{\tilde{D}_{sK}^e} &= \frac{p_s}{RT} \nabla(\ln T) + \nabla \frac{p_s}{RT} \\ &= \frac{p_s}{RT^2} \nabla T + \nabla \frac{p_s}{RT} \\ &= \frac{p_s}{RT^2} \nabla T + \frac{p_s}{R} \nabla \left( \frac{1}{T} \right) + \frac{1}{RT} \nabla p_s \\ &= \frac{p_s}{RT^2} \nabla T - \frac{p_s}{RT^2} \nabla T + \frac{1}{RT} \nabla p_s \\ &= \frac{1}{RT} \nabla p_s = \frac{c}{p} \nabla p_s \approx c \nabla x_s \end{aligned} \quad (2.480)$$

Note that the final expression on the RHS is valid for ideal gases at constant pressure only.

By splitting the combined molar flux (2.393), we obtain:

$$\sum_{r=1}^N \frac{(\mathbf{J}_s^* + c_s \mathbf{v}_m^*) x_r - (\mathbf{J}_r^* + c_r \mathbf{v}_m^*) x_s}{\tilde{D}_{sr}^e} + \frac{\mathbf{J}_s^* + c_s \mathbf{v}_m^*}{\tilde{D}_{sK}^e} \approx -c \nabla x_s \quad (2.481)$$

By simple manipulation, the commonly used mole form of the dusty gas model is achieved:

$$\sum_{r=1}^N \frac{\mathbf{J}_s^* x_r - \mathbf{J}_r^* x_s}{\tilde{D}_{sr}^e} + \frac{\mathbf{J}_s^* + c_s \mathbf{v}_m^*}{\tilde{D}_{sK}^e} \approx -c \nabla x_s \quad (2.482)$$

It is sometimes advantageous to use an explicit expression, similar to (2.406), for the diffusive flux. To achieve such an expression, we must reformulate the model by first re-arranging the terms in the following way:

$$\mathbf{J}_s^* \sum_{r=1}^N \frac{x_r}{\tilde{D}_{sr}^e} - \sum_{r=1}^N \frac{\mathbf{J}_r^* x_s}{\tilde{D}_{sr}^e} + \frac{\mathbf{J}_s^*}{\tilde{D}_{sK}^e} + \frac{c_s \mathbf{v}_m^*}{\tilde{D}_{sK}^e} \approx -c \nabla x_s \quad (2.483)$$

Since the terms occurring for  $r = s$  in the two sums cancel out, we get:

$$\mathbf{J}_s^* \left( \sum_{\substack{k=1 \\ k \neq s}}^N \frac{x_k}{\tilde{D}_{sk}^e} + \frac{1}{\tilde{D}_{sK}^e} \right) - \sum_{\substack{r=1 \\ r \neq s}}^N \frac{\mathbf{J}_r^* x_s}{\tilde{D}_{sr}^e} + \frac{c_s \mathbf{v}_m^*}{\tilde{D}_{sK}^e} \approx -c \nabla x_s \quad (2.484)$$

or, explicitly:

$$\mathbf{J}_s^* \approx D_s^e \left( \sum_{\substack{r=1 \\ r \neq s}}^N \frac{\mathbf{J}_r^* x_s}{\tilde{D}_{sr}^e} - \frac{c_s \mathbf{v}_m^*}{\tilde{D}_{sK}^e} - c \nabla x_s \right) \quad (2.485)$$

where

$$D_s^e \approx \left( \sum_{\substack{k=1 \\ k \neq s}}^N \frac{x_k}{\tilde{D}_{sk}^e} + \frac{1}{\tilde{D}_{sK}^e} \right)^{-1} \quad (2.486)$$

In some cases the convective term on the LHS of (2.482) can be neglected since  $\mathbf{J}_s^* \gg c_s \mathbf{v}_m^*$ . For such problems the dusty gas model (2.482) reduces to:

$$\sum_{\substack{r=1 \\ r \neq s}}^N \frac{\mathbf{J}_s^* x_r - \mathbf{J}_r^* x_s}{\tilde{D}_{sr}^e} + \frac{\mathbf{J}_s^*}{\tilde{D}_{sK}^e} \approx -c \nabla x_s \quad (2.487)$$

This relation can be written in the matrix form:

$$\mathbf{J}_s^* \left( \sum_{\substack{k=1 \\ k \neq s}}^N \frac{x_k}{\tilde{D}_{sk}^e} + \frac{1}{\tilde{D}_{sK}^e} \right) - \sum_{\substack{r=1 \\ r \neq s}}^N \frac{\mathbf{J}_r^* x_s}{\tilde{D}_{sr}^e} \approx -c \nabla x_s \quad (2.488)$$

or more compactly:

$$\mathbf{J}_s^* B_{ss} + \sum_{\substack{r=1 \\ r \neq s}}^N \mathbf{J}_r^* B_{sr} \approx -c \nabla x_s \quad (2.489)$$

with the coefficients:

$$B_{ss} = \left( \sum_{\substack{k=1 \\ k \neq s}}^N \frac{x_k}{\tilde{D}_{sk}^e} + \frac{1}{\tilde{D}_{sK}^e} \right) \quad (2.490)$$

and

$$B_{sr} = -\frac{x_s}{\tilde{D}_{sr}^e} \quad (2.491)$$

In vector notation, the flux relation (2.489) can thus be expressed in terms of the  $[B]$  matrix:

$$[B] \mathbf{J}^* = -c \nabla \mathbf{x} \quad (2.492)$$

After multiplying both sides by  $[B]^{-1}$ , this relation takes a more convenient form:

$$\mathbf{J}^* = -c[B]^{-1} \nabla \mathbf{x} \quad (2.493)$$

It is emphasized that in this description the gas molecule-dust interactions are accounted for by a set of effective Knudsen diffusion coefficients. Therefore, the dusty gas model contains two types of effective binary diffusion coefficients, the effective binary pair diffusivities in the porous medium and the effective Knudsen diffusivities. The effective diffusivities are related to the corresponding molecular diffusivities by:

$$\tilde{D}_{sr}^e = \tilde{D}_{sr} \frac{\varepsilon}{\tau} \quad (2.494)$$

and

$$\tilde{D}_{sK}^e = \tilde{D}_{sK} \frac{\varepsilon}{\tau} \quad (2.495)$$

where the porosity-to-tortuosity factor ( $\frac{\varepsilon}{\tau}$ ) characterizes the porous matrix and is best determined by experiment. Epstein [38] provides physical interpretations of the  $\varepsilon$  and  $\tau$  parameters. For dilute gases, both the molecular bulk and Knudsen diffusivities can be derived from kinetic theory.

#### *Mass based dusty-gas model*

On the mass basis, the dusty gas model can be written in analogy to (2.469) in the following way:

$$-\sum_{r=1}^N \frac{\frac{\mathbf{n}'_s x'_r x'_s}{\omega'_s} - \frac{\mathbf{n}'_r x'_s x'_r}{\omega'_r}}{\rho' \tilde{D}'_{sr}} - \frac{\frac{\mathbf{n}'_s x'_s x'_{N+1}}{\omega'_s}}{\rho' \tilde{D}'_{s,N+1}} = \frac{c'_s \nabla(\ln T)}{c'} + \frac{\nabla c'_s}{c'} \quad (2.496)$$

when  $M_{w_{N+1}} \rightarrow \infty$ ,  $\omega'_s \rightarrow 0$  in accordance with (2.477).

To close the mass form of the dusty gas model, using a similar transformation procedure as employed for the mole based formulation, three novel definitions are required:

$$\mathbf{n}'_s = \mathbf{n}_s \quad (2.497)$$

$$\mathbf{j}'_s = \mathbf{j}_s \quad (2.498)$$

$$\rho'_s = \rho_s \quad (2.499)$$

We multiply the first term on the LHS by  $c'^2/c'^2$  and the second term on the LHS by  $c'/c'$ :

$$-\sum_{r=1}^N \frac{\frac{\mathbf{n}_s}{\omega'_s} (x'_r c') (x'_s c') - \frac{\mathbf{n}_r}{\omega'_r} (x'_s c') (x'_r c')}{(c')^2 \rho' \tilde{D}'_{sr}} - \frac{\frac{\mathbf{n}_s}{\omega'_s} (x'_s c') x'_{N+1}}{c' \rho' \tilde{D}'_{s,N+1}} = \frac{c'_s \nabla(\ln T)}{c'} + \frac{\nabla c'_s}{c'} \quad (2.500)$$

Thereby, all the primed terms of the pseudo-mixture can then be transformed into the actual un-primed variables:

$$-\sum_{r=1}^N \frac{\frac{n_s}{\rho_s} c_r c_s - \frac{n_r}{\rho_r} c_s c_r}{c D_{sr}^e} - \frac{\frac{n_s}{\rho_s} c_s}{D_{sK}^e} = c_s \nabla(\ln T) + \nabla c_s \quad (2.501)$$

Thereafter, the terms containing the actual un-primed mixture variables can be re-written by use of (2.394) and the ideal gas law:

$$\sum_{r=1}^N \frac{\frac{x_r x_s}{\omega_s} \mathbf{j}_s - \frac{x_s x_r}{\omega_r} \mathbf{j}_r}{D_{sr}^e} + \frac{\frac{x_s}{\omega_s} \mathbf{j}_s + \mathbf{v}_m c_s M_w}{D_{sK}^e} = -\rho \nabla x_s \quad (2.502)$$

This form of the mass based dusty gas model equation, which corresponds with the mole based formulation (2.481), is restricted to constant pressure systems.

To enable effective computations it is convenient to rewrite the mole fractions into mass fractions, hence the dusty gas model takes the form:

$$\frac{M_w^2}{M_{w_s}} \sum_{\substack{r=1 \\ r \neq s}}^N \frac{\omega_r \mathbf{j}_s - \omega_s \mathbf{j}_r}{M_{w_r} D_{sr}^e} + \frac{M_w \mathbf{j}_s + \mathbf{v}_m \rho_s M_w}{M_{w_s} D_{sK}^e} = -\frac{\rho}{M_{w_s}} (\omega_s \nabla M_w + M_w \nabla \omega_s) \quad (2.503)$$

From this expression an explicit expression for  $\mathbf{j}_s$  can be obtained:

$$\mathbf{j}_s = D_s^e \left( M_w^2 \sum_{\substack{r=1 \\ r \neq s}}^N \frac{\omega_r \mathbf{j}_r}{M_{w_r} D_{sr}^e} - \frac{\mathbf{v}_m \rho_s M_w}{D_{sK}^e} - \rho (\omega_s \nabla M_w + M_w \nabla \omega_s) \right) \quad (2.504)$$

where

$$D_s^e = \left( M_w^2 \sum_{\substack{r=1 \\ r \neq s}}^N \frac{\omega_r}{M_{w_r} D_{sr}^e} + \frac{M_w}{D_{sK}^e} \right)^{-1} \quad (2.505)$$

In the particular cases in which the convective term can be neglected,  $\mathbf{j}_s \gg \rho \mathbf{v}_m \omega_s$ , the dusty gas model (2.503) reduces to:

$$M_w^2 \sum_{\substack{r=1 \\ r \neq s}}^N \frac{\omega_r \mathbf{j}_s - \omega_s \mathbf{j}_r}{M_{w_r} D_{sr}^e} + \frac{M_w \mathbf{j}_s}{D_{sK}^e} = -\rho (\omega_s \nabla M_w + M_w \nabla \omega_s) \quad (2.506)$$

The model can be written in a matrix form:

$$\mathbf{j}_s \left( M_w^2 \sum_{\substack{k=1 \\ k \neq s}}^N \frac{\omega_k}{M_{w_k} D_{sk}^e} + \frac{M_w}{D_{sK}^e} \right) - M_w^2 \sum_{\substack{r=1 \\ r \neq s}}^N \frac{\omega_s \mathbf{j}_r}{M_{w_r} D_{sr}^e} = -\rho (\omega_s \nabla M_w + M_w \nabla \omega_s) \quad (2.507)$$

A more compact notation is obtained introducing two coefficient matrices:

$$\mathbf{j}_s B_{ss} + \sum_{\substack{r=1 \\ r \neq s}}^N \mathbf{j}_r B_{sr} = -\rho(\omega_s \nabla M_w + M_w \nabla \omega_s) \quad (2.508)$$

The coefficient matrices are defined by:

$$B_{ss} = M_w^2 \sum_{\substack{k=1 \\ k \neq s}}^N \frac{\omega_k}{M_{w_k} D_{sk}^e} + \frac{M_w}{D_{sK}^e} \quad (2.509)$$

and

$$B_{sr} = -M_w^2 \frac{\omega_s}{M_{w_r} D_{sr}^e} \quad (2.510)$$

In vector notation, the mass based dusty gas model becomes:

$$\mathbf{j} = -\rho[B'']^{-1}(\omega \nabla M_w + M_w \nabla \omega) \quad (2.511)$$

From (2.480) a less restricted driving force can be derived avoiding the constant pressure assumption. The extended driving force can be expressed by:

$$\mathbf{d}_s \approx c \frac{\nabla p_s}{p} \approx \frac{\nabla(p x_s)}{RT} = \frac{1}{M_{w_s} RT} (p(\omega_s \nabla M_w + M_w \nabla \omega_s) + M_w \omega_s \nabla p) \quad (2.512)$$

In this case the dusty gas diffusive mass flux can be written as:

$$\mathbf{j} = -\rho[B'']^{-1} \frac{1}{RT} (p\omega \nabla M_w + pM_w \nabla \omega + M_w \omega \nabla p) \quad (2.513)$$

The design of a complete set of *governing equations* for the description of reactive flows requires that the combined fluxes are treated in a convenient way. In principle, several combined flux definitions are available. However, since the mass fluxes with respect to the mass average velocity are preferred when the equation of motion is included in the problem formulation, we apply the species mass balance equations to a  $q$ -component gas system with  $q - 1$  independent mass fractions  $\omega_s$  and an equal number of independent diffusion fluxes  $\mathbf{j}_s$ . However, any of the formulations derived for the multicomponent mass diffusion flux can be substituted into the species mass balance (1.39), hence a closure selection optimization is required considering the specified restrictions for each constitutive model and the computational efforts needed to solve the resulting set of model equations for the particular problem in question.

The notation and definitions used for the molar and mass based concentrations, compositions and velocities characterizing multicomponent mixtures, as well as the relationships between these variables are summarized in Table 2.2.

**Table 2.2** Notation for concentrations and velocities in multicomponent mixtures

Algebraic concentration and velocity relations:

$$c_s = \rho_s / M_{\omega_s} \qquad \rho_s = c_s M_{\omega_s} \qquad (2.514)$$

$$c = \sum_{s=1}^N c_s \qquad \rho = \sum_{s=1}^N \rho_s \qquad (2.515)$$

$$x_s = c_s / c \qquad \omega_s = \rho_s / \rho \qquad (2.516)$$

$$\sum_{s=1}^N x_s = 1 \qquad \sum_{s=1}^N \omega_s = 1 \qquad (2.517)$$

$$M_{\omega} = \sum_{s=1}^N x_s M_{\omega_s} \qquad \frac{1}{M_{\omega}} = \sum_{s=1}^N \frac{\omega_s}{M_{\omega_s}} \qquad (2.518)$$

$$x_s = \frac{\omega_s / M_{\omega_s}}{\sum_{r=1}^N \omega_r / M_{\omega_r}} \qquad \omega_s = \frac{x_s M_{\omega_s}}{\sum_{r=1}^N x_r M_{\omega_r}} \qquad (2.519)$$

$$\mathbf{v}^* = \sum_{r=1}^N \omega_s \mathbf{v}_s \qquad \mathbf{v} = \sum_{r=1}^N \omega_s \mathbf{v}_s \qquad (2.520)$$

$$\mathbf{v} - \mathbf{v}^* = \sum_{r=1}^N \omega_s (\mathbf{v}_s - \mathbf{v}^*) \qquad \mathbf{v}^* - \mathbf{v} = \sum_{r=1}^N x_s (\mathbf{v}_s - \mathbf{v}) \qquad (2.521)$$

Differential composition relations for multicomponent mixtures [9]:

$$\nabla x_s = -\frac{M_{\omega}^2}{M_{\omega_s}} \sum_{\substack{r=1 \\ r \neq s}}^N \left[ \frac{1}{M_{\omega}} + \omega_s \left( \frac{1}{M_{\omega_r}} - \frac{1}{M_{\omega_s}} \right) \right] \nabla \omega_r \qquad (2.522)$$

$$\nabla \omega_s = -\frac{M_{\omega_s}}{M_{\omega}^2} \sum_{\substack{r=1 \\ r \neq s}}^N \left[ M_{\omega} + x_s (M_{\omega_r} - M_{\omega_s}) \right] \nabla x_r \qquad (2.523)$$

Differential composition relations for binary systems [9]:

$$\nabla x_1 = \frac{\frac{1}{M_{\omega_1} M_{\omega_2}} \nabla \omega_1}{\left( \frac{\omega_1}{M_{\omega_1}} + \frac{\omega_2}{M_{\omega_2}} \right)^2} \qquad (2.524)$$

$$\nabla \omega_1 = \frac{M_{\omega_1} M_{\omega_2} \nabla x_1}{(x_1 M_{\omega_1} + x_2 M_{\omega_2})^2} \qquad (2.525)$$

### 2.9.6 Polyatomic Reactive Systems

For polyatomic reactive systems the mixture continuity, momentum and energy equations seemingly remain unchanged compared to the corresponding conservation equations for multicomponent non-reacting mono-atomic gases, as  $m_s$ ,  $m_s \mathbf{C}_s$ , and  $e_s^{\text{total}} = \frac{1}{2} m_s C_s^2 + e_s^{\text{int}}$  are summation invariants. Note that  $e_s^{\text{total}}$  denotes the total energy which equals the sum of the translational and internal energy forms. The polyatomic molecules have rotational and vibrational energy modes and the corresponding internal degrees of freedom [129]. Moreover, for polyatomic reactive systems the species mass balance deviates from the corresponding one for non-reactive systems in that it includes a reaction rate term resulting from collisions of molecules of type  $s$  with all types of molecules [55]. This means that when deriving this particular transport equation from basic principles, the collision term on the RHS of the Boltzmann equation (2.296) must be modified to account for the effects of chemical reactions. Correspondingly, transforming the mixture energy balance in terms of temperature the resulting temperature equation is slightly dif-



ferent from that of mono-atomic gases in that it contains a heat of reaction term. In addition, as expected, the Enskog perturbation solution of the mixture Boltzmann equation (2.289) is more involved than the corresponding one for simple systems containing one type of species only. However, the expressions for the fluxes in terms of the distribution function are unaffected by the reaction taking place in the gas mixture.

### 2.9.6.1 An Outline of the Seminal Friction Coefficient Concept of Maxwell

Maxwell [95, 97] was the first to derive a set of diffusion equations in a form analogous to (2.397) for dilute binary gas mixtures using kinetic theory arguments. Maxwell's [95, 97] seminal idea was that concentration gradients result from the friction between the molecules of different species, hence the proportionality coefficients,  $\hat{C}_{sk}$ , were interpreted as inverse friction or drag coefficients.

The rigorous derivation of the Maxwell-Stefan equations by use of the kinetic theory of dilute gases has already been explained in connection with (2.383) to (2.392). Nevertheless, although not very useful in practical application, it might be informative from a physical point of view to start out from the complete macroscopic species momentum balance when examining the consistent derivation of the Maxwell-Stefan equations in terms of the mass diffusion fluxes. However, it is noted that the following macroscopic derivation is not as rigorous as the alternative kinetic theory approach. The linear momentum principle for species  $s$  states that the rate of change of momentum is balanced by the forces acting on the system and the rate of production of momentum of species  $s$  [110, 159]:

$$\begin{aligned} \frac{D}{Dt} \int_{V_s(t)} \rho_s \mathbf{v}_s dv &= \int_{V_s(t)} \rho_s \mathbf{g}_s dv + \int_{A_s(t)} \mathbf{n} \cdot \mathbf{T}_s da + \int_{V_s(t)} \sum_{r=1}^N \mathbf{P}_{sr} dv \\ &+ \int_{V_s(t)} r_s \mathbf{v}_s^* dv \end{aligned} \quad (2.526)$$

where  $\rho_s \mathbf{g}_s$  represents the body force acting on species  $s$ . The term  $\mathbf{n} \cdot \mathbf{T}_s$  represents the species stress vector. The term  $\mathbf{P}_{sr}$  denotes the force per unit volume exerted by species  $r$  on species  $s$ , and the sum in the balance equation represents the force exerted on species  $s$  by all the other species. The last term  $r_s \mathbf{v}_s^*$  designates the source of species momentum. Note that the velocity of the molecules of species  $s$  generated by chemical reaction,  $\mathbf{v}_s^*$ , need not be equal to the species  $s$  velocity  $\mathbf{v}_s$ .

To convert the system balance description into an Eulerian control volume formulation the transport theorem is employed (i.e., expressed in terms of the species  $s$  velocity,  $\mathbf{v}_s$ ):

$$\frac{D}{Dt} \int_{V_s(t)} f dv = \int_{V_s} \frac{\partial f}{\partial t} dv + \int_{A_s} f \mathbf{v}_s \cdot \mathbf{n} da \quad (2.527)$$

in which  $f$  represents any scalar, vector or tensor valued function.

To convert the area integrals into volume integrals the Gauss theorem is used (App A) in the standard manner.

The transformed momentum balance yields:

$$\int_{V_s} \left( \frac{\partial(\rho_s \mathbf{v}_s)}{\partial t} + \nabla \cdot (\rho_s \mathbf{v}_s \mathbf{v}_s) - \rho_s \mathbf{g}_s - \nabla \cdot \mathbf{T}_s - \sum_{r=1}^N \mathbf{P}_{sr} - r_s \mathbf{v}_s^* \right) dv = 0 \quad (2.528)$$

From Chap. 1 it is known that this balance has to be valid for any volume, hence the integral argument must be equal to zero:

$$\frac{\partial(\rho_s \mathbf{v}_s)}{\partial t} + \nabla \cdot (\rho_s \mathbf{v}_s \mathbf{v}_s) - \rho_s \mathbf{g}_s - \nabla \cdot \mathbf{T}_s - \sum_{r=1}^N \mathbf{P}_{sr} - r_s \mathbf{v}_s^* = 0 \quad (2.529)$$

This balance equation can also be derived from kinetic theory [159]. In the Maxwellian average Boltzmann equation for the species  $s$  type of molecules, the collision operator does not vanish because the momentum  $m_s \mathbf{c}_s$  is not an invariant quantity. Rigorous determination of the collision operator in this balance equation is hardly possible, thus an appropriate model closure for the diffusive force  $\mathbf{P}_{sr}$  is required. Maxwell [95] proposed a model for the diffusive force based on the principles of kinetic theory of dilute gases. The dilute gas kinetic theory result of Maxwell [95] is generally assumed to be an acceptable form for dense gases and liquids as well, although for these mixtures the binary diffusion coefficient is a concentration dependent, experimentally determined empirical parameter.

The elementary modeling of the *diffusion force* is outlined in the sequel. For dilute multicomponent mixtures only elastic binary collisions are considered and out of these merely the unlike-molecule collisions result in a net transfer of momentum from one type of species to another. The overall momentum is conserved since all the collisions are assumed to be elastic (see Sect. 2.4.2.1), hence the net force acting on species  $s$  from  $r$  per unit volume,  $\mathbf{P}_{sr}$  equals the momentum transferred from  $r$  to  $s$  per unit time and unit volume (see e.g., [30] and [109], Sect. 4-2).

The diffusion force yields:

$$\mathbf{P}_{sr} = \mathbf{M}_{sr} Z_{sr} \quad (2.530)$$

where  $\mathbf{M}_{sr}$  represents the momentum flux transferred per collision, and  $Z_{sr}$  denotes the number of collisions between species  $s$  and  $r$  molecules per unit time and unit volume (the collision density).

Several closures have been proposed to calculate the collision density for molecules in gas mixtures [109] (pp. 52–55). To derive these expressions for the collision density one generally perform an analysis of the particle-particle interactions in an imaginary container [80, 109, 135], called the conceptual collision cylinder in kinetic theory, as outlined in Sect. 2.4.2.5. A fundamental assumption in this concept is that the rate of molecular collisions in a gas depends upon the size, number density, and average speed of the molecules. Following Maxwell [95] each type of molecules are considered hard spheres, resembling billiard balls, having diameter  $d_s$ , mass  $m_s$  and number density  $n_s$ . These hard spheres exert no forces on

each other except when they collide. Moreover, the collisions are perfectly elastic and obey the classical conservation laws of momentum and energy. In addition, the particles are uniformly distributed through the gas. Different approximations of the hitherto unknown average molecular speeds  $\langle c_s \rangle_M$  and  $\langle c_r \rangle_M$  can then be made. Suppose that a molecule of type  $s$  moves with an average speed of  $\langle |\mathbf{c}_s| \rangle_M = \langle c_s \rangle_M$  in an imaginary container that contains both  $s$  and  $r$  molecules. Preliminary, in line with the early models, we may assume that the molecules of  $r$  are stationary (this restriction will be removed shortly). Since we are using the billiard ball molecular model, a collision occurs each time the distance between the center of a molecule  $s$  and a molecule  $r$  becomes equal to  $d_{sr} = (d_s + d_r)/2$  in accordance with (2.142). This means that if we construct an imaginary sphere of radius  $d_{sr}$  around the center of molecule  $s$ , a collision occurs every time another molecule  $r$  is located within this sphere as the molecule  $s$  enclosed within the imaginary sphere travels with its average speed sweeping out a cylindrical volume  $\sigma_{AT} \langle c_s \rangle_M = \pi d_{sr}^2 \langle c_s \rangle_M$  per unit time. The total collision cross section is defined by (2.151). If  $n_r$  is the total number of  $r$  molecules per unit mixture volume, the number of centers of  $r$  molecules in the volume swept out is  $\sigma_{AT} \langle c_s \rangle_M n_r$ . This number equals the number of collisions experienced by the one molecule of  $s$  in unit time, hence the collision frequency (2.167) can be expressed by:

$$Z_{s-r} = \sigma_{AT} \langle c_s \rangle_M n_r \quad (2.531)$$

in which the same notation as used in the last part of Sect. 2.4.2 is employed. A reasonable approximation of the molecular speed may be calculated from the Maxwellian distribution function following the kinetic theory presented in Sect. 2.4.2.

Moreover, if there is a total of  $n_s$  molecules of  $s$  per unit volume in addition to the  $r$  molecules, the collision density  $Z_{sr}$  denoting the total number of  $s-r$  collisions per unit volume per unit time is:

$$Z_{sr} = Z_{s-r} n_s = \sigma_{AT} \langle c_s \rangle_M n_r n_s \quad (2.532)$$

If only the  $s$  type of molecules are present, the collision density  $Z_{ss}$  represents the collisions of  $s$  molecules with one another. The expression for this density resembles that for  $Z_{sr}$  but a pre-factor  $1/2$  has to be introduced to avoid counting each collision twice:

$$Z_{ss} = \frac{1}{2} \sigma_{AT} \langle c_s \rangle_M n_s n_s \quad (2.533)$$

This expression coincides with (2.165) when the speed is calculated from the Maxwellian velocity distribution function.

In the collision density formulas presented so far the target molecules  $r$  within the collision cylinder are assumed stagnant, hence only the averaged speed  $\langle c_s \rangle_M$  of the  $s$  molecules is considered. A better estimate of the collision density might be obtained allowing the target molecules to move within the collision cylinder, thus the average relative speeds  $\langle |\mathbf{c}_{\text{rel},sr}| \rangle_M$  and  $\langle |\mathbf{c}_{\text{rel},ss}| \rangle_M$  of the molecules should be used instead of the average speed of the individual species. Furthermore, dealing with a

mixture containing two types of molecules  $s$  and  $r$  of different masses, the  $\langle c_s \rangle_M$  and  $\langle c_r \rangle_M$  values are different. A fairly accurate model is achieved considering that the average relative speed is given by  $\langle |\mathbf{c}_{\text{rel},sr}| \rangle_M = (\langle c_s \rangle_M^2 + \langle c_r \rangle_M^2)^{1/2}$ . This average speed relation is derived using the Maxwellian distribution function as shown by Present [109] (p. 79, p. 53, p. 30). A rigorous collision density model can then be expressed as:

$$Z_{sr} = \sigma_{AT} \langle |\mathbf{c}_{\text{rel},sr}| \rangle_M x_r x_s n^2 = \sigma_{AT} \sqrt{\langle c_s \rangle_M^2 + \langle c_r \rangle_M^2} x_r x_s n^2 \quad (2.534)$$

If the gas contains only type  $s$  molecules, the average relative speed of two molecules becomes  $\langle |\mathbf{c}_{\text{rel},ss}| \rangle_M = (\langle c_s \rangle_M^2 + \langle c_s \rangle_M^2)^{1/2} = \sqrt{2} \langle c_s \rangle_M$ . Hence, the expression for  $Z_{ss}$  has to be modified replacing  $\langle c_s \rangle_M$  by  $\sqrt{2} \langle c_s \rangle_M$ , giving:

$$Z_{ss} = \frac{1}{\sqrt{2}} \sigma_{AT} \langle c_s \rangle_M n_s n_s \quad (2.535)$$

The corresponding expression for the number of collisions of one molecule of  $s$  per unit time, when only  $s$  molecules are present, becomes:

$$Z_s = \sqrt{2} \sigma_{AT} \langle c_s \rangle_M n_s \quad (2.536)$$

It is noted that the collision cross-sectional area, also referred to as the total scattering cross section (2.151), can be approximated in different ways too. In one approach the target particles are approximated as point-like particles. Thus, the cross section of the target particles are not considered in calculating the effective cross-sectional area, so  $\sigma_{AT} \approx \pi d_s^2/4$ . To achieve an improved estimate of the effective cross-sectional area the size of the target particles should be taken into account as well, thus  $\sigma_{AT} = \pi d_{sr}^2$ .

The net *momentum flux* transferred from molecules of type  $s$  to molecules of type  $r$  can be approximated by the difference between the average momentum of molecule  $s$  before and after the collision:

$$\mathbf{M}_{sr} = m_s (\mathbf{v}_s - \mathbf{v}'_s) \quad (2.537)$$

In the literature the net momentum flux transferred from molecules of type  $s$  to molecules of type  $r$  has either been expressed in terms of the average diffusion velocity for the different species in the mixture [109] or the average species velocity is used [148]. Both approaches lead to the same relation for the diffusion force and thus the Maxwell-Stefan multicomponent diffusion equations. In this book we derive an approximate formula for the diffusion force in terms of the average velocities of the species in the mixture. The diffusive fluxes are introduced at a later stage by use of the combined flux definitions. Nevertheless, the given momentum flux formula (2.537) is not useful before the unknown average velocity after the collisions  $\mathbf{v}'_s$  has been determined. For elastic molecular collisions this velocity can be calculated, in

an averaged sense, from the classical momentum conservation law and the definition of the center of mass velocity as elucidated in the following.

The velocity of the center of mass, as defined relative to a fixed point in space, can be obtained from the expression given for position vector of the center of mass (2.104):

$$\mathbf{G} = \frac{m_s \mathbf{v}_s + m_r \mathbf{v}_r}{m_s + m_r} \quad (2.538)$$

If all possible particle-particle approaches are considered, the ensemble average velocities after the collision will be equal to  $\mathbf{G} = \mathbf{G}' = \text{Constant}$ , because all directions of reflection or rebound are assumed to occur with equal likelihood in kinetic theory of dilute gases [109]. By ensemble averaging, we may write:

$$\mathbf{v}'_s = \mathbf{v}'_r = \mathbf{G}' = \mathbf{G} \quad (2.539)$$

One recalls from (1.345) that the ensemble averaged of a species  $k$  velocity  $\langle \mathbf{c}'_k \rangle_e$  is defined by:

$$\mathbf{v}'_k = \langle \mathbf{c}'_k \rangle_e = \frac{1}{N} \sum_{i=1}^N \mathbf{c}'_{k,i} \quad (2.540)$$

where  $N$  is the number of events (collisions) observed.

An ensemble averaged momentum balance considering  $N$  binary collisions between  $s$  and  $r$  molecules is obtained by averaging (2.107). The result is:

$$m_s \mathbf{v}_s + m_r \mathbf{v}_r = m_s \mathbf{v}'_s + m_r \mathbf{v}'_r \quad (2.541)$$

Inserting (2.539) into (2.541) gives:

$$m_s \mathbf{v}_s + m_r \mathbf{v}_r = m_s \mathbf{v}'_s + m_r \mathbf{v}'_r = m_s \mathbf{G}' + m_r \mathbf{G}' = (m_s + m_r) \mathbf{G}' \quad (2.542)$$

Solving for  $\mathbf{v}'_s = \mathbf{G}'$  the relation becomes:

$$\mathbf{v}'_s = \mathbf{G}' = \frac{m_s \mathbf{v}_s + m_r \mathbf{v}_r}{m_s + m_r} = \text{Constant} \quad (2.543)$$

By assuming that an ensemble average velocity equals a Maxwellian average velocity, we might introduce (2.543) into (2.537). In this way we get:

$$\mathbf{M}_{sr} = m_s \left( \mathbf{v}_s - \frac{m_s \mathbf{v}_s + m_r \mathbf{v}_r}{m_s + m_r} \right) \quad (2.544)$$

If we multiply the first term on the RHS by  $\frac{m_s + m_r}{m_s + m_r}$ , the relation can be manipulated as:

$$\begin{aligned}
\mathbf{M}_{sr} &= m_s \left( \mathbf{v}_s \left( \frac{m_s + m_r}{m_s + m_r} \right) - \frac{m_s \mathbf{v}_s + m_r \mathbf{v}_r}{m_s + m_r} \right) \\
&= m_s \left( \frac{m_s \mathbf{v}_s + m_r \mathbf{v}_s - m_s \mathbf{v}_s - m_r \mathbf{v}_r}{m_s + m_r} \right) \\
&= m_s \left( \frac{m_r \mathbf{v}_s - m_r \mathbf{v}_r}{m_s + m_r} \right) \\
&= \frac{m_s m_r (\mathbf{v}_s - \mathbf{v}_r)}{m_s + m_r}
\end{aligned} \tag{2.545}$$

By inserting (2.534) and (2.545) into (2.530), the diffusion force can be expressed as:

$$\mathbf{P}_{sr} = \mathbf{M}_{sr} Z_{sr} = x_r x_s (\mathbf{v}_s - \mathbf{v}_r) \frac{m_s m_r \pi n^2 d_{sr}^2 \sqrt{\langle c_s \rangle_M^2 + \langle c_r \rangle_M^2}}{m_s + m_r} \tag{2.546}$$

It has been proposed to insert a proportionality (drag or friction) coefficient that does not depend on the mole fractions and the velocities  $\mathbf{v}_s$  and  $\mathbf{v}_r$ . The diffusion force is thus expressed as:

$$\mathbf{P}_{sr} = x_r x_s (\mathbf{v}_s - \mathbf{v}_r) f_{sr} \tag{2.547}$$

The binary friction coefficient has been related to the binary diffusivity by the following relation [95, 148]:

$$f_{sr} = \frac{p}{\tilde{D}_{sr}} \tag{2.548}$$

The diffusion force thus becomes <sup>37</sup>:

$$\mathbf{P}_{sr} = \frac{p x_r x_s (\mathbf{v}_s - \mathbf{v}_r)}{\tilde{D}_{sr}} \tag{2.549}$$

By inserting (2.549) into (2.529), the species momentum equation yields:

$$\begin{aligned}
\frac{\partial(\rho_s \mathbf{v}_s)}{\partial t} + \nabla \cdot (\rho_s \mathbf{v}_s \mathbf{v}_s) &= \rho_s \mathbf{g}_s + \nabla \cdot \mathbf{T}_s + \sum_{r=1}^N \mathbf{P}_{sr} + r_s \mathbf{v}_s^* \\
&= \rho_s \mathbf{g}_s - \nabla p_s + \nabla \cdot \boldsymbol{\sigma}_s + p \sum_{r=1}^N \frac{x_r x_s (\mathbf{v}_r - \mathbf{v}_s)}{\tilde{D}_{sr}} + r_s \mathbf{v}_s^*
\end{aligned} \tag{2.550}$$

In deriving (2.550), the species stress tensor has been decomposed in the standard manner:

$$\mathbf{T}_s = -p_s \mathbf{e} + \boldsymbol{\sigma}_s \tag{2.551}$$

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<sup>37</sup> This model was first obtained by Maxwell [95] for binary systems. Present [109] (Sect. 8-3) outlines a more accurate treatment by the moment transfer method which is not restricted to the billiard-ball molecular representation.

where  $\sigma_s$  is the species  $s$  viscous stress tensor.

The balance (2.550) can be simplified to obtain the Maxwell-Stefan equation, due to the following assumption:

$$\frac{\partial(\rho_s \mathbf{v}_s)}{\partial t} + \nabla \cdot (\rho_s \mathbf{v}_s \mathbf{v}_s) - \rho_s \mathbf{g}_s - \nabla \cdot \sigma_s - r_s \mathbf{v}_s^* \ll p \sum_{r=1}^N \frac{x_r x_s (\mathbf{v}_r - \mathbf{v}_s)}{\tilde{D}_{sr}} - \nabla p_s \quad (2.552)$$

It has been shown that this inequality is valid for a wide variety of conditions [159]. That is, (2.550) can be reduced to:

$$p \sum_{r=1}^N \frac{x_r x_s (\mathbf{v}_r - \mathbf{v}_s)}{\tilde{D}_{sr}} \approx \nabla p_s = p \nabla x_s + x_s \nabla p \quad (2.553)$$

If the pressure gradient in the last term on the RHS is small, the Maxwell-Stefan equation (2.392) is reproduced for the particular cases in which the driving force can be approximated by the mole fraction gradient, the gravity force is the only body force acting on the system and the thermal diffusion is neglectable.

The result is:

$$\sum_{r=1}^N \frac{x_r x_s (\mathbf{v}_r - \mathbf{v}_s)}{\tilde{D}_{sr}} - \nabla x_s \gg \frac{x_s}{p} \nabla p, \quad (2.554)$$

Therefore, the Maxwell-Stefan equations might be considered a particular approximate form of the species momentum equation.

### 2.9.6.2 Applications of Multicomponent Mass Diffusion Flux Models in Chemical Reactor Engineering

In chemical engineering multicomponent mass diffusion phenomena might be important in describing several unit operations like reaction and separation vessels containing either gas or liquid mixtures. Examples of practical applications of the different multicomponent diffusion flux model expressions are outlined in this subsection. For convenience, only dilute gas mixtures are considered for which the kinetic theory of dilute gases is valid. The modeling of multicomponent mass diffusion in fixed packed bed catalyst pellets is examined. This modeling problem has been chosen because it is well known from introductory chemical reaction engineering subjects.

#### *Relevance and previous investigations*

Heterogeneous catalysis is of utmost significance in many fields of gas conversion and processing in chemical industries. Fixed packed bed reactors are widely used for heterogeneous catalysis of many of these processes. Accurate modeling of intra-particle heat and mass transport is a prerequisite for the design of many industrial processes and the interpretation of experiments. To describe the mass diffusion processes within

the pores in catalyst pellets, three fundamentally different types of mass diffusion mechanisms [70, 71, 94] are distinguished:

- *Bulk diffusion* that are significant for large pore sizes and high system pressures in which gas molecule-molecule collisions dominate over gas molecule-wall collisions.
- *Knudsen diffusion* becomes predominant when the mean-free path of the molecular species is much larger than the pore diameter and hence molecule-wall collisions become important.
- *Surface diffusion* of adsorbed molecular species along the pore wall surface. This mechanism of transport becomes dominant for micro-pores and for strongly adsorbed species. Extensions of the Maxwell-Stefan bulk diffusion model have been proposed in order to provide a realistic description of the combined bulk, Knudsen and surface diffusion mechanisms, apparently with limited success [70, 71].

Fick's first law [40] is strictly only valid for binary mixtures. Hence, due to the shortcoming of the well-known Fick's Law of binary diffusion, numerous models for multicomponent diffusion are proposed in the literature to describe these diffusion fluxes. The Wilke [161] and Maxwell-Stefan [96, 142] diffusion flux models assume bulk diffusion, whereas the dusty gas model [62, 94] describes the combined bulk and Knudsen diffusion fluxes in the gas transition transport regime. As a simplification to the dusty gas model, the Wilke model in combination with the Bosanquet formula [11] has been proposed. However, the validity of Knudsen diffusion modeling by the dusty gas and Wilke-Bosanquet models are subjected to criticism in the literature, see for example, the recent review by Krishna [76]. Mathematical modeling of intra-particle mass and heat transport in porous pellets has thus been widely investigated by numerous researchers, e.g., [12, 34, 51, 125, 127, 128, 155, 156], because the intra-particle transport limitations often play an important role in the design of chemical reactors. Most mass diffusion problems in chemical reactor processes involve transport of multicomponent mixtures. Numerous modeling approaches have frequently been adopted considering the intra-particle heat and mass transfer limitations. An efficiency factor is used in the simpler pseudo-homogeneous reactor models to account for the intra-particle transport limitations. Hence, the solid material is not explicitly taken into account. The efficiency factor is normally computed by use of the more rigorous heterogeneous reactor models consisting of a set of equations describing the heat and mass transport processes within the pellets. The intra-particle mass diffusion fluxes may be described by the Maxwell-Stefan, Wilke, dusty gas, or the Wilke-Bosanquet models. A survey of the use of multicomponent diffusion flux closures in chemical reaction engineering for the analysis of internal pellet heat and mass transfer limitations for processes operated in packed fixed bed reactors are provided in the following.

Apécetche et al. [1] studied viscous and diffusive transport with simultaneous reaction in non-isobaric porous catalyst particles by use of the dusty gas model. A binary gaseous mixture under isothermal conditions was studied taking into account mass transfer due to the following mechanisms; viscous flow, non-equimolar



flow, bulk diffusion and Knudsen diffusion. An irreversible,  $m$ -th order reaction kinetics with respect to the gaseous reactant was assumed. It was shown that the non-isobaric effectiveness factor is significantly different from the isobaric one. A maximum pressure gradient of about 10% in the catalyst pellet was produced by Knudsen diffusion.

Burghardt and Aerts [12] proposed a method for evaluation of the pressure change in an isothermal porous pellet within which a single chemical reaction takes place, accompanied by mass transfer by Knudsen diffusion, bulk diffusion and viscous convective flow of the reacting mixture. The pressure change did also depend on the reaction and on the mixture composition on the pellet surface. It was concluded that the pressure changes in a catalyst pellet under conditions normally encountered in industry are most likely so small that they can be neglected in process simulations.

Graaf et al. [51] used the dusty gas model to investigate the relative importance of Knudsen and bulk diffusion for the intra-particle diffusion limitation problem for the methanol synthesis. In their steady-state model, they neglected the pressure gradient and assumed isothermal conditions throughout the spherical particle. Their simulation results indicated that both bulk and Knudsen diffusion mechanisms should be incorporated in the single pellet model to obtain reliable results.

Salmi and Wärnå [125] neglected the effect of Knudsen diffusion and applied the Maxwell-Stefan and Wilke models in their transport model for the catalyst pellet. Moreover, pressure changes inside the pellet were neglected and steady-state conditions were assumed to prevail. They assumed isotropic pore structure catalyst properties and included the energy balance equation in their model. The pellet equations were combined with the corresponding balances of the bulk phase collectively constituting a heterogeneous reactor model. For the water-gas shift reaction and methanol synthesis their simulation results indicated that the differences between the Maxwell-Stefan and Wilke models were minor on the level of a fixed-bed reactor, but becomes of interest for detailed calculations of single pellets.

Elnashaie and Abashar [34] developed a mathematical model to investigate the phenomena of diffusion and chemical reactions in porous catalyst pellets for steam reforming. The rigorous dusty gas model was compared to the simpler Wilke-Bosanquet model under the assumptions of steady-state, negligible viscous flow and isothermal conditions. It was found that at low steam to methane ratios the simplified diffusion model is adequate for simulating the reforming process, while at high steam to methane ratios the implementation of the dusty gas model is essential for accurate prediction of the behavior for this gas-solid system.

More recently, Solsvik and Jakobsen [140] performed a numerical study comparing several closures for mass diffusion fluxes of multicomponent gas mixtures; the Wilke, Maxwell-Stefan, dusty gas, and Wilke-Bosanquet models, on the level of the single catalyst pellet and the impacts of the mass diffusion flux closures employed for the pellet, on the reactor performance. For this investigation, the methanol synthesis operated in a fixed packed bed reactor was the chemical process adopted. In the mathematical modeling study of a novel combined catalyst/sorbent pellet, Rout et al. [121] investigated the performance of the sorption-enhanced steam methane reforming (SE-SMR) process at the level of a single pellet. Different closures

for multicomponent mass diffusion fluxes, the effect of viscous flow, and the significance of Knudsen diffusion were analyzed. Moreover, deviating effects of choosing the random-pore, multi-grain, and the parallel-pore models were studied. Solsvik and Jakobsen [137] extended the study of the combined catalyst/sorbent pellet including also the effects of pellet structure changes due to product layer generation. In this numerical analysis, both the dusty gas and Maxwell-Stefan models were adopted in the analysis of different pellet model description complexities and the sensitivity to model parameters. Rout and Jakobsen [122] further investigated possible reactor performance optimizations employing such a combined pellet reflecting both catalyst and adsorbent properties. It is noted that the mass diffusion flux closures based on the mass average velocity definition are not frequently employed in the literature. On the other hand, the mole based diffusion flux models are not consistent with the continuum mechanical reactive flow model as the fundamental energy and momentum balances are conventionally derived based on the mass average velocity definition due to the physical laws applied; the Navier-Stokes and first laws of thermodynamics. However, the novel mass based pellet equations are adopted in the recent modeling work of Kuijlaars et al. [77], Rout et al. [121] and Solsvik and Jakobsen [136, 138, 140]. For the steam methane reforming (SMR) process, methanol synthesis, and dimethyl ether production, Solsvik and Jakobsen [136, 138] derived a pellet model on both a mass and mole basis and compared the simulation results of the two model formulations. Unexpectedly, deviations between the simulation results of the mole and mass formulated pellet models were obtained. Inconsistency between the mass and mole formulations were also observed in the pellet modeling study of Rout and Jakobsen [122]. For this reason, Solsvik et al. [139] presented a throughout modeling and simulation study of mass and mole based pellet models with the aim to elucidate the effects of different modeling assumptions on the simulation results in order to propose reduced pellet model formulations that give identical simulation results for the mole and mass formulations. The SMR process and the methanol synthesis were adopted for this investigation because the two processes cover various aspects of a chemical reaction; for example, (i) one of them is very endothermic, the other exothermic, (ii) on a net basis one of them produce gas molecules, the other consumes gas molecules, and (iii) one of them is strongly diffusion limited, while the other is not. Some general conclusions regarding model discrimination can be drawn. Compared to the Wilke and Wilke-Bosanquet models the more rigorous Maxwell-Stefan equations and the dusty gas model should rather be used in industrial reaction engineering applications as these model formulations are rigorous and ensure  $\sum_{s=1}^N \mathbf{j}_s = 0$  and  $\sum_{s=1}^N \omega_s = 1$ , whereas these constraints are not always satisfied when the Wilke approximation is employed. Moreover, the simplifying assumption of a constant total pressure and thus negligible gas velocity and convective transport in porous pellets is generally a good approximation. However, such model reductions may strongly influence the consistency between the mass and mole based models.

### *Models for pellet porosity and pore structure*

The relationship between the structure of a porous medium and transport phenomena occurring within the void space of the material is of great importance because the internal architecture of the porous media significantly influences the transport processes occurring within them. Hence, there are two essential aspects for the understanding of chemical processes in porous media; the structural, which is associated with the topological and morphological characteristics of the interstitial void space, and the second aspect makes a reference to the transport mechanisms and physico-chemical interactions taking place at the pore level. The effective diffusivity is a measure of the diffusivity that accounts for: (i) not all area normal to the flux direction is available for molecules to diffuse in a porous particle, (ii) diffusion paths are tortuous, (iii) pore cross-sections vary, and (iv) internal void fraction. A geometrical model of the pore system is adopted in order to convert the molecular diffusivity into the effective diffusivity. Hence, the effective diffusivity is determined based on the molecular diffusivity and the pore structure of the porous pellet. The optimum model is a realistic representation of the geometry of the voids that can be described in terms of easily measurable physical properties of the pellet. The structure of porous media is often characterized in terms of parameters such as the voidage fraction (porosity), pore size distribution, specific surface area, pore network lattice size and connectivity.

Smith [134] discusses the simple parallel-pore and random-pore models, which are extensively adopted in chemical reactor engineering describing the effective diffusivities of porous material. The parallel-pore model presents a mono-disperse pore-size distribution in a porous pellet with the following effective diffusivity [3, 126]:

$$D^e = \frac{\epsilon}{\tau} D \quad (2.555)$$

where  $\epsilon$  denotes the pellet porosity and  $\tau$  represents the tortuosity. The random pore model supposes that the pellet consists of an assembly of small particles. When the particles themselves contain pores, there exists a strongly bi-modal pore size distribution. Hence, transport in the pellet is assumed to occur by a combination of diffusion through the inter-particle and intra-particle voids. The resultant expression for the effective diffusivity may be written as:

$$D^e = D_1 \epsilon_1^2 + \frac{\epsilon_2^2 (1 + 3\epsilon_1)}{1 - \epsilon_1} D_2 \quad (2.556)$$

where  $\epsilon_1$  denotes the inter-particle voids and  $\epsilon_2$  is the void fraction of intra-particle channels. The random pore model can also be applied to mono-disperse systems:

$$D^e = D \epsilon^2 \quad (2.557)$$

The non-catalytic heterogeneous solid fluid reaction shrinking core model [41, 78, 130, 158] provides an overall or effective reaction rate constituting an approximate

description of the external film resistance, the internal diffusion resistance and the chemical reaction resistance.

For a reacting pellet at some intermediate stage of conversion, the following steps can occur in series:

- Gaseous species A diffuses through the film surrounding the pellet to its surface.
- Gaseous species A penetrates and diffuses through the blanket of product solid to reach the reaction front.
- Gaseous species A reacts with reactant B in the narrow reaction zone.
- Gaseous reaction products diffuse through the product layer from the reaction zone to the surface of the particle.
- Gaseous reaction products diffuse into the main gas stream.

The resulting effective reaction rate,  $r_{\text{eff},A}$ , can be expressed as:

$$r_{\text{eff},A} \approx \frac{4\pi C_{A0}}{\left[ \frac{1}{R^2 k_{mA}} + \frac{1}{D_{eA}} \left( \frac{1}{r_c} - \frac{1}{R} \right) + \frac{1}{r_c^2 a k_s C_{S0}} \right]} \quad (2.558)$$

where  $k_{mA}$  is the mass transfer coefficient of species A from the bulk of the fluid phase to the solid surface across the film,  $C_{S0}$  is the concentration of solid reactant in the unreacted core which is assumed to be constant for uniform particles,  $C_{A0}$  is the concentration of fluid reactant A in the bulk of fluid stream,  $R$  is the radius of the particle,  $r_c$  is the radius of the unreacted core,  $a$  is the stoichiometric coefficient representing the number of moles of fluid species A that will react with 1 mole of solid reactant S,  $k_s$  is the reaction rate constant based on the reacting surface area, and  $D_{eA}$  is the effective diffusivity of fluid A in the ash layer. The three terms in the denominator represent the three resistances in series for the reaction considered; external film diffusional-, internal diffusion- and chemical reaction resistances, respectively. The shrinking core model is used to describe situations in which solid particles are being consumed either by dissolution or reaction thus the amount of the particle material being consumed is shrinking. This model applies to areas like the formation of an ash layer around a burning coal particle, catalyst regeneration, and adsorbent particle adsorption and desorption processes.

The grain- or multigrain model consists of separate model equations for characteristic grains or micro-particles and the macro-scale pellet. The characteristic micro-grain is described by the following diffusion-reaction partial- differential equation for the product species  $s$ :

$$\frac{\partial \rho_s(r, t)}{\partial t} + \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 j_{A,r}^{mg}(r, t)) + R_A(r, t) \quad (2.559)$$

where the reaction is supposed to take place in the grains only, and  $r$  is the radial coordinate for the micro-particle.

The following initial and boundary conditions are normally employed:

$$\rho_s(r, t) = \rho_s(r, t_0), \quad \forall r \quad (2.560)$$

$$\frac{\partial j_{A,r}^{mg}(r, t)}{\partial r} = 0, \quad r = 0, \quad t > 0 \quad (2.561)$$

$$j_{A,r}^{mg}(r_S, t) = -k_L^{mg}(\rho_s(R, t) - \rho_s(r_S, t)), \quad r = r_S, \quad t > 0 \quad (2.562)$$

where  $k_L^{mg}$  denotes a local mass transfer coefficient for the micro-grains, and  $r_S$  is the radius of the micro-grain.

The pellet equation is expressed as:

$$\frac{\partial \rho_s(R, t)}{\partial t} + \frac{1}{R^2} \frac{\partial}{\partial R} (R^2 j_{A,R}(R, t)) + k_L^{mg} a^{mg} (\rho_s(R, t) - \rho_s(r_S, t)) \quad (2.563)$$

where the last term denotes the effective reaction rate at any location  $R$  in the pellet,  $a^{mg}$  represent the micro-grain area concentration and  $R$  is the radial coordinate in the pellet.

The following initial and boundary conditions are normally employed:

$$\rho_s(R, t) = \rho_s(R, t_0), \quad \forall R \quad (2.564)$$

$$\frac{\partial j_{A,R}(R, t)}{\partial R} = 0, \quad R = 0, \quad t > 0 \quad (2.565)$$

$$j_{A,R_S}(R, t) = k_{L,p} a_p (\rho_s(\mathbf{r}, t) - \rho_s(R_S, t)) \quad R = R_S, \quad t > 0 \quad (2.566)$$

where  $R_S$  denotes the radius of the pellet,  $K_{L,p}$  the pellet mass transfer coefficient, and  $a_p$  is the pellet area concentration.

This fundamental form of the grain model is rather time consuming to solve, thus several simplified forms have been proposed over the years. Debling and Ray [31] and Kittilsen et al. [64] examined similar multi-grain models and model simplifications employed in polymerization processes. The grain models by [44, 54, 145, 146] consider pellets that are formed by compacting fine grains of particles with or without some binding agents. The pellet overall shape and the shape of the individual grains that make up the pellet is usually irregular. However, to allow a convenient analysis of the grain pellet problem, the pellet is normally considered spherical made up of individual spherical grains of equal size. There are normally two cases postulated on the basis of physical reasoning: (a) A region of chemical control in which the pellets react uniformly throughout the pellet volume. (b) A region of diffusion control with a sharp reaction zone. Rout et al. [123] did employ a similar grain model for describing the multicomponent mass diffusion fluxes and overall reaction rate in sorbent particles for the SE-SMR process.

A variety of modeling approaches for the geometrical pellet structure are given in the literature. Further details are given by, e.g., [33, 56, 124]. It is noticed that in practical reaction engineering, the classical models are most frequently used due to the complexity of the pellet structure.

**Table 2.3** Diffusion flux closures based on the mass average velocity definition

Wilke:

$$\mathbf{j}_s = -\rho D'_{sm} \nabla \omega_s \quad \text{where} \quad D'_{sm} = \frac{1-\omega_s}{M_\omega \sum_{\substack{r=1 \\ r \neq s}}^N \frac{\omega_r}{M_{\omega r} D_{sr}}} \quad (2.450)$$

Wilke-Bosanquet:

$$\mathbf{j}_s = -\rho D''_{s,\text{eff}} \nabla \omega_s \quad \text{where} \quad \frac{1}{D''_{s,\text{eff}}} = \frac{1}{D'_{sm}} + \frac{1}{D_{s,K}} \quad (2.454)$$

Maxwell-Stefan:

$$\mathbf{j}_s = \frac{-\rho \omega_s \nabla \ln(M) - \rho \nabla \omega_s + M \omega_s \sum_{\substack{r=1 \\ r \neq s}}^N \frac{\mathbf{j}_r}{M_{\omega r} D_{sr}}}{M_\omega \sum_{\substack{r=1 \\ r \neq s}}^N \frac{\omega_r}{M_{\omega r} D_{sr}}} \quad (2.421)$$

Dusty gas:

$$\mathbf{j}_s = \frac{M_\omega^2 \sum_{\substack{r=1 \\ r \neq s}}^N \frac{\omega_s \mathbf{j}_r}{M_{\omega r} D_{sr}} - \frac{\mathbf{v}_s M}{D_{sK}} - \rho(\omega_s \nabla M_\omega + M_\omega \nabla \omega_s)}{M_\omega^2 \sum_{\substack{r=1 \\ r \neq s}}^N \frac{\omega_r}{M_{\omega r} D_{sr}} + \frac{M}{D_{sK}}} \quad (2.504)$$

### Pellet equations

For multicomponent mixtures the governing species mass balance can be written on the vector form:

$$\frac{\partial(\rho \omega_s)}{\partial t} + \nabla \cdot (\rho \mathbf{v}_m \omega_s) = -\nabla \cdot \mathbf{j}_s + \mathbf{r}_s \quad (2.567)$$

where  $\omega_s$ ,  $\mathbf{j}_s$  and  $r_s$  denote the mass fractions of species  $s$ , the diffusion flux of species  $s$ , and the  $q$  independent reactions, respectively.

For multicomponent systems the diffusive flux terms may be written in accordance with the approximate Wilke bulk flux equation (2.450), the approximate Wilke-Bosanquet combined bulk and Knudsen flux for porous media (2.454), the rigorous Maxwell-Stefan bulk flux equations (2.421), and the consistent dusty gas combined bulk and Knudsen diffusion flux for porous media (2.504). The different mass based diffusion flux models are listed in Table 2.3. The corresponding molar based diffusion flux models are listed in Table 2.4. In most simulations, the catalyst pellet is approximated by a porous spherical pellet with center point symmetry. For such spherical pellets a representative system of pellet model equations, constitutive laws and boundary conditions are listed in Tables 2.5, 2.6 and 2.7, respectively.

### Viscous flow in pellet pores

In pellet model analysis in which the convective transport of heat and species mass in porous catalyst pellets have to be taken into account simulating catalytic reactor processes, either the Maxwell-Stefan mass flux equations (2.416) or dusty gas model for the mass fluxes (2.513) might be used. The possible viscous flow in the catalyst pores is driven by a pressure gradient induced by the potential non-uniform spatial species composition and temperature evolution created by the chemical reactions.

**Table 2.4** Diffusion flux closures based on the molar average velocity definition

Wilke:

$$\mathbf{J}_s = -c D_{sm} \nabla x_s \quad \text{where} \quad D_{sm} = \frac{1-x_s}{\sum_{\substack{r=1 \\ r \neq s}}^N \frac{x_r}{D_{sr}}} \quad (2.439)$$

Wilke-Bosanquet:

$$\mathbf{J}_s = -c D_{s,\text{eff}} \nabla x_s \quad \text{where} \quad \frac{1}{D_{s,\text{eff}}} = \frac{1}{D_{sm}} + \frac{1}{D_{s,K}} \quad (2.452)$$

Maxwell-Stefan:

$$\mathbf{J}_s = \frac{-c \nabla x_s + \sum_{\substack{r=1 \\ r \neq s}}^N \frac{\mathbf{J}_r x_s}{D_{sr}}}{\sum_{\substack{r=1 \\ r \neq s}}^N \frac{x_r}{D_{sr}}} \quad (2.406)$$

Dusty gas:

$$\mathbf{J}_s = \frac{\sum_{\substack{r=1 \\ r \neq s}}^N \frac{\mathbf{J}_r x_s}{D_{sr}} - \frac{c_s \mathbf{v}^*}{D_{s,K}} - c \nabla x_s}{\sum_{\substack{r=1 \\ r \neq s}}^N \frac{x_r}{D_{sr}} + \frac{1}{D_{s,K}}} \quad (2.485)$$

**Table 2.5** Mass and molar based pellet equations in spherical coordinates*Molar based equations.*

Continuity:

$$\epsilon_p \frac{\partial c}{\partial t} + \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 u_r^s c) = \sum_s S_s \quad (2.571)$$

Species mass balance:

$$\epsilon_p \frac{\partial}{\partial t} (c x_s) + \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 u_r^s c x_s) = -\frac{1}{r^2} \frac{\partial}{\partial r} (r^2 J_{s,r}) + S_s \quad (2.572)$$

Heat balance:

$$\begin{aligned} & \left( (1 - \epsilon_p) C p_p'' \rho_p + \epsilon_p c \sum_{s=1}^N x_s C p_s'' \right) \frac{\partial T}{\partial t} \\ & = -c \sum_{s=1}^N x_s C p_s v_r^s \frac{\partial T}{\partial r} - \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 Q_r) + \hat{S} \end{aligned} \quad (2.573)$$

*Mass based equations.*

Continuity:

$$\epsilon_p \frac{\partial \rho}{\partial t} + \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 v_r^s \rho) = 0 \quad (2.574)$$

Species mass balance:

$$\epsilon_p \frac{\partial}{\partial t} (\rho \omega_s) + \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 v_r^s \rho \omega_s) = -\frac{1}{r^2} \frac{\partial}{\partial r} (r^2 j_{s,r}) + S_s'' \quad (2.575)$$

Heat balance:

$$\begin{aligned} & \left( (1 - \epsilon_p) C p_p'' \rho_p + \epsilon_p \rho \sum_{s=1}^N \omega_s C p_s'' \right) \frac{\partial T}{\partial t} \\ & = -\rho \sum_{s=1}^N \omega_s C p_s v_r^s \frac{\partial T}{\partial r} - \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 Q_r) + \hat{S} \end{aligned} \quad (2.576)$$

The pressure gradient in porous media is usually related to the consistent viscous gas velocity through a correlation inspired by the *Darcy's law* [29] (see e.g., [9, 71] and [132], p. 197):

$$\mathbf{v}_m = -\frac{B_0}{\mu} \nabla p \quad (2.568)$$

**Table 2.6** Constitutive laws

Ideal gas law:

$$p = cRT = \frac{\rho RT}{M_w} \quad (2.577)$$

Darcy's law (viscous gas flow) [70]:

$$\mathbf{v} = -\frac{B}{\mu} \nabla p \quad (2.578)$$

Permeability (Poiseuille flow relationship for cylindrical pores) [70]:

$$B = \frac{d_{\text{pore}}^2}{32} \quad (2.579)$$

Heat flux (Fourier's law):

$$\mathbf{Q}_r = -k \frac{\partial T}{\partial r} \quad (2.580)$$

Mole and mass source terms:

$$S_s = (1 - \epsilon_p) \rho_p r_s \quad (2.581)$$

$$S_s'' = (1 - \epsilon_p) \rho_p M_{\omega_s} r_s \quad (2.582)$$

Heat source term:

$$\hat{S} = (1 - \epsilon_p) \rho_p \sum_{k=1}^q (-\Delta H_{r_k}) r_k \quad (2.583)$$

**Table 2.7** Initial and boundary conditions*Molar based equations*

Initial conditions:

$$\begin{cases} x_s = x_s^b \\ J_{s,r} = 0 \\ T = T^b \\ Q_r = 0 \\ c = c^b \end{cases} \quad \text{for } t = 0, \forall r \quad (2.584)$$

Boundary conditions for symmetry point,  $r = 0$ :

$$J_{s,r} = 0 \quad (2.586)$$

$$Q_r = 0 \quad (2.588)$$

Boundary conditions for surface,  $r = r_p$ :

$$-k_s (c_s^b - x_s c) = J_{s,r} + u_r^s c x_s \quad (2.590)$$

$$Q_r + c C p_g T v_r = -h(T^b - T) \quad (2.592)$$

$$c = c^b \quad (2.594)$$

*Mass based equations*

Initial conditions:

$$\begin{cases} \omega_s = \omega_s^b \\ j_{s,r} = 0 \\ T = T^b \\ Q_r = 0 \\ \rho = \rho^b \end{cases} \quad \text{for } t = 0, \forall r \quad (2.585)$$

Boundary conditions for symmetry point,  $r = 0$ :

$$j_{s,r} = 0 \quad (2.587)$$

$$Q_r = 0 \quad (2.589)$$

Boundary conditions for surface,  $r = r_p$ :

$$-k_s (\rho_s^b - \omega_s \rho) = j_{s,r} + v_r^s \rho \omega_s \quad (2.591)$$

$$Q_r + \rho C p_g'' T v_r = -h(T^b - T) \quad (2.593)$$

$$\rho = \rho^b \quad (2.595)$$

Generally, the permeability  $B_0$  ( $m^2$ ) has to be determined experimentally. However, for simple structures the permeability coefficient  $B_0$  can be determined analytically. Considering a cylindrical pore, for example, the permeability can be calculated from the Poiseuille flow relationship [71]:

$$B_0 = \frac{d_0^2}{32} \quad (2.569)$$

For the multi-grain model [155]:



$$B_0 = \frac{2\epsilon_p}{9\tau(1-\epsilon)} S^2 \quad (2.570)$$

in which  $S$  is the radius of the micro-particle.

Solving this flow model for the velocity the pressure is calculated from the ideal gas law. The temperature therein is obtained from the heat balance and the mixture density is estimated from the sum of the species densities. It is noted that the viscous velocity is normally computed from the pressure gradient by use of a phenomenologically derived constitutive correlation, known as Darcy's law, which is based on laminar shear flow theory [139]. Laminar shear flow theory assumes no slip condition at the solid wall, inducing viscous shear in the fluid. Knudsen diffusion and slip flow at the solid matrix separate the gas flow behavior from Darcy-type flow. Whenever the mean free path of the gas molecules approaches the dimensions of pore diameter, the individual gas molecules are in motion at the interface and contribute an additional flux. This phenomena is called slip flow. In slip flow, the layer of gas next to the surface is in motion with respect to the solid surface. Strictly, the Darcy's law is valid only when the flow regime is laminar and dominated by viscous forces. The theoretical foundation of the dusty gas model considers that the model is applied to a transition regime between Knudsen and continuum bulk diffusion. To estimate the combined flux, the model is based on the assumption that the combined flux can be expressed as a linear sum of the Knudsen flux and the convective flux due to laminar flow.

## 2.10 Mean Free Path Concept

In this section the transport properties are determined by use of the empirical method suggested by Maxwell [95], on the basis of Clausius' mean free path concept. That is, instead of determining the transport properties from the rather theoretical Enskog solution of the Boltzmann equation, for practical applications we may often resort to the much simpler but still fairly accurate mean free path approach (e.g., [20], Sect. 5.1; [48], Sect. 9.6; [119], Chap. 20). Actually, the form of the relations resulting from the mean free path concept are about the same as those obtained from the much more complex theories, and even the values of the pre-factors are considered sufficiently accurate for many reactor modeling applications.

### 2.10.1 Transport Properties

The overall aim in this analysis is to determine a rough estimate of the transfer fluxes in dilute one-component gases using the elementary mean free path concept in kinetic theory. In this approach it is assumed that the only means for transport of information in the fluid is via molecular collisions. Due to the physical similarity

of the flux phenomena of mass, momentum and energy, a common mathematical formalism is outlined (e.g., [55], Sect. 2; [90], Sect. 3.4.2; [109], Sect. 3-4; [162] app E;). Considering a dilute gas containing  $n$  molecules per unit volume inducing a macroscopic transfer flux of property  $\psi$ . The symbol  $\psi$  denotes any property of a single molecule that can be changed by collisions, and  $\langle\psi\rangle_M$  represents the average value of  $\psi$  for the gas. The molecules are assumed to move in a geometrical configuration in which  $\frac{\partial\langle\psi\rangle_M}{\partial x} = \frac{\partial\langle\psi\rangle_M}{\partial y} = 0$ , so that the molecular motion transport the property  $\langle\psi\rangle_M$  in the  $z$ -direction only. For illustrative purposes we consider a gas confined between two infinite parallel planes denoted by  $z = z_0$  and  $z = z_2$ . Imagine a net flux of the properties in the positive  $z$ -direction through a plane at an arbitrary location  $z = z_1$  between the two planes located at  $z = z_0$  and  $z = z_2$ . Let  $F_\psi$  denote the net molecular flux of the property  $\psi$  in the  $z$ -direction.

At each collision it is assumed to be an equalizing transfer of properties between the two molecules, so in consequence  $F_{z_1}$  is determined by the relative location of the last collision experienced by a molecule before it crosses the plane at  $z = z_1$ . This particular distance is thus expected to be related to the mean free path,  $l$ . It is supposed throughout this analysis that the mean free path is small compared to the dimensions of the vessel containing the gas.

It may be expected that on the average molecules crossing the plane  $z = z_1$  from the  $z_1 - l$  side will transfer the property  $\psi_{z_1-l}$  and those crossing from the  $z_1 + l$  side will transfer the property  $\psi_{z_1+l}$ . Hence,  $F_{z_1} = \Gamma\langle\psi\rangle_M|_{z_1-l} - \Gamma\langle\psi\rangle_M|_{z_1+l}$ , where  $\Gamma_{z_1-l}$  denotes the number of molecules per unit area per second crossing the plane  $z = z_1$  from the  $z_1 - l$  side and  $\Gamma_{z_1+l}$  denotes the number of molecules per unit area per second crossing the plane  $z = z_1$  from the  $z_1 + l$  side. This means that  $\Gamma_{z_1-l} = \Gamma_{z_1+l} = \Gamma_{z_1}$ , where  $\Gamma_{z_1} = \frac{1}{6}\langle|\mathbf{C}|\rangle_M n$ . The factor  $\frac{1}{6}$  accounts for the fact that only one-sixth of the molecules on plane  $\Gamma_{z_1-l}$  move in the  $(+z)$ -direction.<sup>38</sup> Hence:

$$F_{\psi,z_1} = \frac{1}{6}\langle|\mathbf{C}|\rangle_M n (\langle\psi\rangle_M|_{z_1-l} - \langle\psi\rangle_M|_{z_1+l}) \quad (2.596)$$

The properties  $\langle\psi\rangle_M|_{z_1-l}$  and  $\langle\psi\rangle_M|_{z_1+l}$  in (2.596) may then be expanded in a Taylor series about  $z = z_1$ , since the mean free path is small compared to the distance over which  $\langle\psi\rangle_M$  changes appreciably. Neglecting terms of order higher than one the result is<sup>39</sup>:

<sup>38</sup> Consider isotropic molecular motion in a Cartesian coordinate system. If there are  $n$  molecules per unit volume, about one-third of them have velocities along the  $x$ -direction. Half of these, i.e.,  $\frac{1}{6}n$  per unit volume, move in the  $(+x)$ -direction and the other half of them move in the  $(-x)$ -direction. Accordingly, one-sixth of the  $N$  molecules move in the  $(+y)$ -direction, another one-sixth of the them move in the  $(-y)$ -direction, another one-sixth of them in the  $(+z)$ -direction, and finally the last one-sixth of them will move in the  $(-z)$ -direction.

<sup>39</sup> The subscript  $z_1$  is omitted since the choice of the position  $z = z_1$  was arbitrary.

$$F_{\psi, z_1} = \frac{1}{6} \langle |C| \rangle_M n (\langle \psi \rangle_M|_{z-l} - \langle \psi \rangle_M|_{z+l}) = \frac{2l \langle |C| \rangle_M}{6} n \left( \frac{\langle \psi \rangle_M|_{z-l} - \langle \psi \rangle_M|_{z+l}}{2l} \right) \quad (2.597)$$

$$\approx - \frac{l \langle |C| \rangle_M}{3} n \frac{d \langle \psi \rangle_M}{dz} \quad (2.598)$$

It has also been assumed that the gradient of the property  $\langle \psi \rangle_M$  is constant over distances of the order  $l$ .

To determine the species mass diffusion a concentration gradient is induced by assuming that the species number concentration is different at each of the planes  $z_0, z_1, z_2$ . To estimate the viscosity we create a gradient in the  $z$ -momentum by assuming that the molecules at the plane  $z_0$  are moving in the negative  $z$ -direction, at the plane  $z_1$  the molecules are stationary, and those at plane  $z_2$  are moving in the positive  $z$ -direction. To induce a thermal conduction flux the three planes are taken to be at different temperatures. Then, the specific fluxes are achieved letting the symbol  $F_\psi$  successively represent the  $y$ -component of the flux of momentum through a plane with normal in the  $z$ -direction, the flux of energy through the same plane, and the mass flux of species  $c$  through the same plane, respectively. The symbol  $\langle \psi \rangle$  represents correspondingly the  $y$ -direction momentum per molecule of mass  $m$ ,  $m v_y$ , the energy per particle ( $me$ ), and the mass per molecule of species  $c$ ,  $m_c$ .

Comparing the fluid dynamic closures with the corresponding kinetic theory results we see that:

$$F_{mv_y} = -\frac{1}{3} \langle |C| \rangle_M l n m \frac{dv_y}{dz} = P_{yz} = -\mu \frac{dv_y}{dz} \quad (2.599)$$

$$F_{me} = -\frac{1}{3} \langle |C| \rangle_M l n m \frac{de}{dT} \left|_V \frac{dT}{dz} \right. = q_z = -k \frac{dT}{dz} \quad (2.600)$$

$$F_{m\omega_c} = -\frac{1}{3} \langle |C| \rangle_M l n m \frac{d\omega_c}{dz} = j_z = -\rho D \frac{d\omega_c}{dz} \quad (2.601)$$

The molecular fluxes can be extended to systems containing gradients in the other two space dimensions as well, denoting a complete three dimensional flux formulation.

It is noted that in determining the viscosity parameter we consider a spatially uniform fluid in a state of shear such that  $\mathbf{v} = v_y(z)\mathbf{e}_y$ . In the heat conduction case we imagine that a gas is heated at constant volume so that all the energy supplied is increasing the energy of the molecules, thus  $n[d(me)/dT] = \rho C_v$ , where  $C_v = \frac{3k}{2m}$  is the specific heat per unit mass at constant volume. The mass diffusion flux is determined considering a binary mixture in which both the total pressure and temperature are uniform. The form of the species mass flux used above deviates from the standard literature on elementary kinetic theory in that the mass fraction is used instead of the species number density. A brief discussion of the two formulations is given by Rohsenow and Choi ([119], p. 495).

The standard self-diffusion flux can be derived in a similar way. The flux of particles in the positive  $z$ -direction that crosses the  $z_1$  plane is equal to the number of molecules that reach the same plane from  $z_1 - l$ , minus those that reach it from  $z_1 + l$ . The result is [90]:

$$\begin{aligned}
\Gamma_{z1} &= \Gamma|_{z1-l} - \Gamma|_{z1+l} = \frac{1}{6} \langle |\mathbf{C}| \rangle_M (\langle n \rangle_M|_{z-l} - \langle n \rangle_M|_{z+l}) \\
&= \frac{2l \langle |\mathbf{C}| \rangle_M}{6} \left( \frac{\langle n \rangle_M|_{z-l} - \langle n \rangle_M|_{z+l}}{2l} \right) \\
&\approx -\frac{l \langle |\mathbf{C}| \rangle_M}{3} \frac{d \langle n \rangle_M}{dz} = -D \frac{d \langle n \rangle_M}{dz}
\end{aligned} \tag{2.602}$$

Comparing the two last terms, we may conclude:  $D = \frac{1}{3} l \langle |\mathbf{C}| \rangle_M$ .

The molecular flux models are still not closed as the mean free path  $l$  and the molecular speed quantities  $\langle |\mathbf{C}| \rangle_M$  are not determined yet. A frequently used closure is examined in the next paragraph.

### 2.10.2 Mean Free Path

In this section approximate mathematical models determining the molecular mean free path are derived. It is anticipated that for dilute gases the mean free path is a significant parameter that governs the mechanism of transfer, defined as the mean distance traveled by a molecule between two successive collisions [119]. The basic physical interpretation of the transfer phenomenon is thus that a molecule traveling a free path of a certain distance is in effect transferring momentum, energy and mass over that distance. To derive a simple expression for the mean free path we preliminarily examine the molecular motion from the point of view of an elementary kinetic theory of dilute gases adopting the billiard ball molecular model. Consider a pure gas composed of a collection of rigid, non-attracting spherical molecules of diameter  $d_1$ , mass  $m_1$ , and number density  $n_1$  colliding at random. A molecule is singled out as it travels in straight paths from one collision to the next, anticipating that the molecular speed and direction of motion change with each collision. It is then further imagined that at a given instant all the molecules but the one in question are frozen in position, whereas this particular molecule moves with an average speed  $\langle |\mathbf{c}_1| \rangle_M$ . At the instant of a collision, the center to center distance of the two molecules is  $d_1$  (see Fig. 2.7). The total collision cross section or target area,  $\sigma_{AT}$ , of the moving molecule is then given by  $\sigma_{AT} = \pi d_1^2$ . In time  $t$  the moving molecule sweeps out a cylindrical volume of length  $\langle |\mathbf{c}_1| \rangle_M t$  and cross section  $\sigma_{AT}$  (see Fig. 2.10). Any molecule whose center is in this cylinder will be struck by the moving molecule. The number of collisions in time  $t$  is given by  $\sigma_{AT} n_1 \langle |\mathbf{c}_1| \rangle_M t$ , where  $n$  is the number of molecules present in a unit volume, assumed to be uniformly distributed in space. A crude estimate of the mean free path,  $l_1$ , is then given by the ratio of the distance traveled in time  $t$  over the number of collisions in this time [157]:

$$l_1 = \frac{\langle |\mathbf{c}_1| \rangle_M t}{\sigma_{AT} n_1 \langle |\mathbf{c}_1| \rangle_M t} = \frac{1}{\sigma_{AT} n_1} \tag{2.603}$$

The corresponding collision frequency is defined as the average number of collisions per unit time experienced by any one molecule of type 1:

$$Z_{1-1} = \sigma_{AT} n_1 \langle |\mathbf{c}_1| \rangle_M = \frac{\langle |\mathbf{c}_1| \rangle_M}{l_1} \quad (2.604)$$

The mean time between successive collisions of molecules of type 1, called the *collision time*  $\tau_1$ , is approximated by:

$$\tau_1 = \frac{1}{Z_{1-1}} = \frac{l_1}{\langle |\mathbf{c}_1| \rangle_M} \quad (2.605)$$

Several extensions of the crude model sketched above have been derived over the years, for example considering the situation that all the molecules in the cylindrical volume move with the same average speed. A third model providing results being in better agreement with the Enskog relations is obtained assuming that all the molecules possess a Maxwellian speed distribution. The Maxwellian representation of the collision frequency of one molecule of type  $m_1$  with similar molecules (2.166) is commonly rewritten using the ideal gas law:

$$Z_{1-1} = \frac{2Z_{11}}{n_1} = 4n_1 d_1^2 \sqrt{\frac{\pi kT}{m_1}} = 4 \frac{p_1}{kT} d_1^2 \sqrt{\frac{\pi kT}{m_1}} = 4p_1 d_1^2 \sqrt{\frac{\pi}{m_1 kT}} \quad (2.606)$$

The mean free path,  $l_1$ , traveled by a molecule of type  $m_1$  between successive collisions in a given time  $t$  is found by dividing the total distance traveled by all molecules of type  $m_1$  in this time by the total number of the collisions between them:

$$l_1 = \frac{n_1 \langle |\mathbf{c}_1| \rangle_M t}{\frac{n_1 t}{\tau_1}} = \langle |\mathbf{c}_1| \rangle_M \tau_1 = \frac{\langle |\mathbf{c}_1| \rangle_M}{Z_{1-1}} \quad (2.607)$$

From this formula it is seen that to calculate  $l_1$  we need to determine the mean molecular speed  $\langle |\mathbf{c}_1| \rangle_M$ . For real systems the average molecular speed is difficult to determine. Assuming that the system is sufficiently close to equilibrium the velocity distribution may be taken to be Maxwellian. For molecules in the absolute Maxwellian state the peculiar velocity equals the microscopic molecular velocity, i.e.,  $\mathbf{C}_1 = \mathbf{c}_1$ , because the macroscopic velocity is zero  $\mathbf{v}_1 = 0$ , hence it follows that the speed of the microscopic molecular velocity equals the thermal speed:  $\langle C_1 \rangle_M = \langle |\mathbf{C}_1| \rangle_M = \langle c_1 \rangle_M = \langle |\mathbf{c}_1| \rangle_M$ .

The mean value of a generalized function of the molecular velocity for a gas in the absolute Maxwellian state is defined by:

$$n \langle \psi \rangle_M = \int_{-\infty}^{\infty} \psi f d\mathbf{c} = n \left( \frac{m}{2\pi kT} \right)^{3/2} \int_{-\infty}^{\infty} \psi \exp\left(-\frac{mC^2}{2kT}\right) d\mathbf{c} \quad (2.608)$$

The present form of the integral is not really defined in a consistent manner as the integrand contains the peculiar speed  $C$ , which is defined by  $C = |\mathbf{C}|$ , whereas the integration is over the velocity space  $d\mathbf{c}$ . Transforming from Cartesian coordinates

$(C_x, C_y, C_z)$  to spherical polar coordinates  $(C, \theta, \phi)$ , we get with spherical symmetry:  $d\mathbf{C} = dC = C^2 \sin \theta d\theta d\phi dC$  (e.g., [20], p. 70; [48], p. 242; [163], p. 34).

The mean value of the thermal speed  $C$  ( $= |\mathbf{C}|$ ) can then be derived as follows<sup>40</sup>:

$$\begin{aligned}
 \langle C \rangle_M &= \left(\frac{m}{2\pi kT}\right)^{3/2} \int_{-\infty}^{\infty} C \exp\left(-\frac{mC^2}{2kT}\right) d\mathbf{C} \\
 &= \left(\frac{m}{2\pi kT}\right)^{3/2} \int_0^{\infty} C^3 \exp\left(-\frac{mC^2}{2kT}\right) \int_0^{2\pi} \int_0^{\pi} \sin \theta d\theta d\phi dC \\
 &= 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} \int_0^{\infty} C^3 \exp\left(-\frac{mC^2}{2kT}\right) dC \\
 &= 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} \times \frac{1}{2} \left(\frac{m}{2kT}\right)^{-2} = \left(\frac{8kT}{\pi m}\right)^{1/2} \quad (2.609)
 \end{aligned}$$

Thus, for a molecule of type 1 the mean value of the peculiar speed  $\langle C_1 \rangle_M$  for a gas in the Maxwellian state yields:

$$\langle C_1 \rangle_M = \langle c_1 \rangle_M = \sqrt{\frac{8kT}{\pi m_1}} = 2\sqrt{\frac{2kT}{\pi m_1}} \quad (2.610)$$

The mean free path can then be determined from (2.607) and (2.606):

$$\begin{aligned}
 l_1 &= \langle |\mathbf{c}_1| \rangle_M \tau_1 = \frac{\langle |\mathbf{c}_1| \rangle_M}{Z_{1-1}} = \left(2\sqrt{\frac{2kT}{\pi m_1}}\right) \left(\frac{1}{4n_1 d_1^2 \sqrt{\frac{\pi kT}{m_1}}}\right) \quad (2.611) \\
 &= \frac{1}{\sqrt{2} n_1 d_1^2 \pi} = \frac{kT}{\sqrt{2} p_1 d_1^2 \pi}
 \end{aligned}$$

<sup>40</sup> In these manipulations we have used a mathematical formula solving odd integrals on the form:

$$\int_0^{\infty} x^n \exp(-ax^2) dx$$

The solution for  $n = 3$  is (e.g., [20], Sect. 1.4; [90], pp. 526–527):

$$\int_0^{\infty} \exp(-ax^2) dx = \frac{1}{2} a^{-2}.$$

### 2.10.3 Transport Coefficients

In this section we derive theoretical expressions for the transport coefficients (i.e., viscosity, thermal conductivity, and diffusivity) for dilute gases.

Using the elementary mean free path theory (2.603), the viscosity, thermal conductivity<sup>41</sup> and self-diffusion coefficients in (2.599) and (2.601) are estimated to be (e.g., [39], Sect. 6.7 and Chap. 7; [106], Chap. 3; [109]; [157], Chap. 5):

$$\mu_1 = \frac{1}{2}\rho_1 l_1 \langle C_1 \rangle_M = \frac{1}{\pi d_1^2} \sqrt{\frac{m_1 kT}{\pi}} \quad (2.612)$$

$$k_1 = \frac{1}{2}\rho_1 l_1 \langle C_1 \rangle_M C_{v,1} = \mu_1 C_{v,1} \quad (2.613)$$

$$D_{11} = \frac{1}{2}l_1 \langle C_1 \rangle_M = \mu_1 / \rho_1 \quad (2.614)$$

In a one-component gas it is conceptually still possible to label a certain subset of particles with 1 and the complement, 2. The resulting motion of the conceptually labeled subgroup of particles is called *self-diffusion*. Diffusion in a two-component system is called *mutual diffusion*.

The following set of parameter values may be more common because they are obtained adopting a refined proportionality coefficient in the flux expressions and the more accurate mean free path relation (2.611). The parameter values are<sup>42</sup> [109] (Sect. 3-5) [106] (Chap. 3) [9] (Sects. 1-4, 9-3 and 17-3):

$$\mu_1 = \frac{1}{3}\rho_1 l_1 \langle C_1 \rangle_M = \frac{2}{3\pi d_1^2} \sqrt{\frac{m_1 kT}{\pi}} \quad (2.615)$$

$$k_1 = \frac{1}{3}\rho_1 l_1 \langle C_1 \rangle_M C_{v,1} = \mu_1 C_{v,1} = \frac{1}{\pi d_1^2} \sqrt{\frac{k^3 T}{\pi m_1}} \quad (2.616)$$

The self diffusivity which is valid for two species of identical mass and size yields:

$$D_{11} = \frac{1}{3}l_1 \langle C_1 \rangle_M = \mu_1 / \rho_1 = \frac{2}{3} \left( \frac{kT}{\pi^3 m_1} \right)^{1/2} \frac{1}{nd_1^2} = \frac{2}{3} \left( \frac{k^3}{\pi^3 m_1} \right)^{1/2} \left( \frac{T^{3/2}}{p_1 d_1^2} \right) \quad (2.617)$$

<sup>41</sup> In this section we denote the thermal conductivity by the symbol  $k$  to distinguish this parameter from the Boltzmann constant.

<sup>42</sup> Maxwell [95] was able to obtain these fairly accurate expressions for the transport coefficients which describe their primary dependence of upon temperature, pressure, mass and size of the molecules in the gas based on rather crude arguments. Historically, the mean free path theory given by Maxwell [95] predates the more accurate theory based on the Boltzmann equation by about half a century.

For species of differing mass and size, the mean free paths, velocities, and collision frequencies will be different. The derivation of the binary diffusivity is more complicated but may be expressed as (e.g., [9], Sect. 17-3 and [39, 106]):

$$D_{12} = \frac{2}{3} \left( \frac{k}{\pi} \right)^{3/2} \left( \frac{1}{2m_1} + \frac{1}{2m_2} \right)^{1/2} \left( \frac{T^{3/2}}{p(\frac{d_1+d_2}{2})^2} \right) \quad (2.618)$$

A similar result was obtained by Present [109] (p. 149) for the rigid-sphere molecular model:

$$D_{12} = \frac{1}{3} l_1 \langle C_1 \rangle_M = \frac{3}{8} \left( \frac{\pi k T}{2\mu} \right)^{1/2} \frac{1}{n\pi d_{12}^2} \quad (2.619)$$

The pressure dependence expressed by these relations is fairly accurate for pressures up to about 10–20 atmospheres. At higher pressures, multi-body collisions become important and the pressure dependence is greater. Experimental evidence also show that a temperature dependence of  $T^{3/2}$  is too weak leading to the search for more accurate relations as derived by use of the Enskog approach.

Alternative estimates of the transport coefficients can be obtained from the rigorous Chapman-Enskog expansion method of mono-atomic gases at low densities (e.g., [20, 35, 36, 39] and [90], p. 202)). The transport coefficients deduced from the Chapman-Enskog kinetic theory with the rigid elastic spheres interaction model yield (e.g., [20], Sects. 10.1–10.2; [55] Sect. 8.2; [90], p. 202):

$$\mu_1 = \frac{5}{16d_1^2} \sqrt{\frac{m_1 k T}{\pi}}, \quad (2.620)$$

$$k_1 = \frac{5}{2} \mu_1 C_{v1} = \frac{75}{64d_1^2} \sqrt{\frac{k^3 T}{m_1 \pi}} \quad (2.621)$$

$$D_{11} = \frac{3}{8n_1 d_1^2} \sqrt{\frac{k T}{m_1 \pi}} \quad (2.622)$$

The binary diffusivity can also be determined in a similar manner considering a binary mixture of dilute gases:

$$D_{12} = \frac{3}{16n_1 d_{12}^2} \sqrt{\frac{2k T}{\pi \mu}} \quad (2.623)$$

The Chapman-Enskog kinetic theory actually gives general expressions for the transport properties in terms of the intermolecular potential energy which is related to the intermolecular force as expressed by (2.54) and (2.55). The molecular interaction is most frequently described by the empirical Lennard-Jones 12-6 potential.



The transport coefficients like viscosity, thermal conductivity and self-diffusivity for a pure mono-atomic gas and the diffusivity for binary mixtures obtained from the rigorous Chapman-Enskog kinetic theory with the Lennard-Jones interaction model yield (e.g., [9], Sects. 1-4, 9-3 and 17-3; [55], Sect. 8.2):

$$\mu_1 = \frac{5}{16} \frac{\sqrt{\pi m_1 k T}}{\pi \sigma_1^2 \Omega_{\mu,1}} \quad (2.624)$$

$$k_1 = \frac{25}{32} \frac{\sqrt{\pi m_1 k T}}{\pi \sigma_1^2 \Omega_{k,1}} C_{v1} \quad (2.625)$$

$$D_{11} = 3.2027 \times 10^{-5} \sqrt{\frac{T}{M_{w1}}} \frac{1}{c \sigma_1^2 \Omega_{D,11}} \quad (2.626)$$

$$D_{12} = 0.0018583 \sqrt{T^3 \left( \frac{1}{M_{w1}} + \frac{1}{M_{w2}} \right)} \frac{1}{p \sigma_{12}^2 \Omega_{D,12}} \quad (2.627)$$

where the units of the transport coefficients are; viscosity  $\mu_1$  [Pa  $\times$  s], conductivity  $k_1$  [W/mK], diffusivities  $D_{11}$  and  $D_{12}$  [m<sup>2</sup>/s], and the properties  $p$  [atm], and  $T$  [K].

The  $\sigma_1$  is a characteristic diameter of the molecules of type 1, often called the collision diameter, and may be defined differently for each molecular model. In the Lennard-Jones potential  $\sigma_1$  has the significance of being the distance from the center of mass of the two molecules to the point at which the potential changes from repulsive to attractive [39]. To calculate  $\sigma_{12}$  an analog of the rigid sphere model is generally adopted:  $\sigma_{12} = (\sigma_1 + \sigma_2)/2$ . This approach has little theoretical justification and is not accurately verified by experimental data. The collision integrals<sup>43</sup>  $\Omega_{\mu,1}$ ,  $\Omega_{k,1}$ ,  $\Omega_{D,11}$ , and  $\Omega_{D,12}$  account for the details of the paths that the molecules take during a binary collision and are usually of order unity. In one view these integrals are interpreted as describing the deviation from the rigid sphere behavior. The  $\varepsilon$  quantity in the Lennard-Jones potential is a characteristic energy denoting the maximum energy of attraction between a pair of molecules. For binary mixtures  $\varepsilon_{12}$  is usually approximated by a geometric average of the contributions from the two species  $\varepsilon_{12} \approx \sqrt{\varepsilon_1 \varepsilon_2}$ . By use of these formulas accurate calculations of the transport coefficients can thus be performed provided that the Lennard-Jones potential parameters like  $\varepsilon_1$  and  $\sigma_1$  are known. Extensive lists of these parameters are given for many substances by Hirschfelder et al. [55] and Bird et al. [9], among others.

<sup>43</sup> Chapman and Cowling [20] have shown that in kinetic theory the transport coefficients can be expressed in terms of the Sonine polynomial expansion coefficients which are complicated combinations of the bracket integrals. In the given solutions these integrals are written as linear combinations of a set of these *collision integrals*. See also Hirschfelder et al. [55], Sect. 7-4.

### 2.10.4 Dilute Gas Hypothesis

The phrase *dilute gas* indicates that the physical volume  $n[\frac{4}{3}\pi d^3]$  occupied by the gas particles (molecules) is small compared to the container volume  $V$  available to the gas. Mathematically this condition can be expressed as:

$$n \left[ \frac{4}{3} \pi d^3 \right] \ll V, \quad (2.628)$$

or

$$\frac{n \left[ \frac{4}{3} \pi d^3 \right]}{V} \ll 1, \quad (2.629)$$

where  $n$  denotes the number of particles and  $d$  is the radius of the particle.

A real gas is also considered dilute provided that the mean free path  $l$  is much larger than the particle size, i.e.,  $l \gg d$ .

Assuming that the molecules are rigid elastic spheres a typical value for the mean free path for a gas, say oxygen, can be calculated from (2.611). Consider a typical room temperature at 300 (K) and a pressure of 101325 (Pa). The collision diameter of molecular oxygen can be set to  $3.57 \times 10^{-10}$  (m) in accordance with the data given by Laidler [80], example 1.4. We can then calculate the mean free path  $l$  for oxygen from (2.611):

$$\begin{aligned} l &= \frac{RT}{\sqrt{2}\pi d^2 N_a p} \\ &= \frac{8.314(\text{JK}^{-1}\text{mol}^{-1}) \times 300(\text{K})}{\sqrt{2}\pi [3.57 \times 10^{-10}(\text{m})]^2 \times 6.022 \times 10^{23}(\text{mol}^{-1}) \times 101325(\text{Pa})} \\ &= 7.22 \times 10^{-8}(\text{m}) \end{aligned} \quad (2.630)$$

Since the molecular diameters for the different gases are of the same order, the mean free path in any gas at the given temperature and pressure is of the order  $10^{-5}$  (cm). In this case it follows that the mean free path is about hundred times the diameter of the molecule, thus the gas is dilute. However, it is noted that at higher gas pressure, say 10132500 (Pa), the mean free path is reduced and comparable with the dimensions of a molecule. In this case the assumption of molecular chaos may not be valid so the gas cannot be considered dilute [20].

### 2.10.5 Continuum Hypothesis

A dilute gas mixture is assumed to behave as a continuum when the mean free path of the molecules is much smaller than the characteristic dimensions of the problem geometry [5, 42, 43, 68, 129, 154, 164]. A relevant dimensionless group of variables, the Knudsen number,  $\text{Kn}$ , is defined as:

$$Kn = \frac{l}{L}, \quad (2.631)$$

where  $l$  is the mean free path of the molecules and  $L$  a characteristic dimension of the apparatus region in which the relevant physical phenomena take place (e.g., the thickness of boundary layers in which large gradients appear, the diameter of catalyst pores, the reactor diameter, etc). In general the *continuum hypothesis* is considered valid for  $Kn < 0.01$ .

By use of the typical numerical value for the mean free path (2.611) for a gas at temperature 300 K and pressure 101325 Pa, this condition indicates that the continuum assumption is valid provided that the characteristic dimension of the apparatus is  $L > 0.001$  cm. Nevertheless, it is noted that at low gas pressures, say 10 Pa, the mean free path is increased and might be comparable with the characteristic dimensions of the apparatus. In particular, for low pressures and small characteristic dimensions we might enter a flow regime where the continuum assumption cannot be justified.

The gas flow regimes are generally characterized as:

$$Kn < 0.01 - 0.001 \quad \text{Continuum flow} \quad (2.632)$$

$$0.01 < Kn \leq 0.1 \quad \text{Slip flow} \quad (2.633)$$

$$0.1 < Kn \leq 10 \quad \text{Transition flow} \quad (2.634)$$

$$Kn > 10 \quad \text{Free molecular flow} \quad (2.635)$$

In the *slip flow regime* velocity slip, and species mass- and temperature jump phenomena occur in the vicinities of the boundaries. In this regime, the ordinary gas dynamics conservation equations might still be employed with sufficient modifications of the boundary conditions. The *free molecular flow regime* occurs at the verge of large Knudsen number where the gas is very rarefied. However, the molecular collisions with the vessel walls prevail thus some law of molecular reflection on the vessel wall is required. In this flow regime the mean free path  $l$  is much larger than  $L$ , and the equilibrium Maxwell velocity distribution might be considered. In the *transitional regime* between the slip flow regime and the free molecule region, the collisions of the molecules with the vessel walls and the mutual collisions of the molecules in the oncoming flow have about equal importance. The analysis becomes challenging, and the molecular gas dynamics methods must be adopted.

## 2.11 Ideal Gas Law

The description of the behavior of an ideal gas in terms of the macroscopic state variables<sup>44</sup>  $p$ ,  $V$ ,  $n$ , and  $T$  can be related to simple averages of microscopic quantities such as the mass and speed of the molecules in the gas [20, 39, 109, 149, 157].

<sup>44</sup> A state variable is a precisely measurable physical property which characterizes the state of a system, independently of how the system was brought to that state.

From the point of view of kinetic theory, an ideal gas consists of a large number of molecules making elastic collisions with each other and with the walls of the container containing the gas, and there are no intermolecular attractive forces. In such an ideal gas, all the internal energy is in the form of kinetic energy and any change in internal energy is accompanied by a change in temperature. The ideal gas law can thus be viewed as arising from the kinetic pressure of the ideal gas molecules colliding with the walls of a container in accordance with Newton's laws.

For convenience, the underlying model assumptions employed deriving the ideal gas law are briefly summarized prior to the model derivation:

- The ideal gas molecules are considered hard spheres without internal structure (mono-atomic molecules).
- Out of the three possible types of degrees of freedom for molecular motion, i.e., translation, rotation and vibrational, only three translational degrees of freedom are present for the ideal gas molecules with no internal structure (mono-atomic molecules).
- The intermolecular collisions are elastic.
- The molecular collisions with the wall are elastic.
- The molecules in an ideal gas move randomly, even though the molecules experience intermolecular interactions and collisions with the walls:

$$\langle C^2 \rangle = \langle C_x^2 \rangle + \langle C_y^2 \rangle + \langle C_z^2 \rangle = 3\langle C_x^2 \rangle \quad (2.636)$$

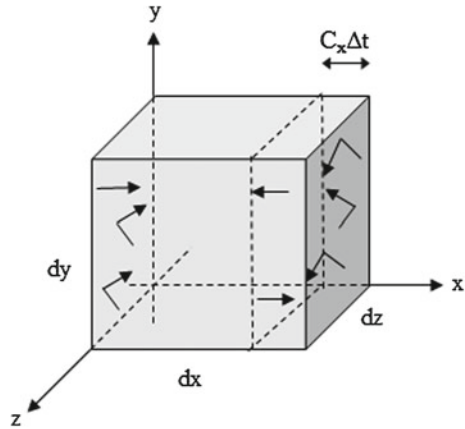
The random molecular movement requires that:

$$\langle C_x^2 \rangle = \langle C_y^2 \rangle = \langle C_z^2 \rangle. \quad (2.637)$$

- In an ideal gas, the molecules are separated, on the average, by distances that are large compared with their diameters. The gas molecules are thus considered point particles. Moreover, the collisions are considered instantaneous.
- The attractive forces between molecules are considered negligible. The equivalent condition of low density is to be understood such that the molecules of the gas are so far apart that they do not interact except during collisions.
- The average kinetic energy is considered proportional to temperature through the kinetic energy equipartition theorem.
- No external forces are acting on the system. In the absence of external forces, there is no preferred position for a molecule in the container, and no preferred direction for its velocity vector. Actually gravity is such an external force acting on the gas in the container, thus the density of molecules at the bottom of the container will be slightly greater than at the top. However, the variation over a normal sized container is generally negligible. Hence, the molecular movement is considered random in accordance with (2.637).

Under these idealized conditions, both the system momentum and kinetic energy are conserved in the molecular collisions, thus the intermolecular collisions have no effect on the total momentum in any direction. For this reason, the molecular

**Fig. 2.12** Gas molecules in a rectangular container. In a time interval  $\Delta t$ , the molecules closer to the right wall than a distance  $C_x \Delta t$  will hit the right wall if they are moving to the right



collisions can be omitted in the subsequent analysis calculating the pressure that an ideal gas exerts on the container walls. The ideal gas pressure is due to the collisions between the gas molecules and the container walls which are solely induced by the translational motion of the molecules. Pressure is defined as a force per unit area and, by Newton's second law, this force equals the rate of change of momentum of the gas molecules colliding with the wall. That is, Newton's second law can be expressed as:

$$\mathbf{F} = m\mathbf{a} = \frac{d\mathbf{p}}{dt} = \frac{d(m\mathbf{C})}{dt} \quad (2.638)$$

For simplicity, consider a rectangular container of volume  $V$  containing  $N$  gas molecules, each of mass  $m$  moving with a speed  $C$ . To calculate the force exerted by these molecules on the right hand wall, which is perpendicular to the  $x$  axis and has area  $A$ , a simple geometrical analysis is required. The molecules hitting this wall in a time interval  $\Delta t$  are those that are within a distance  $C_x \Delta t$  of the wall (see Fig. 2.12) and are moving to the right. The number of molecules hitting the right hand wall during the time interval  $\Delta t$  is  $\frac{1}{3}$  times the number per unit volume  $N/V$  times the volume  $C_x \Delta t A$  times  $\frac{1}{2}$  because, on average, only half the molecules moving along the  $x$ -axis are moving to the right. In other words, on average,  $N/3$  of the molecules moving along a given axis, whereas  $N/6$  of the molecules move towards each of the walls. That is, the number of molecules that hit the right hand wall in the time interval  $\Delta t$  is  $\frac{1}{6} \frac{N}{V} C_x \Delta t A$ . The  $x$  component of momentum of a molecule is  $+mC_x$  before it hits the wall, and  $-mC_x$  after an elastic collision with the wall. The change in momentum thus has the magnitude  $2mC_x$ . The magnitude of the total change in momentum  $|\Delta \mathbf{p}|_x$  of all molecules moving along the  $x$ -axis during a time interval  $\Delta t$  is  $2mC_x$  times the number of molecules that hit the wall during this interval:

$$|\Delta \mathbf{p}|_x = (2mC_x) \times \left( \frac{1}{6} \frac{N}{V} C_x \Delta t A \right) = \frac{1}{3} \frac{N}{V} m C_x^2 A \Delta t \quad (2.639)$$

From Newton's third law, the magnitude of the force exerted by the wall on the molecules and by the molecules on the wall is equal and may be approximated by  $|\Delta \mathbf{p}|_x / \Delta t$ . The pressure is the magnitude of this force divided by the area  $A$ :

$$p_x = \frac{F_x}{A_x} = \frac{1}{A_x} \frac{|\Delta \mathbf{p}|_x}{\Delta t} = \frac{1}{3} \frac{N}{V} m C_x^2 \quad (2.640)$$

or

$$p_x V = \frac{1}{3} N m C_x^2 \quad (2.641)$$

To allow for the fact that all the molecules in a container do not have the same speed,  $C_x^2$  is replaced with the average speed  $\langle C_x^2 \rangle$ . The latter relation can then be written in terms of the kinetic energy  $\frac{1}{2} m C_x^2$  associated with the motion along the  $x$  axis:

$$p_x V = \frac{2}{3} N \langle \frac{1}{2} m C_x^2 \rangle \quad (2.642)$$

In kinetic theory, in accordance with the kinetic energy equipartition theorem, the kinetic temperature  $T$  of a gas at a uniform state at rest or in uniform translation is defined directly in terms of the average peculiar speeds of the molecules, by the three dimensional relation  $\frac{1}{2} m \langle C^2 \rangle_M = \frac{3}{2} k T$  obtained from (2.200) and (2.199). In accordance with (2.200) and (2.192) the static pressure  $p$  of a gas in equilibrium is given by  $p = 3 p_x = n m \langle C_x^2 \rangle_M = \frac{1}{3} n m \langle C^2 \rangle_M = k n T$ . Considering the mass  $M$  of gas contained in a volume  $V$ , the number of mono-atomic molecules  $N$  in the mass  $M$  is  $M/m$ , and the number density  $n$  is therefore  $N/V$ . The thermodynamic pressure is then given by  $pV = NkT$ . Alternatively one can write  $N = n N_a$ , where  $n$  is the number of moles of gas present and  $N_a$  is Avogadro's number. Then, the *ideal gas law*, yields:

$$pV = nRT \quad (2.643)$$

where  $R = k N_a$  is the universal gas constant. This formula may also be valid for a gas not in equilibrium provided that the molecules possess only translational energy.

### 2.11.1 Non-Ideal Gases

The ideal gas law is not accurately followed at high pressure because the molecular size becomes important as the molecules are packed closer together. Likewise, at low temperatures the molecular interactions may become more important and can cause deviations from the ideal gas behavior. For such system conditions, more complex equations of state formulations are required.

Considering real non-ideal gases, the basic kinetic theory for ideal gases must be modified to account for the anomalous real gas behavior caused by the fact that real gas molecules attract each other and have finite volumes. The van der Waals equation

of state, among other equations of state formulations proposed in the literature, includes parameters that relate to molecular size and interactions:

$$p = \frac{nRT}{V - nb} - \frac{an^2}{V^2} \quad (2.644)$$

## 2.12 Extending the Kinetic Theory to Denser Gases

The preceding sections in this chapter deal with the kinetic theory of dilute gases summarizing the statistical modeling concepts, deriving the governing conservation equations and fairly accurate relations determining the transport coefficients from first principles. The starting point for the kinetic theory of dilute mono-atomic gases is the Boltzmann equation determining the evolution of the distribution function in time and space. The formulation of the collision term is restricted to gases that are sufficiently dilute so that only binary collisions need to be taken into account. It is also required that the molecular dimensions are small in comparison with the mean distance between the molecules, hence the transfer of molecular properties is solely regarded as a consequence of the free motion of molecules between collisions. Obviously, these restrictions are not met in dense gases, so the dilute gas results are not acceptable for higher-density systems (e.g., [39], p. 356). After recognizing these model restrictions, Enskog [37] made a first attempt to extend the kinetic theory of dilute mono-atomic gases to slightly higher densities.

Enskog's [37] kinetic theory extension consists in the introduction of corrections that account for the fact that for dense gases the molecular diameter is no longer small compared with the average intermolecular distance. The fundamental postulate is that as a dilute gas is compressed two novel effects become important because the molecules have finite volumes. First, it is expected that during a molecular collision momentum and energy are transferred over a distance equal to the separation of the molecules. In the particular case of rigid spherical molecules this collisional transfer of momentum and energy takes place instantaneously and results in a transfer over the distance between their centers. Second, the collision frequency may be altered. One possible mechanism is that the collision frequency is increased because the particle diameter is not negligible small compared with the average distance between the molecules. However, the collision frequency may also decrease because the molecules are close enough to shield one another from oncoming molecules. Nevertheless, the probability of multiple simultaneous collisions is considered negligible. In the following subsections the derivation of Enskog's equation is examined [37].

### 2.12.1 Boltzmann Equation Collision Frequency Reformulation

To derive the Enskog's equation for a dense gas, Enskog [37] did departure from the kinetic theory of dilute mono-atomic gases that is described by the Boltzmann

equation determining the evolution of the single distribution function in time and space. Moreover, the original formulation of the collision term is restricted to gases that are sufficiently dilute so that only binary collisions need to be taken into account. Even for the dilute gas Boltzmann equation, the choice of using the Maxwellian billiard ball- or rigid sphere model representing the molecules allows a reformulation of the collision frequency and the collision term. That is, it has been shown that the collision frequency (2.160) which is formulated in terms of the solid angle  $d\Omega_{g'}$  and used in the Boltzmann equation (2.184) for dilute gas, can be expressed in an alternative form in terms of the alternative solid angle  $d\mathbf{k}$ . Hence, before the Enskog modifications to the Boltzmann equation are treated, this prerequisite collision frequency reformulation is outlined in this subsection.

In the analysis of a binary collision between molecules with velocities  $\mathbf{c}_1$  and  $\mathbf{c}_2$  the direction of the line of centers at collision can be specified by the unit vector  $\mathbf{k}$  along the apse-line (i.e., in the particular case of rigid spherical molecules, the apse-line corresponds to the line joining the centers of the two molecules at the instant of contact), Fig. 2.7. This unit vector is precisely characterized by the polar angles  $(\psi, \phi)$ . Therefore, instead of describing the deflection<sup>45</sup> with the angles  $(\theta, \phi)$ , it is more convenient to use the angles  $(\psi, \phi)$  since in these variables the final velocity  $\mathbf{g}'_{21}$  is more simply related to the initial velocity  $\mathbf{g}_{21}$  (i.e., by symmetry the projections of  $\mathbf{g}_{21}$  and  $\mathbf{g}'_{21}$  on  $\mathbf{k}$  are equal and of opposite sign:  $\mathbf{k} \cdot \mathbf{g}_{21} = -\mathbf{k} \cdot \mathbf{g}'_{21}$ , as discussed in Sect. 2.4.2.2). In particular, in Sect. 2.4.2 we found that when the collision term in (2.184) is expressed in terms of the impact parameter (i.e.,  $b db d\phi$ ),  $\mathbf{c}'$  and  $\mathbf{c}'_1$  should be given as functions of  $\mathbf{c}$ ,  $\mathbf{c}_1$ ,  $b$  and  $\phi$ . Alternatively, when the collision term is rewritten in terms of  $\sigma_A(\theta, g)d\Omega'$  the velocities  $\mathbf{c}'$  and  $\mathbf{c}'_1$  must be given as functions of  $\mathbf{c}$ ,  $\mathbf{c}_1$  for given  $\Omega'$ , through the law of collision. We can then, for example, use (2.132)–(2.134) expressed in the particular reference frame chosen (i.e., the center of force frame). However, a third and more common approach (i.e., made possible by the use of the hard sphere molecular model thus available both for dilute and dense gases) is to use the unit vector  $\mathbf{k}$  to describe the scattering. That is, we express the scattering cross section in terms of the variable  $\mathbf{k}$  rather than  $\theta$ . Therefore, when the scattering cross section is expressed in terms of the unit vector  $\mathbf{k}$ , (2.132)–(2.134) can be used directly to compute  $\mathbf{c}'$  and  $\mathbf{c}'_1$  as these relations are independent of the laboratory frame. The latter formulation plays a fundamental role in the applications of kinetic theory to denser gases, hence it is worthwhile to display its derivation in further details.

The scattering cross section is expressed in terms of the variable  $\mathbf{k}$ , simply by defining a function  $s_A(\psi, g)$  by [109, 117]:

$$s_A(\psi, g) \sin \psi d\psi d\phi = \sigma_A(\theta, g) \sin \theta d\theta d\phi \quad (2.645)$$

<sup>45</sup> The deflection angle  $\theta$  is defined as the angle between the final and initial velocities:  $\theta = \pi - 2\psi$ . It appears that the phrase scattering is used for the case of Maxwellian billiard ball particles, whereas the phrase deflection is used in the more general case considering a center of force.



in such a way that the number of particles deflected into the corresponding differential surface element of a sphere of unit radius per unit time (2.139) becomes:

$$I\sigma_A(\theta, g) \sin \theta d\theta d\phi = Is_A(\psi, g) \sin \psi d\psi d\phi \quad (2.646)$$

By trigonometric manipulations using (2.146), we obtain:

$$s_A(\psi, g) = \sigma_A(\theta, g) \frac{\sin \theta d\theta d\phi}{\sin \psi d\psi d\phi} = 4\sigma_A(|\pi - 2\psi|; g) \cos \psi \quad (2.647)$$

where we have required that  $s_A$  is a positive factor by using a positive angle:  $\theta = |\pi - 2\psi|$ .

It appears that the variable  $\mathbf{k}$  will be convenient shortly calculating the collision term because it allows us to write down the number of scattered particles in a form independent of the particular system of coordinates used in the previous calculations (i.e., the laboratory frame). Trigonometrical considerations imply that:

$$\cos \psi = \mathbf{k} \cdot \mathbf{e}_{g'} = \mathbf{k} \cdot \frac{\mathbf{g}'_{21}}{|\mathbf{g}'_{21}|} \quad (2.648)$$

or,

$$\psi = \arccos(\cos \psi) = \arccos\left(\frac{\mathbf{k} \cdot \mathbf{g}'_{21}}{g}\right) \quad (2.649)$$

and we introduce a novel quantity

$$d\mathbf{k} = \sin \psi d\psi d\phi \quad (2.650)$$

denoting a differential area of a sphere of unit radius. Hence,  $\psi$  and  $\phi$  represent the polar angles around  $\mathbf{k}$ .

It follows that the number of particles scattered into the differential area element per unit time, given by (2.646), can be rewritten using (2.648)–(2.650). The result is:

$$\begin{aligned} I\sigma_A(\theta, g) \sin \theta d\theta d\phi &= Is_A(\psi, g) \sin \psi d\psi d\phi = Is_A(\psi, g) d\mathbf{k} \\ &= Is_A\left(\arccos\left(\frac{\mathbf{k} \cdot \mathbf{g}'_{21}}{g}\right), g\right) d\mathbf{k} \\ &= Is_A(\arccos(\mathbf{k} \cdot \mathbf{e}_{g'}), |\mathbf{g}'_{21}|) d\mathbf{k} = Is_A(\mathbf{k}, \mathbf{g}'_{21}) d\mathbf{k} \end{aligned} \quad (2.651)$$

which is independent of the laboratory reference frame, as it is expressed in a system of coordinates moving with the center of mass.

For hard spheres (2.651) takes a particularly simple form, using (2.149), (2.647) and (2.648), we get:

$$s_A(\mathbf{k}, \mathbf{g}'_{21}) = s_A(\arccos(\frac{\mathbf{k} \cdot \mathbf{g}'_{21}}{g}), g) = 4\sigma_A(\psi, g)\mathbf{k} \cdot \mathbf{e}_{g'} = 4(\frac{d_{12}^2}{4})\mathbf{k} \cdot \mathbf{e}_{g'} = d_{12}^2\mathbf{k} \cdot \mathbf{e}_{g'} \quad (2.652)$$

Making an inversion of the trajectory with respect to the origin  $O$  and reversing the velocities, the unit vector along the apse-line changes sign, whereas the deflection angle  $\theta$  does not change in these transformations [117]. Hence, in accordance with the Liouville law for elastic collisions, the cross sections of the two processes are the same and consistently  $s(\mathbf{k}', \mathbf{g}_{21}) = s(\mathbf{k}, \mathbf{g}_{21}) = s(-\mathbf{k}, \mathbf{g}_{21})$ .

Reformulating (2.651), using (2.648) and (2.652), we get:

$$|\mathbf{g}_{21}|I\sigma_A(\theta, g)d\Omega' = |\mathbf{g}_{21}|Is_A(\mathbf{k}, \mathbf{g}'_{21})d\mathbf{k} = Id_{12}^2\mathbf{k} \cdot \mathbf{g}_{21}d\mathbf{k} \quad (2.653)$$

or, simply

$$g\sigma_A(\theta, g)d\Omega' = d_{12}^2\mathbf{k} \cdot \mathbf{g}_{21}d\mathbf{k} = d_{12}^2gd\mathbf{k} \cos \psi \quad (2.654)$$

It follows that the elementary area  $bd\phi db$  is the projection of  $d_{12}^2d\mathbf{k}$  on a plane normal to  $\mathbf{g}_{21}$ , where  $\mathbf{g}_{21} = \mathbf{c}_2 - \mathbf{c}_1$ , and if  $\psi$  is the angle between  $\mathbf{g}_{21}$  and  $\mathbf{k}$  we get:

$$gbd\phi db = d_{12}^2gd\mathbf{k} \cos \psi = d_{12}^2\mathbf{k} \cdot \mathbf{g}_{21}d\mathbf{k} \quad (2.655)$$

The collision frequency can now be obtained from (2.160) as:

$$f(\mathbf{r}, \mathbf{c}, t)f_1(\mathbf{r}_1, \mathbf{c}_1, t)d_{12}^2\mathbf{g}_{21} \cdot \mathbf{k}d\mathbf{k}d\mathbf{c}_1d\mathbf{c}d\mathbf{r} \quad (2.656)$$

This formulation of the collision frequency is valid for the rigid sphere molecular model and forms the basis for the Enskog's equation development.

### 2.12.2 Enskog's Equation

For dilute mono-atomic gases we have shown that the evolution of the distribution function is given by the Boltzmann equation as expressed by (2.184). Hence, considering dense gases it might be natural to start out from this result. Enskog [37] derived a modified Boltzmann equation for the evolution of the distribution function supposedly valid for denser gases. No changes was made to the LHS of the equation, whereas an extended form of the collision term was introduced due to the finite size of the molecules. More precisely, Enskog [37] considered a mono-atomic gas composed of rigid spherical molecules of diameter  $d$ . The restriction to rigid spheres was made because multi-body collisions need not be considered, as for this special molecular model there are essentially no three-body and higher order collisions. For dense gas, the binary molecular collisions were assumed elastic just as for dilute gas. The major aim was to take into account the mechanisms of instantaneous momentum and energy transfer over the distance separating the centers of the two colliding molecules,  $d_{12} = d$ . Another important goal was to extend the collision frequency formula correcting for the finite size of the molecules. Considering the impact of

collisions for dilute mono-atomic gases we have shown in the foregoing paragraphs that we need to know the numbers of pairs of molecules both lying in the element  $d\mathbf{r}$  which are going to collide in the time interval  $dt$  and elementary knowledge from scattering theory. Hence, during a time interval  $dt$  the expected number of collisions in the volume element  $d\mathbf{r}$  about  $\mathbf{r}$  between molecules in the velocity ranges  $d\mathbf{c}$  about  $\mathbf{c}$  and  $d\mathbf{c}_1$  about  $\mathbf{c}_1$ , with the infinitesimal solid angle in the range  $d\Omega'$  about  $\Omega'$ , is given by the collision term on the RHS of (2.184).

For convenience, the Maxwell-Boltzmann equation (2.67) with the collision operator definition (2.69) is rewritten here defining the point of departure in Enskog's model development:

$$\frac{\partial f}{\partial t} + \mathbf{c} \cdot \frac{\partial f}{\partial \mathbf{r}} + \mathbf{F} \cdot \frac{\partial f}{\partial \mathbf{c}} = \int_{-\infty}^{\infty} \int_{4\pi} (f' f'_1 - f f_1) g \sigma_A(\Omega) d\Omega' d\mathbf{c}_1 \quad (2.67)$$

By use of (2.654) or (2.656), the collision operator in the Maxwell-Boltzmann equation (2.67) can be reformulated. The reformulated Maxwell-Boltzmann equation is given as:

$$\frac{\partial f}{\partial t} + \mathbf{c} \cdot \frac{\partial f}{\partial \mathbf{r}} + \mathbf{F} \cdot \frac{\partial f}{\partial \mathbf{c}} = \int_{-\infty}^{\infty} \int_{4\pi} (f' f'_1 - f f_1) d_{12}^2 (\mathbf{g}_{12} \cdot \mathbf{k}) d\mathbf{k} d\mathbf{c}_1 \quad (2.657)$$

### 2.12.2.1 Enskog's Boltzmann Equation Modifications

Just as in the Boltzmann theory [10], in Enskog's theory [37] the state of the gas is characterized by a single-particle distribution function  $f(\mathbf{r}, \mathbf{c}, t)$  defined such that  $f(\mathbf{r}, \mathbf{c}, t) d\mathbf{r} d\mathbf{c}$  gives the number of molecules in the volume element between  $\mathbf{r}$  and  $\mathbf{r} + d\mathbf{r}$  and with velocities between  $\mathbf{c}$  and  $\mathbf{c} + d\mathbf{c}$  at time  $t$ . Moreover, Enskog proposed that the basic assumptions of molecular chaos and elastic molecular collisions hold also for dense gas. So far it has been shown that the collision frequency (2.160) which is formulated in terms of the solid angle  $d\Omega_{g'}$  and used in the Boltzmann equation (2.184) for dilute gas, can be expressed in an alternative form (2.656) in terms of the alternative solid angle  $d\mathbf{k}$ . In addition to this minor collision frequency manipulation, Enskog [37] considered that in a dense gas the volume of the molecules is comparable with the total volume occupied by the gas. The effect of this relative volume change is to reduce the volume in which the centre of any one molecule can lie, and thus to increase the probability of a collision. The collision term on the RHS of Boltzmann equation (2.184) was thus modified by Enskog [37] in order to take these effects into account. First, the frequency of collisions (2.656) is changed by a pre-factor  $\chi$ , to increase the probability of a collision for a dense gas:

$$\chi f(\mathbf{r}, \mathbf{c}, t) f_1(\mathbf{r}_1, \mathbf{c}_1, t) d_{12}^2 \mathbf{g} \cdot \mathbf{k} d\mathbf{k} d\mathbf{c}_1 d\mathbf{c} d\mathbf{r} \quad (2.658)$$

where  $\chi$  is a free volume correction function that is unity for dilute gases, and increases with increasing gas density towards infinity as the gas density approaches

the state of closest packing where no motion is possible.  $\chi$  is considered a function of position but, by the assumption of molecular chaos, not on velocity.

The correction function  $\chi$  is related to the virial expansion of the equation of state and fitted to experimental data [55]. Enskog ([37], p. 9) and Chapman and Cowling ([20], p. 299) gave an approximate relation for the value for  $\chi$  for a fairly rare uniform gas:

$$\chi \approx 1 + \frac{5}{8}b\rho \quad (2.659)$$

where  $b\rho = 2\pi n\sigma_A^3/3$ ,  $b = 2\pi\sigma_A^3/m$  and  $\rho = mn$ .

Second, due to the finite size of the colliding molecules the centers of the two molecules are not at the same point. If, at the instant of collision, the center of the first molecule is at  $\mathbf{r}$ , the center of the second one is at  $\mathbf{r} \pm d_{12}\mathbf{k}$ . For this reason the two distribution functions should be evaluated at different points, so that for the direct collision  $f(\mathbf{r}_1, \mathbf{c}_1, t)$  is replaced by  $f(\mathbf{r} - d_{12}\mathbf{k}, \mathbf{c}_1, t)$ . The correction function is determined at the point of contact between the two particles, hence the collision frequency for the direct collision is approximated as:

$$\chi(\mathbf{r} - \frac{1}{2}d_{12}\mathbf{k}) f(\mathbf{r}, \mathbf{c}, t) f(\mathbf{r} - d_{12}\mathbf{k}, \mathbf{c}_1, t) d_{12}^2 \mathbf{g} \cdot \mathbf{k} d\mathbf{k} d\mathbf{c}_1 d\mathbf{c} d\mathbf{r} \quad (2.660)$$

As for dilute gases, corresponding to any direct collision specified by the variables  $\mathbf{c}, \mathbf{c}_1, \mathbf{k}$  there is an analogous inverse collision in which  $\mathbf{c}, \mathbf{c}_1$  are the velocities of the molecules after the collision, while  $-\mathbf{k}$  is the direction of the apse-line. In such a collision the center of the second molecule is at  $\mathbf{r} + d_{12}\mathbf{k}$ , while the point of contact is at  $\mathbf{r} + \frac{1}{2}d_{12}\mathbf{k}$ . The correction function is still determined at the point of contact between the two particles, hence the collision frequency for the inverse collision is approximated as:

$$\chi(\mathbf{r} + \frac{1}{2}d_{12}\mathbf{k}) f(\mathbf{r}, \mathbf{c}, t) f(\mathbf{r} + d_{12}\mathbf{k}, \mathbf{c}_1, t) d_{12}^2 \mathbf{g} \cdot \mathbf{k} d\mathbf{k} d\mathbf{c}_1 d\mathbf{c} d\mathbf{r} \quad (2.661)$$

It follows that the Enskog's equation describing the evolution of the distribution function for a dense gas of rigid spherical molecules is analogous to the Boltzmann equation (2.184) but containing the modified collision term on the following form:

$$\begin{aligned} \frac{\mathcal{D}f}{\mathcal{D}t} = & \int \int [\chi(\mathbf{r} + \frac{1}{2}d_{12}\mathbf{k}) f'(\mathbf{r}, \mathbf{c}', t) f'_1(\mathbf{r} + d_{12}\mathbf{k}, \mathbf{c}_1, t) \\ & - \chi(\mathbf{r} - \frac{1}{2}d_{12}\mathbf{k}) f(\mathbf{r}, \mathbf{c}, t) f_1(\mathbf{r} - d_{12}\mathbf{k}, \mathbf{c}_1, t)] d_{12}^2 (\mathbf{g} \cdot \mathbf{k}) d\mathbf{k} d\mathbf{c}_1 \end{aligned} \quad (2.662)$$

This extended Boltzmann equation is called the *Enskog equation*.

Enskog [37] further considered that a prerequisite in order to solve this equation is that all quantities must be evaluated at a common point. Assuming that the conditions in the dense gas are sufficiently smooth, each of the functions  $\chi(\mathbf{r} \pm \frac{1}{2}d_{12}\mathbf{k})$ ,  $f_1(\mathbf{r} - d_{12}\mathbf{k}, \mathbf{c}_1, t)$  and  $f'_1(\mathbf{r} + d_{12}\mathbf{k}, \mathbf{c}'_1, t)$  on the RHS of (2.662) was expanded in a Taylor

series near  $\mathbf{r}$ , neglecting the third- and higher-order terms. Then, Enskog's equation can be written as [69]:

$$\frac{\partial f}{\partial t} + c_i \frac{\partial f}{\partial x_i} + F_i \frac{\partial f}{\partial c_i} = J_0(ff) + J_1(ff) + J_2(ff) \quad (2.663)$$

where

$$J_0(ff) = \chi \int_{-\infty}^{\infty} \int_{4\pi} (f'_1 f' - f_1 f) d_{12}^2 (\mathbf{g}_{12} \cdot \mathbf{k}) d\mathbf{k} d\mathbf{c}_1 \quad (2.664)$$

$$J_1(ff) = d_{12} \int_{-\infty}^{\infty} \int_{4\pi} \left\{ \chi \left[ f' \frac{\partial f'_1}{\partial x_i} + f \frac{\partial f_1}{\partial x_i} \right] + \frac{1}{2} \frac{\partial \chi}{\partial x_i} (f'_1 f' - f_1 f) \right\} k_i d_{12}^2 (\mathbf{g}_{12} \cdot \mathbf{k}) d\mathbf{k} d\mathbf{c}_1 \quad (2.665)$$

$$J_2(ff) = \frac{d_{12}^2}{2} \int_{-\infty}^{\infty} \int_{4\pi} \left\{ \chi \left[ f' \frac{\partial^2 f'_1}{\partial x_i \partial x_j} - f \frac{\partial^2 f_1}{\partial x_i \partial x_j} \right] + \frac{\partial \chi}{\partial x_i} \left[ f' \frac{\partial f'_1}{\partial x_i} + f \frac{\partial f_1}{\partial x_i} \right] + \frac{1}{4} \frac{\partial^2 \chi}{\partial x_i \partial x_j} (f'_1 f' - f_1 f) \right\} k_i k_j d_{12}^2 (\mathbf{g}_{12} \cdot \mathbf{k}) d\mathbf{k} d\mathbf{c}_1 \quad (2.666)$$

where all quantities are evaluated at  $\mathbf{r}$ .

In Enskog's equation (2.662),  $(\mathbf{c}, \mathbf{c}_1)$  and  $(\mathbf{c}', \mathbf{c}'_1)$  are the velocities of two molecules before and after collision, respectively, and they are connected by the relations (being analogue to the dilute mono-atomic gas relations (2.133) and (2.134)):

$$\mathbf{c}' = \mathbf{c} + (\mathbf{k} \cdot \mathbf{g}_{21}) \mathbf{k} \quad (2.667)$$

$$\mathbf{c}'_1 = \mathbf{c}_1 + (\mathbf{k} \cdot \mathbf{g}_{21}) \mathbf{k} \quad (2.668)$$

in which  $\mathbf{g}_{21} = \mathbf{c}_2 - \mathbf{c}_1$  is the relative linear velocity and  $\mathbf{k}$  is the unit vector in the direction of the line which joins the two molecules centers at collision pointing from the molecule labeled by 1 to the other. Moreover,  $d_{12}$  is the diameter of the molecule and  $d\mathbf{k} = \sin \psi d\psi d\phi$ ;  $0 \leq \psi \leq \pi/2$  is the angle between  $\mathbf{k}$  and  $\mathbf{g}_{21}$  while  $0 \leq \phi \leq 2\pi$  is the angle between the plane containing  $\mathbf{k}$  and  $\mathbf{g}_{21}$  and a reference plane through  $\mathbf{g}_{21}$ . The plus or minus sign corrections refer to collisions that take  $(\mathbf{c}, \mathbf{c}_1)$  or  $(\mathbf{c}', \mathbf{c}'_1)$  as initial velocities, respectively.

### 2.12.3 Flux Vectors

In Sect. 2.5 the flux of molecular property  $\psi$  across a small surface element  $dA$  in a dilute gas at low pressure was considered. For dilute gases the molecules could be considered to be point masses. In dense gases, however, the finite size of the molecules

must be taken into account and, thus the instantaneous *collisional transfer* of the molecular property  $\psi$  across  $dA$ . That is, the instantaneous transfer due to collisions between molecules whose centers lie on opposite side of  $dA$  while the line joining their centers cuts  $dA$  must be taken into account.

The sign convention is define by  $\mathbf{n}$  being the unit normal to  $dA$ , located at  $\mathbf{r}$ , pointing from the negative to the positive side. Consider a collision between a molecule having velocity  $\mathbf{c}$  and a molecule having velocity  $\mathbf{c}_1$ . If the first molecule lies on the positive side of  $dA$  and the second on the negative side, the inner product  $\mathbf{k} \cdot \mathbf{n}$  is positive. At collision, the line joining the centers of the molecules must cut  $dA$ , so the center of the first molecule must lie within a cylinder having  $dA$  as base and whose generators are parallel to  $\mathbf{k}$  and of length  $d$ . Thus, the volume of this cylinder is  $d(\mathbf{k} \cdot \mathbf{n})dA$ . The mean positions of the centers of the two molecules at the instant of the collision are  $\mathbf{r} + \frac{1}{2}d\mathbf{k}$  and  $\mathbf{r} - \frac{1}{2}d\mathbf{k}$ , and the mean position of the point of contact is  $\mathbf{r}$ . Hence, the average number of such collisions per unit time at  $t$ , in which  $\mathbf{c}$ ,  $\mathbf{c}_1$  and  $\mathbf{k}$  lie in the range  $d\mathbf{c}$ ,  $d\mathbf{c}_1$  and  $d\mathbf{k}$ , respectively, is, by analogy with (2.660):

$$\chi(\mathbf{r})f(\mathbf{r} + \frac{1}{2}d_{12}\mathbf{k}, \mathbf{c}, t)f_1(\mathbf{r} - \frac{1}{2}d_{12}\mathbf{k}, \mathbf{c}_1, t)d_{12}^3\mathbf{g} \cdot \mathbf{k}d\mathbf{k}d\mathbf{c}_1d\mathbf{c}(\mathbf{k} \cdot \mathbf{n})dA \quad (2.669)$$

For convenience, henceforth a new notation is introduced:

$$d\Gamma = d_{12}^3\mathbf{g} \cdot \mathbf{k}d\mathbf{k}d\mathbf{c}_1d\mathbf{c} \quad (2.670)$$

Each such collision causes the transfer of a quantity  $(\psi - \psi')$  of the molecular property  $\psi$  across  $dA$ , so the total transfer by collisions of this type, per unit time and per unit area, is:

$$\chi(\mathbf{r}) \int \int \int (\psi' - \psi)f(\mathbf{r} + \frac{1}{2}d_{12}\mathbf{k}, \mathbf{c}, t)f_1(\mathbf{r} - \frac{1}{2}d_{12}\mathbf{k}, \mathbf{c}_1, t)(\mathbf{k} \cdot \mathbf{n})d\Gamma \quad (2.671)$$

in which the integration is over all values of the variables such that  $(\mathbf{g}_{21} \cdot \mathbf{k})$  and  $(\mathbf{k} \cdot \mathbf{n})$  are positive. That is, the condition  $(\mathbf{g}_{21} \cdot \mathbf{k}) > 0$  ensures that the molecules collide, whereas the condition  $(\mathbf{k} \cdot \mathbf{n})$  is a consequence of the definition of  $\mathbf{k}$  and  $\mathbf{n}$ .

The resulting *flux vector* associated with the collisional transfer of property  $\psi$  is expressed as:

$$\Phi_\psi = \chi(\mathbf{r}) \iiint_{\substack{\mathbf{g}_{21} \cdot \mathbf{k} > 0 \\ \mathbf{k} \cdot \mathbf{n} > 0}} (\psi' - \psi)f(\mathbf{r} + \frac{1}{2}d_{12}\mathbf{k}, \mathbf{c}, t)f_1(\mathbf{r} - \frac{1}{2}d_{12}\mathbf{k}, \mathbf{c}_1, t)\mathbf{k}d\Gamma \quad (2.672)$$

The summational invariant quantities like mass, momentum and energy, certain simplifying manipulations are possible because  $\psi + \psi_1 = \psi' + \psi'_1$ . We may then let the variables of integration  $\mathbf{c}$  and  $\mathbf{c}_1$  be interchanged. This operation is equivalent to interchanging the roles of the two colliding molecules, so that  $\mathbf{k}$  is replaced by  $-\mathbf{k}$ ,  $\mathbf{g}_{21}$  is replaced by  $-\mathbf{g}_{21}$ , and  $\psi' - \psi$  by  $\psi'_1 - \psi_1$  which is equal to  $-(\psi' - \psi)$ . Consequently, the integrand of (2.672) is unchanged but the region of integration is

now restricted by the condition  $\mathbf{g}_{21} \cdot \mathbf{k} > 0$  and  $\mathbf{k} \cdot \mathbf{n} < 0$ . The flux vector associated with the collisional transfer of a summational invariant  $\psi$  is, therefore, equal to:

$$\begin{aligned} \Phi_{\psi, \text{collision}} & \quad (2.673) \\ &= \frac{1}{2} \chi(\mathbf{r}) \iiint_{\mathbf{g}_{21} \cdot \mathbf{k} > 0} (\psi' - \psi) f(\mathbf{r} + \frac{1}{2} d_{12} \mathbf{k}, \mathbf{c}, t) f_1(\mathbf{r} - \frac{1}{2} d_{12} \mathbf{k}, \mathbf{c}_1, t) \mathbf{k} d\Gamma \end{aligned}$$

If the conditions in the gas are sufficiently smooth,  $f(\mathbf{r} \pm \frac{1}{2} d_{21} \mathbf{k})$  may be expanded in a Taylor series around  $\mathbf{r}$ , so that  $\Phi$  may be approximated as:

$$\begin{aligned} \Phi_{\psi, \text{collision}} &= \frac{1}{2} \chi(\mathbf{r}) \iiint_{\mathbf{g}_{21} \cdot \mathbf{k} > 0} (\psi' - \psi) f(\mathbf{r}, \mathbf{c}, t) f_1(\mathbf{r}, \mathbf{c}_1, t) \mathbf{k} d\Gamma \quad (2.674) \\ &+ \frac{1}{4} d_{12} \chi(\mathbf{r}) \iiint_{\mathbf{g}_{21} \cdot \mathbf{k} > 0} (\psi' - \psi) \left( \mathbf{k} \cdot f(\mathbf{r}, \mathbf{c}, t) f_1(\mathbf{r}, \mathbf{c}_1, t) \nabla_r \ln \frac{f(\mathbf{r}, \mathbf{c}, t)}{f_1(\mathbf{r}, \mathbf{c}_1, t)} \right) \mathbf{k} d\Gamma \end{aligned}$$

The kinetic flux contribution due to the flow of molecules across the surface is given by (2.186):

$$\Phi_{\psi, \text{kinetic}} = \int_{-\infty}^{\infty} \psi f \mathbf{C} d\mathbf{c} \quad (2.675)$$

The total flux of the property  $\psi$  is then the sum of the two contributions:

$$\Phi_{\psi} = \Phi_{\psi, \text{kinetic}} + \Phi_{\psi, \text{collision}} \quad (2.676)$$

The Chapman-Enskog solution method, as discussed in Sect. 2.8 for a dilute mono-atomic gas, can be applied to the Enskog's equation as well. Solving the Enskog's equation by the perturbation method to determine  $f$ , we find that the *zero-order approximation* (i.e.,  $f \approx f^{(0)}$ ) of the *pressure tensor* and the *heat flux* vector are obtained from (2.675) with  $\psi = m\mathbf{c}$  and  $\psi = \frac{1}{2} m C^2$ , respectively:

$$\mathbf{p}_{\text{kinetic}}^{(0)} = \Phi_{m\mathbf{c}, \text{kinetic}}^{(0)} = nkT\mathbf{e} \quad (2.677)$$

$$\mathbf{q}_{\text{kinetic}}^{(0)} = \Phi_{mC^2, \text{kinetic}}^{(0)} = 0 \quad (2.678)$$

However, in this case the product  $nkT$  is not equal to the static pressure in the gas, because the collisional contribution to the pressure does not vanish. With  $f \approx f^{(0)}$ , the collisional flux relation (2.674) gives for the *pressure tensor* (i.e., with  $\psi = m\mathbf{c}$ ):

$$\Phi_{m\mathbf{c}, \text{collision}}^{(0)} = \frac{1}{2} \chi(\mathbf{r}) \iiint_{\mathbf{g}_{21} \cdot \mathbf{k} > 0} m(\mathbf{c}' - \mathbf{c}) f^{(0)}(\mathbf{r}, \mathbf{c}, t) f_1^{(0)}(\mathbf{r}, \mathbf{c}_1, t) \mathbf{k} d\Gamma \quad (2.679)$$

This integral can be integrated analytically, thus the result is [39]:

$$\mathbf{p}_{\text{collision}}^{(0)} = \Phi_{mc, \text{collision}}^{(0)} = \frac{2}{3} \pi n d_{12}^3 \chi n k T \mathbf{e} \quad (2.680)$$

Combining (2.676), (2.677) and (2.680) we conclude that in a zero-order theory, the pressure tensor assumes the form:

$$\begin{aligned} \mathbf{p}^{(0)} &= \mathbf{p}_{\text{kinetic}}^{(0)} + \mathbf{p}_{\text{collision}}^{(0)} = n k T \mathbf{e} + \frac{2}{3} \pi n d_{12}^3 \chi n k T \mathbf{e} \\ &= (1 + \frac{2}{3} \pi n d_{12}^3 \chi) n k T \mathbf{e} \end{aligned} \quad (2.681)$$

From this analysis, it follows that in a zero-order theory the kinetic theory approximates the static pressure as:

$$p^{(0)} = \frac{1}{3} \mathbf{p}^{(0)} : \mathbf{e} = (1 + \frac{2}{3} \pi n d_{12}^3 \chi) n k T \quad (2.682)$$

The static pressure in equilibrium is related to the temperature and density of the gas through this equation of state. A comparison with the ideal gas law defined in (2.643) might be informative.

In a similar manner, with  $f \approx f^{(0)}$  the collisional part of the molecular *heat flux* (i.e.,  $\psi = \frac{1}{2} m C^2$ ) is found from (2.674):

$$\Phi_{mC^2, \text{collision}}^{(0)} = \frac{1}{2} \chi(\mathbf{r}) \iiint_{\mathbf{g}_{21} \cdot \mathbf{k} > 0} \frac{1}{2} m (C'^2 - C^2) f^{(0)}(\mathbf{r}, \mathbf{c}, t) f_1^{(0)}(\mathbf{r}, \mathbf{c}_1, t) \mathbf{k} d\Gamma \quad (2.683)$$

In a zero-order theory the analytical solution to this integral is zero [39]:

$$\mathbf{q}_{\text{collision}}^{(0)} = \Phi_{\frac{1}{2}mC^2, \text{collision}}^{(0)} = 0 \quad (2.684)$$

Combining (2.676), (2.678) and (2.684) we conclude that in a zero-order theory, the heat flux vector assumes the form:

$$\mathbf{q}^{(0)} = \mathbf{q}_{\text{kinetic}}^{(0)} + \mathbf{q}_{\text{collision}}^{(0)} = 0 \quad (2.685)$$

In the *first order approximation* considering that the gas is not in the uniform steady-state, a first approximation to  $f$  is given by  $f = f^{(0)}(1 + \Phi^{(1)})$ . The solution procedure is thus analogous to the dilute gas approach outlined in Sect. 2.8.2. However, for dense gas the perturbation function,  $\Phi^{(1)}$ , differs from the corresponding perturbation function (2.267) for a dilute gas only in that the term involving  $\nabla \ln T$  is multiplied by  $(1 + \frac{2}{3} \pi n d_{12}^3 \chi)/\chi$  and the term involving  $\nabla \mathbf{v}$  by  $(1 + \frac{4}{15} \pi n d_{12}^3 \chi)/\chi$ . The dense gas perturbation function is given by:

$$\Phi^{(1)} = -\frac{1}{n\chi} \left\{ (1 + \frac{2}{3} \pi n d_{12}^3 \chi) \mathbf{A} \cdot \nabla \ln T + (1 + \frac{4}{15} \pi n d_{12}^3 \chi) \mathbf{B} : \nabla \mathbf{v} \right\} \quad (2.686)$$



The first order *pressure tensor* approximations are given as [39]:

$$\begin{aligned} \mathbf{p}^{(1)} &= \mathbf{p}_{\text{kinetic}}^{(1)} + \mathbf{p}_{\text{collision}}^{(1)} \\ &= p\mathbf{e} - \kappa(\nabla \cdot \mathbf{v})\mathbf{e} - 2 \left[ \frac{1}{\chi} \left( 1 + \frac{4}{15} \pi n d_{12}^3 \chi \right)^2 \mu^{(0)} + \frac{3}{5} \kappa \right] \mathbf{S} \end{aligned} \quad (2.687)$$

where

$$\begin{aligned} \mathbf{p}_{\text{kinetic}}^{(1)} &= \Phi_{mc, \text{kinetic}}^{(1)} + \Phi_{mc, \text{kinetic}}^{(0)} \\ &= xnkT\mathbf{e} - \frac{2}{\chi} \left( 1 + \frac{4}{15} \pi n d_{12}^3 \chi \right) \mu^{(0)} \mathbf{S} \end{aligned} \quad (2.688)$$

$$\begin{aligned} \mathbf{p}_{\text{collision}}^{(1)} &= \Phi_{mc, \text{collision}}^{(1)} + \Phi_{mc, \text{collision}}^{(0)} \\ &= \frac{2}{3} \pi n d_{12}^3 \chi n k T \mathbf{e} - \frac{8}{15} \pi n d_{12}^3 \left( 1 + \frac{4}{15} \pi n d_{12}^3 \chi \right) \mu^{(0)} \mathbf{S} - \kappa \left[ \frac{6}{5} \mathbf{S} + (\nabla \cdot \mathbf{v}) \mathbf{e} \right] \end{aligned} \quad (2.689)$$

in which

$$\kappa = \frac{4}{9} n^2 d_{12}^4 \chi (\pi m k T)^{1/2} \quad (2.690)$$

By application of the same solution procedure, the first order *heat flux* approximations are given as [39]:

$$\mathbf{q}^{(1)} = \mathbf{q}_{\text{kinetic}}^{(1)} + \mathbf{q}_{\text{collision}}^{(1)} = - \left[ \frac{1}{\chi} \left( 1 + \frac{2}{5} \pi n d_{12}^3 \chi \right)^2 k^{(0)} + C_v \kappa \right] \nabla T \quad (2.691)$$

where

$$\begin{aligned} \mathbf{q}_{\text{kinetic}}^{(1)} &= \Phi_{\frac{1}{2}mC^2, \text{kinetic}}^{(1)} + \Phi_{\frac{1}{2}mC^2, \text{kinetic}}^{(0)} \\ &= - \frac{1}{\chi} \left( 1 + \frac{2}{5} \pi n d_{12}^3 \chi \right) k^{(0)} \nabla T \end{aligned} \quad (2.692)$$

$$\begin{aligned} \mathbf{q}_{\text{collision}}^{(1)} &= \Phi_{\frac{1}{2}mC^2, \text{collision}}^{(1)} + \Phi_{\frac{1}{2}mC^2, \text{collision}}^{(0)} \\ &= - \left[ \frac{2}{5} \pi n d_{12}^3 \left( 1 + \frac{2}{5} \pi n d_{12}^3 \chi \right) k^{(0)} + C_v \kappa \right] \nabla T \end{aligned} \quad (2.693)$$

It is seen that for mono-atomic dense gases both the pressure tensor,  $\mathbf{p}^{(1)}$ , and the heat flux vector  $\mathbf{q}^{(1)}$ , contain two flux contributions (i.e., a kinetic- and a collisional flux contribution) [20, 39, 55].

The *transport coefficients* for a moderately dense gas can be extracted from these results. A comparison of Newton's viscosity law (1.77) from continuum mechanics with (2.687) and of Fourier's law (2.580) with (2.691), approximate values of the transport coefficients (i.e., for the dynamic viscosity and the conductivity) can be determined. The dynamic viscosity,  $\mu^{(1)}$ , is given by:

$$\mu^{(1)} = \frac{1}{\chi} \left( 1 + \frac{4}{15} \pi n d_{12}^3 \chi \right)^2 \mu^{(0)} + \frac{3}{5} \kappa \quad (2.694)$$

The thermal conductivity,  $k^{(1)}$ , is given by the expression:

$$k^{(1)} = \frac{1}{\chi} \left( 1 + \frac{2}{5} \pi n d_{12}^3 \chi \right)^2 k^{(0)} + C_v \kappa \quad (2.695)$$

In the zero-order approximation, the dynamic viscosity and the conductivity are given by:

$$\mu^{(0)} = 1.0160 \times \frac{5}{16 d_{12}^2} \left( \frac{m k T}{\pi} \right)^{1/2} \quad (2.696)$$

$$k^{(0)} = 2.5 C_v \mu^{(0)} \quad (2.697)$$

The zero-order approximation transport coefficient values corresponds to the dilute gas values (2.620) and (2.621), respectively.

### 2.12.4 Enskog's Macroscopic Equations of Change

Analogous to the equation of change of mean molecular properties for dilute gas that was examined in Sect. 2.6, similar macroscopic conservation equations may be derived for dense gas from the Enskog equation. Multiplying the Enskog's equation (2.663) with the summation invariant property,  $\psi$ , and integrating over  $\mathbf{c}$ , the result is the *Enskog's equation of change* on the form:

$$\frac{\partial}{\partial t} \int \psi f d\mathbf{c} + \nabla_r \cdot \int (\psi \mathbf{c} f) d\mathbf{c} + \mathbf{F} \cdot \int f \nabla_c \psi d\mathbf{c} = I_0 + I_1 + I_2 \quad (2.698)$$

where  $I_i = \int \psi J_i(f f) d\mathbf{c}$ ,  $i = 0, 1, 2$ .

Analogous to the analysis of dilute gas in Sect. 2.6, it is easily proved that the integral  $I_0$  vanishes as it is an identical integral with a pre-factor that is independent of the integration. Moreover, by invoking some manipulations considering the equivalence of collisions and their inverses, and by interchanging the roles of the two colliding molecules, the integral  $I_1$  can be written as [39]:

$$I_1 = \frac{1}{2} \nabla_r \cdot \chi \iiint (\psi - \psi') f f_1 \mathbf{k} d\mathbf{\Gamma} \quad (2.699)$$

The last part of  $J_2(f f)$  gives a zero contribution to the integral  $I_2$  due to the same reason that  $I_0$  vanishes. The remainder two parts can after several manipulations be approximated as [39]:

$$I_2 = \frac{1}{4} d_{12} \nabla_r \cdot \chi \iiint (\psi - \psi') \left( \mathbf{k} \cdot f f_1 \nabla_r \ln \frac{f}{f_1} \right) \mathbf{k} d\Gamma \quad (2.700)$$

A comparison of the resulting fluxes  $I_i$ ,  $i = 0, 1, 2$  with (2.674) reveals that:

$$I_0 + I_1 + I_2 = -\nabla_r \cdot \Phi_\psi \quad (2.701)$$

The *Enskog's macroscopic equation of change* (2.698) may thus be written as:

$$\frac{\partial}{\partial t} \int \psi f d\mathbf{c} + \nabla_r \cdot \int (\psi \mathbf{c} f) d\mathbf{c} + \mathbf{F} \cdot \int f \nabla_c \psi d\mathbf{c} = -\nabla_r \cdot \Phi_\psi \quad (2.702)$$

This equation is a generalization of the macroscopic moment equation for dilute gas to dense gas of identical, rigid spherical molecules.

If we choose  $\psi$  as the summational invariants  $m$ ,  $m\mathbf{C}$  and  $mC^2$ , we obtain the Cauchy set of conservation equations named the continuity (2.217), the equation of motion (2.223), and the equation of energy (2.230). The only difference in the final result is that the pressure tensor,  $\mathbf{p}$ , and the heat flux vector,  $\mathbf{q}$ , are made up of two parts (i.e., a kinetic and a collisional contribution):

$$\mathbf{p} = \mathbf{p}_{\text{kinetic}} + \mathbf{p}_{\text{collision}} \quad (2.703)$$

$$\mathbf{q} = \mathbf{q}_{\text{kinetic}} + \mathbf{q}_{\text{collision}} \quad (2.704)$$

The kinetic parts corresponds to the dilute gas pressure tensor and heat flux, as defined by (2.270) with (2.271) and (2.272), respectively.

Substitution of the first order dense gas flux approximations (2.687) and (2.691) into the conservation equations results in the set of non-equilibrium gas dynamics equations (i.e., sometimes named the Navier-Stokes equations) for a mono-atomic dense gas. If the zero order dense gas flux approximations were employed instead, the outcome is the set of equilibrium Euler equations.

## 2.13 Governing Equations for Polydispersed Multiphase Systems

To describe polydispersed multiphase systems the Boltzmann equation can be extended by including the dependency of the internal property coordinates such as the particle size and shape in the definition of the distribution function. In this way a statistical balance formulation can be obtained by means of a distribution function on the form:  $p(\xi, \mathbf{r}, \mathbf{v}_\xi, \mathbf{c}, t) d\xi d\mathbf{r} d\mathbf{v}_\xi d\mathbf{c}$ , defined as the probable number of particles with internal properties in the range  $d\xi$  about  $\xi$ , with a velocity range in property space  $d\mathbf{v}_\xi$  about  $\mathbf{v}_\xi$ , located in the spatial range  $d\mathbf{r}$  about the position  $\mathbf{r}$ , with a velocity range  $d\mathbf{c}$  about  $\mathbf{c}$ , at time  $t$ . The particular Boltzmann type of equation is given by:

$$\frac{\partial p}{\partial t} + \nabla_{\mathbf{r}} \cdot (\mathbf{c} p) + \nabla_{\mathbf{c}} \cdot (\mathbf{F} p) + \nabla_{\xi} \cdot (\mathbf{v}_\xi p) + \nabla_{\mathbf{v}_\xi} \cdot (\mathbf{a}_\xi p) = \mathcal{I} \quad (2.705)$$

The first term on the LHS denotes the time variation of the distribution function  $p$ . The second term on the LHS represents the change in the number density distribution because of fluid particle convection into and out of the range  $d\mathbf{r}$ . The third term on the LHS represents the change in the number density distribution because of acceleration of the fluid particle into and out of the range  $d\mathbf{c}$  in the standard manner. However, in this case the net force  $\mathbf{F}$  acting to accelerate or decelerate the fluid particle includes the body and drag forces (per unit mass). The fourth term on the LHS represents the change in the number density distribution because of transport processes in the property space for example due to fluid particle growth into and out of the range  $d\xi$ . The fifth term on the LHS represents the change in the number density distribution because of accelerations in the property space for example due to acceleration of the fluid particle interface into and out of the range  $d\mathbf{v}_\xi$ . The term on the RHS represents the rate of change in the number density distribution due to particle coalescence, breakage and collisions.

A critical review of the population balance model derivation shows that there exist several transport equations of this type having different theoretical origin and interpretations [141]. The different model versions have specific inherent advantages and disadvantages. Following the same procedure as outlined in Sects. 2.6 and 2.6.1 deriving the governing single phase conservation equations from the original Boltzmann equation, the extended Boltzmann equation can be multiplied by a generalized property function whereupon the resulting equation is integrated over the whole velocity space to give a generic transport equation for the conserved multiphase quantities [118]. In particular, considering that the property function is unity a transport equation for the number distribution function  $f(\xi, \mathbf{r}, t)$  is obtained [82]. This transport equation is generally referred to as the *population balance equation*.

Hulburt and Katz [58] applied this approach to derive a transport equation for the number distribution function describing particulate systems considering growth, nucleation and agglomeration processes. Reyes Jr [118] and Lafi and Reyes [79] derived an extended set of mass, momentum and energy equations to describe poly-dispersed bubbly flows using a fluid particle continuity equation analogous to the Boltzmann's transport equation. In a similar manner Laurent et al. [88] derived the governing conservation equations for poly-dispersed dense sprays of evaporating liquid droplets. Lathouwers and Bellan [83–87] and Chao et al. [16, 17] proposed a similar model for poly-dispersed gas-solid multicomponent reactive processes in fluidized beds. The main challenge in formulating these equations is related to the definition of the collision operator. So far this approach has been restricted to the formulation of the population balance equation. That is, in most cases a general transport equation which is complemented with postulated source term formulations for the particle behavior is used. Randolph [112] and Randolph and Larson [113] used this approach deriving a microscopic population balance equation for the purpose of describing the behavior of particulate systems. Ramkrishna [111] provides further details on a different statistical approach considering also fluid particle systems. The population balance modeling framework is further discussed in Chap. 9.

## 2.14 Multifluid Models with Granular Flow Closures

Enskog's dense gas theory for rigid spheres has also been used as basis developing multifluid granular flow models. The modifications suggested extending the dense gas kinetic theory to particulate flows are discussed in Chap. 4.

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