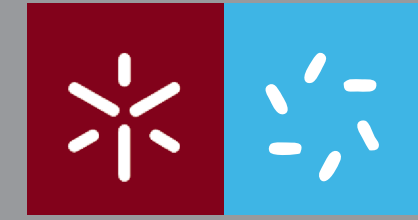


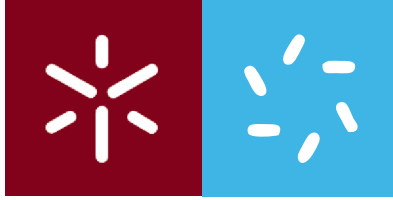


Benjamin Anwasia

**On the hydrodynamic limits of the
Boltzmann equation for reactive mixtures**

Universidade do Minho
Escola de Ciências





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Boltzmann equation for reactive mixtures**

Tese de Doutoramento
Doutoramento em Matemática Aplicada

Trabalho efetuado sob a orientação da
**Professora Doutora Ana Jacinta Pereira da
Costa Soares**

e sob co-orientação da
**Professora Doutora Ana Patrícia Carvalho
Gonçalves**

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Acknowledgements

First and foremost, praises and thanks to God the almighty to whom I am irredeemably indebted to and without whom nothing is possible.

To be involved in a task like writing a thesis would require supports of various kinds from some persons. So I wish to use this opportunity to express my appreciation to those who have one way or the other contributed to making this work a reality.

I would like to express my sincere gratitude to my supervisors Prof. Ana Jacinta Soares and Prof. Patrícia Gonçalves, for accepting to supervise this research in the first place and for the invaluable guidance throughout this research. I would also like to thank them for their time, patience, support, and encouragement throughout my studies, and for providing me with the environment to make this program a successful one, as well as for teaching me how to present the results obtained from my research in a clear and concise manner. I would not have hoped for better supervisors.

I am extremely grateful to my parents Chief Dr. and Mrs. B. N Anwasia (JP) for their prayers, love, support, and sacrifices because there is no limit to the thing they did to ensure I have a good education. Special thanks to my brothers: Engr. Frank Chijioke Anwasia and Henry Kaine Anwasia, to my sisters: Mrs. Chibuzor Obiora, Mrs. Henrietta Oyakhilome, Mrs. Chinelo Nwajei, Mrs. Deborah Okoko, Mrs. Cordelia Iteye, and Anthonia Anwasia. I am extending my heartfelt thanks to my Nephews: Stephen Obiora, Joseph Obiora, Paul Anwasia, Tobechukwu Obiora, Edoseina Oyakhilome, Oseaga Oyakhilome, Chinedum Nwajei, David Nwajei, Efezino Iteye, Majesty Iteye and Nieces: Blessing Obiora, Faith Anwasia, Oserere Oyakhilome, Faith Oyakhilome, Nkiruka Nwajei, Ifeoma Anwasia Nora Okoko, Onyiye Anwasia, High-Praise Iteye and Glory Iteye. You all contributed in one way or the other to what I am today.

To my late brother Kester Uzowulu Anwasia, although you did not live to see this day, I hope I made you proud.

To Alex Obinikpo thank you for the moral support, encouragement, and incredible friendship over the years. I would like to thank all the friends I made along the way in my quest to study abroad. In Barcelona: Precious Olakunlemi Akinsulire, Romanus Abia and Dr. John Afa. In Porto: Dr. Aliyu Ahmad Yusuf, Dr. Salisu Mamman Abdurrahman, Dr. Olaide Aderoju, Dr. Yomi Aboderin, Dr. Francis Nwaebonyi, Babatunde Akinsunmi, Dr. John Ogbonna, Sadiq Abubakar, Shamsuddeen Mohammad, and Mubarak Ojewale. To exhaust this list will be an impossible task. Therefore, to everyone who, in one way or the other, contributed to making this work a reality that I could not remember at this moment, I say a big thank you.

Finally, this thesis was supported by Centro de Matemática, Universidade do Minho, Fundação para a Ciência e a Tecnologia (FCT) through the PhD grant PD/BD/128188/2016, and Program Pessoa of Cooperation between Portugal and France reference 406/4/4/2017/S.

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Benjamin Anwasia

November 2020

Resumo

O principal objetivo desta tese é o estudo de misturas gasosas multicomponentes – sistemas gasosos com três ou mais espécies misturadas ao nível molecular – e a dedução de modelos macroscópicos da mecânica de fluidos a partir de uma descrição cinética das partículas que constituem a mistura. Mais especificamente, consideram-se equações cinéticas de tipo Boltzmann que descrevem a evolução de misturas quimicamente reativas, com estrutura monatômica ou poliatômica, que participam numa reação química reversível de tipo bi-molecular e deduzem-se, no limite hidrodinâmico, modelos macroscópicos que descrevem como as espécies se propagam no espaço devido ao processo de difusão e como se transformam quimicamente devido ao processo de reação. Para obter estes modelos macroscópicos, diferentes regimes de adimensionamento das equações cinéticas são considerados, correspondendo a diferentes regimes químicos. O primeiro regime descreve um estado físico em que as colisões mecânicas são dominantes relativamente à reação química, enquanto o segundo regime corresponde a um estado em que as colisões mecânicas e reativas têm a mesma relevância na evolução. No primeiro regime, obtêm-se, como limite hidrodinâmico das equações cinéticas, um sistema de reação-difusão em que o processo de difusão é modelado pelas equações de Maxwell-Stefan. No segundo regime, obtêm-se as equações de Maxwell-Stefan reativas, com termos adicionais que descrevem a difusão das espécies reativas. As propriedades matemáticas dos modelos cinéticos considerados, relacionadas com as leis de conservação, o equilíbrio termodinâmico, o teorema H e as taxas de produção química, que são fundamentais para a análise desenvolvida nesta tese, são estabelecidas e estudadas rigorosamente.

Palavras-chave: Equações de Boltzmann para misturas de gases, Limites hidrodinâmicos, Equações de Maxwell-Stefan, Teoria cinética e de transporte de gases, Dinâmica de gases rarefeita, Misturas de gases reativos.

Abstract

The purpose of this thesis is to study multicomponent gaseous mixtures – systems composed of three or more species mixed at a molecular level – and derive macroscopic models of fluid mechanics from a kinetic description of particles that constitute the mixture. Specifically, this thesis considers Boltzmann-type kinetic equations that model the evolution of reactive monatomic and polyatomic gaseous mixtures participating in a bi-molecular reversible chemical reaction and derive, in the hydrodynamic limit, macroscopic models that describe how the species spread in space due to diffusion and how the species are transformed into each other as a result of the chemical reaction. To obtain these macroscopic models, different scalings of the Boltzmann-type kinetic equations, which correspond to different chemical regimes, are considered. The first regime describes a physical situation in which mechanical collisions are dominant with respect to chemical reaction, whereas the other regime corresponds to a situation in which mechanical and reactive collisions are of the same relevance in the evolution. In the former regime, reaction-diffusion systems where the diffusion process is modelled by the Maxwell-Stefan equations are obtained as hydrodynamic limits of the scaled kinetic equations, while in the latter regime, the reactive Maxwell-Stefan equations, with additional terms describing the diffusion of the reactive species, are obtained. Moreover, the mathematical properties of the considered kinetic models related to the conservation laws, thermodynamic equilibrium, $\mathcal{H}$ -theorem, and chemical production rates, which are fundamental for the analysis developed in this thesis, are stated and studied in detail.

Keywords: Boltzmann equations for gas mixtures, Hydrodynamic limits, Maxwell-Stefan equations, Kinetic and transport theory of gases, Rarefied gas dynamics, Reactive gas mixtures.

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Chapter 1

Introduction

This thesis deals with the problem of deriving macroscopic models of fluid mechanics from a microscopic description of the particles that makes up the fluid. This type of problem is referred to as the problem of hydrodynamic limits.

The question of hydrodynamic limits was formulated as a mathematical problem by David Hilbert in his famous sixth problem titled “Mathematical Treatment of the Axioms of Physics”. This problem was one of the twenty-three mathematics problems Hilbert posed in 1900. Also, it was one of the ten problems he presented at the international congress of mathematicians, which held in Paris, that same year. In Hilbert’s exact words [65]:

“The investigations on the foundations of geometry suggest the problem: To treat in the same manner, by means of axioms, those physical sciences in which mathematics plays an important part; in the first rank are the theory of probabilities and mechanics. As to the axioms of the theory of probabilities, it seems to me desirable that their logical investigation should be accompanied by a rigorous and satisfactory development of the method of mean values in mathematical physics, and in particular in the kinetic theory of gases. Important investigations by physicists on the foundations of mechanics are at hand; I refer to the writings of Mach, Hertz, Boltzmann and Volkmann. It is therefore very desirable that the discussion of the foundations of mechanics be taken up by mathematicians also. Thus Boltzmann’s work on the principles of mechanics suggests the problem of developing mathematically the limiting processes, there merely indicated, which lead from the atomistic view to the laws of motion of continua.”

In the mathematical formulation of Hilbert’s sixth problem, the term “atomistic view” nowadays can lead to at least three very different theories. These theories are as follows.

1. Molecular dynamics: this is the N-body problem of classical mechanics with elastic collisions, in which for simplicity, the bodies are assumed to be spherical and possessing equal mass [79].
2. Interacting particle systems: these are spatio-temporal stochastic processes used to describe the evolution of particles under some kind of interaction between the particles [81].
3. The kinetic theory: this is based on the concept that all measurable macroscopic quantities (“observables”) can be expressed in terms of microscopic averages [72].

The subject of hydrodynamic limits deals with the formal or rigorous derivation of macroscopic models from a microscopic (i.e., atomistic) description of matter. More precisely, from either molecular dynamics, interacting particle systems, or the kinetic theory. These microscopic descriptions are either deterministic, stochastic, or statistical.

The deterministic microscopic description of matter involves the use of Newton's second law of motion¹ [104] to obtain the equation of motion of each particle (or molecule) in the system under consideration. More precisely, if one assumes that the particles (endowed with their position vector $\mathbf{x}_i(t)$ and velocity vector $\mathbf{v}_i(t)$, where $i = 1, \dots, \mathcal{N}$, with $\mathcal{N}$ the number of molecules in the system) are mass points obeying the laws of classical mechanics (that is, neglecting quantum and relativistic effects) and that the laws of interaction between the particles are perfectly known, then the equation of motion of each particle is obtained by applying Newton's second law of motion. In three dimensions, the equation of motion for each particle consist of 6 first order ordinary differential equations in 6 unknowns constituting the components of the two vectors $(\mathbf{x}_i, \mathbf{v}_i)$. The time evolution of the system can then be computed by solving the resulting $6\mathcal{N}$ ordinary differential equations in $6\mathcal{N}$ unknowns which corresponds to the components of the $2\mathcal{N}$ vectors $(\mathbf{x}_i, \mathbf{v}_i)$. A prerequisite for this computation is the knowledge of the $6\mathcal{N}$ initial conditions $\mathbf{x}_i(0)$, $\mathbf{v}_i(0)$, which describe the initial state of the system. However, solving this initial value problem for a system comprising of many particles say, $\mathcal{N} \simeq 10^{25}$: which is the number of molecules in one metre cubed of a gas at standard temperature and pressure² is a hopeless task, see [34] page two for reasons. A typical example of the deterministic microscopic description of matter is molecular dynamics.

The stochastic description of matter deals with a system made up of finitely or infinitely many particles [81]. The system is such that, in the absence of interaction between the particles, it would evolve according to independent finite or countable state Markov chains. On the other hand, when the particles interact, the evolution of an individual particle is no longer Markovian. However, the global configuration (i.e., the system as a whole) evolves according to a Markov process. This Markov process is a large and complex one, and it differs in many aspects from processes like Brownian motion on Euclidean spaces, which had a lot of influence on the development of the standard Markov process theory. Consequently, while there are some connections with the Markov process, there is a substantial difference from it too. Interacting particle systems are typical examples of stochastic microscopic description of matter.

The statistical description of matter utilises the concept of probability instead of certainty, see, for example, [34]. More precisely, in this approach, a given particle will not have a definite position and velocity, but only different probabilities of having different positions and velocities. This type of description makes sense only if the system under consideration is made up of a very large number of particles so that it can be treated as a continuum. Furthermore, this approach uses the notion of probability distribution

¹Newton's second law of motion states that "The change in motion is proportional to the motive force impressed and is made in the direction of the right line in which that force is impressed." Mathematically, this law can be written as $F = ma$, where F is the acting force, m represents mass and a represents acceleration.

²The number of molecules $\mathcal{N}$ in a volume $v = 1.00m^3$ of a gas at standard temperature $T = 273.15K$ and pressure $p = 10^5Pa$ can be computed using the ideal gas law : $pv = \mathcal{N}k_B T$, where $k_B = 1.38 \times 10^{-23}J/K$ is the Boltzmann constant. Therefore $N = \frac{pv}{k_B T} = \frac{10^5 \times 1}{273.15 \times 1.38 \times 10^{-23}} = 2.65 \times 10^{25}$

function³ (also known as the number density) to describe the evolution of the particles in the system. There are two slightly different ways to view the distribution function : it can be seen as an approximation of the true density of the particles in phase space (on a scale which is much larger than the typical distance between particles), or it can reflect the lack of knowledge of the true positions of particles. The kinetic theory is a typical example of statistical microscopic description of matter.

In this thesis, the focus is on the derivation of macroscopic models of fluid mechanics from a statistical description of matter, more precisely, from the kinetic theory. For the derivation of macroscopic models from molecular dynamics (i.e., from the deterministic microscopic description of matter), see, for example, [88] for the formal derivation of the Euler system of equations for compressible fluids. For general methods that allow one to deduce macroscopic models of interacting particle systems from their underlying stochastic dynamics, see [73].

The method of hydrodynamic limits studied here provides an alternative approach to the classical method used to derive macroscopic models of fluid mechanics, such as the classical Euler equations [51] and the Navier-Stokes equations [89, 106] of fluid dynamics. These equations were from inception obtained by applying Newton's second law of motion to infinitely small elements of volume in a fluid, see, for example, chapter one of [78]. Indeed, all hydrodynamic models can be obtained in this way. However, despite the universality of this approach, it has one crucial disadvantage, namely, the fact that transport coefficients and equations of state are obtained either from phenomenological arguments or from experimental data, and they are not related to microscopic data resulting from molecular interactions. On the other hand, in the method of hydrodynamic limits, transport coefficients and equations of state are obtained in terms of parameters of the kinetic model.

This thesis is organised as follows. In chapter 2, a brief introduction of the kinetic theory is given and kinetic models for multi-species non-reactive and reactive systems, respectively, are presented together with the properties of the models that are important for the work developed in this thesis. Chapter 3, deals with the continuum physics derivation of macroscopic diffusion models from multi-species mixtures. This is followed by showing how macroscopic models can be derived from the kinetic theory and the problems studied in this thesis. The main contributions of this thesis to the subject of hydrodynamic limits are given chapters 4, 5 and 6. More precisely, in Chapter 4, the derivation of an isothermal diffusion model where the diffusion process is modelled by the Maxwell-Stefan equations is treated. In chapter 5, an extension of the Maxwell-Stefan equations which is referred to as the reactive Maxwell-Stefan equations is obtained. Chapter 6, deals with the derivation of a non-isothermal diffusion model where the diffusion process is again modelled by the Maxwell-Stefan equations. Chapter 7 is dedicated to conclusions and some future perspectives. Finally, an appendix is included where some technical computations are given.

³This represents the density of particles in the system which at a given time say t are located at position say $\mathbf{x}$ and have velocity $\mathbf{v}$

Chapter 2

Kinetic Theory

The Kinetic theory is a branch of non-equilibrium statistical physics. It dates back to the works of: Daniel Bernoulli, John Herapath, John James Waterston, James Prescott Joule, Karl Krönig, Rudolf Clausius, and James Clerk Maxwell, who are considered as the founding fathers of what is, referred to as “Elementary Kinetic Theory”. The foundations of the modern kinetic theory were laid by James Clerk Maxwell [83, 84, 85], who proposed a general transport equation for arbitrary macroscopic quantities (“observables”) associated with microscopic averages. This transport equation relates the time evolution of macroscopic quantities with transport of particles, collision between particles and action due to external forces. In 1872, Ludwig Eduard Boltzmann [19, 20] reformulated Maxwell’s equation in terms of a single integro-differential equation, which represents the evolution of a probability distribution function.

The goal of kinetic theory is the modelling of any system composed of a large number of particles, such as a gas (fluid) or plasma, from a microscopic point of view. The state of the system is, described using the concept of a distribution function in the particle phase space. This phase space is composed of macroscopic variables, like time t and position in physical space $\mathbf{x}$, as well as microscopic variables $\mathbf{c}$, which describe the state of the particles. If one assumes that the particles obey the laws of classical mechanics (i.e., non-relativistic and non-quantum), then $\mathbf{c}$ will be the velocity components, and in this case, we simply write $\mathbf{v}$ instead of $\mathbf{c}$. However, extra microscopic variables should be added if one would want to take into account non-translational degrees of freedom of the particles: internal energy, spin variables, etc., as it happens when dealing with polyatomic gases. Furthermore, suppose that the system is contained in a bounded or unbounded domain say, $\bar{\Omega} \subset \mathbb{R}^{dim(\mathbf{x})}$ and observed over a time interval say, $[0, \infty)$, then the distribution function is a non-negative function $f(t, \mathbf{x}, \mathbf{c})$ with $(t, \mathbf{x}, \mathbf{c}) \in \mathbb{R}_+ \times \bar{\Omega} \times \mathbb{R}^{dim(\mathbf{c})}$.

In what follows, the case where the microscopic variables which describe the state of the particles are the velocity variables $\mathbf{v}$ will be considered. Therefore, the distribution function to be considered is of the form $f \equiv f(t, \mathbf{x}, \mathbf{v})$. Furthermore, we will work in three dimensional space so that $(t, \mathbf{x}, \mathbf{v}) \in \mathbb{R}_+ \times \Omega \times \mathbb{R}^3$, where $\Omega \subset \mathbb{R}^3$.

The function f is not directly observable however, it allows one to compute measurable macroscopic quantities, such as mass density, macroscopic velocity, temperature, pressure tensor, stress tensor, internal energy density, heat flux, etc. In addition, for any fixed time $t \geq 0$, the quantity $f(t, \mathbf{x}, \mathbf{v}) d\mathbf{x} d\mathbf{v}$ represents the density (number) of particles in an infinitesimal volume element $d\mathbf{x} d\mathbf{v}$ centred at $(\mathbf{x}, \mathbf{v})$.

This number changes in time as a result of transport and collisions between the particles.

2.1 Transport Equations and Particle Interactions

In this section, we will consider a system of $S \geq 2$ species composed of a large number of particles and describe how the distribution functions $f_i(t, \mathbf{x}, \mathbf{v}_i)$ with $i \leq 1 \leq S$ change in time due to free transport and collisions.

2.1.1 Transport Equations

In the absence of collisions between the particles and the walls of the domain Ω , the particles in the system move in straight lines with constant velocity $\mathbf{v}_i$, as dictated by Newton's first law of motion¹ [104]. If one assumes that each particle of mass m_i is subject to an external force $\mathbf{F}$, which is independent of the velocity of each particle $\mathbf{v}_i$, that is, $\mathbf{F} := \mathbf{F}(t, \mathbf{x})$, and that this force may be due to gravity or electric fields, but not magnetic, then the translational motion (i.e., the equation of motion) of the distribution functions $f_i = f(t, \mathbf{x}, \mathbf{v}_i)$ can be obtained by any of the following two methods.

- This method involves following the motion of an ensemble of particles in a volume element of phase space spanned by the position and velocity of the particles. More precisely, if one considers a collection of particles which at time t have positions and velocities in the range $d\mathbf{x} d\mathbf{v}_i$ near $\mathbf{x}$ and $\mathbf{v}_i$. Then at an infinitesimal time $\bar{t} = t + dt$ later, these collection of particles will have positions and velocities in the range $d\bar{\mathbf{x}} d\bar{\mathbf{v}}_i$ near $\bar{\mathbf{x}} = \mathbf{x} + \mathbf{v}_i dt$ and $\bar{\mathbf{v}}_i = \mathbf{v}_i + \frac{1}{m_i} \mathbf{F} dt$ as a result of their motion under the influence of the force $\mathbf{F}$. See, for example, [40, 66, 67, 94, 99, 111] for more details.
- This method involves following the motion of an ensemble of particles through a fixed volume in the phase space spanned by the position and velocity of the particles. More precisely, if one considers a control volume $d\mathbf{x} d\mathbf{v}_i$ in the phase space, containing a collection of particles with a given range of particles positions and velocities between $\mathbf{x}$ and $\mathbf{x} + d\mathbf{x}$, $\mathbf{v}_i$ and $\mathbf{v}_i + d\mathbf{v}_i$. Then the number of particles in the control volume $d\mathbf{x} d\mathbf{v}_i$ of the phase space changes as the positions and velocities of the particles change. The net accumulation of particles in this range in time dt is given by $\frac{\partial f_i}{\partial t} d\mathbf{x} d\mathbf{v}_i dt$. This change in the number of particles within the control volume is due to the number of particles entering and leaving this range $d\mathbf{x} d\mathbf{v}_i$ due to random motion of the particles. See, for example, [99, 109] for more details.

Either of the above methods lead to the following linear transport equations for the species

$$\frac{\partial f_i}{\partial t} + \mathbf{v}_i \cdot \frac{\partial f_i}{\partial \mathbf{x}} + \mathbf{F} \cdot \frac{\partial f_i}{\partial \mathbf{v}} = 0, \quad i = 1, 2, \dots, S. \quad (2.1.1)$$

¹Newton's first law of motion states that "Every body perseveres in its state of being at rest or of moving uniformly straight forward except insofar as it is compelled to change its state by forces impressed."

The equations defined in (2.1.1) above are sometimes called the Vlasov equation [1, 2, 3].

In the absence of external forces equation (2.1.1) reduces to the free transport equation:

$$\frac{\partial f_i}{\partial t} + \mathbf{v}_i \cdot \frac{\partial f_i}{\partial \mathbf{x}} = 0, \quad i = 1, 2, \dots, S. \quad (2.1.2)$$

Remark 2.1.1. *In this thesis, we will neglect the effects due to external forces. Therefore, in what follows, we will use equation (2.1.2) to describe how the distribution functions change due to free streaming.*

2.1.2 Particle Interactions

An approximation to the rate of change of the distribution functions $f_i = f_i(t, \mathbf{x}, \mathbf{v}_i)$ due to particle interactions can be obtained using the following assumptions.

- (i) Only binary collisions are considered: this means that collisions involving more than two particles are neglected. These binary collisions occur between particles of the same species as well as between particles of different species.
- (ii) Interactions between the particles and the walls of the domain Ω are neglected.
- (iii) Collisions between the particles are elastic: this means that mass, momentum and energy are conserved in the collision process.
- (iv) Collisions are localised both in time and space: this means that the typical duration and impact parameter of the interacting processes are negligible when compared to the typical time and space scales of the description, respectively.
- (v) The collisions are microreversible: this means that the microscopic dynamics are time reversible or in other words, the probability that the velocities of the colliding pair before collision (pre-collision velocities) are changed into the velocities after collision (post-collision velocities) is the same as the probability that post-collision velocities are changed into pre-collision velocities.
- (vi) The velocities of the two particles which are about to collide are uncorrelated before their interaction, but becomes correlated after collision: this means that particles that have already collided are expected not to re-collide in future.
- (vii) The effects of external forces on the magnitude of the collision cross-section are neglected.

2.1.3 Collision Operator

Using assumptions (i) to (vii) above, a mathematical expression for the rate at which the distribution functions f_i changes as a result of collision between the particles is given by:

$$Q(f_i, f_{i*}) + \sum_{\substack{j=1 \\ j \neq i}}^S Q(f_i, f_j). \quad (2.1.3)$$

The term $Q(f_i, f_{i*})$ above describe collisions between particles of the same species and the subscript i and i^* are used to distinguish their velocities. This term will be referred to as the mono-species collision operator and is defined as follows:

$$Q(f_i, f_{i*}) = \int_{\mathbb{R}^3} \int_{\mathbb{S}^2} [f'_i f'_{i*} - f_i f_{i*}] B_i(\mathbf{v}_i - \mathbf{v}_{i*}, \boldsymbol{\omega}) d\boldsymbol{\omega} d\mathbf{v}_{i*}. \quad (2.1.4)$$

The term $Q(f_i, f_j)$ given in equation (2.1.3) above describe collisions between particles of different species. This term will be referred to as the bi-species collision operator and it is defined as follows:

$$Q(f_i, f_j) = \int_{\mathbb{R}^3} \int_{\mathbb{S}^2} [f'_i f'_j - f_i f_j] B_{ij}(\mathbf{v}_i - \mathbf{v}_j, \boldsymbol{\omega}) d\boldsymbol{\omega} d\mathbf{v}_j. \quad (2.1.5)$$

In equations (2.1.4) and (2.1.5) above, the following notations have been used:

$$\begin{aligned} f'_i &= f(t, \mathbf{x}, \mathbf{v}'_i), & f'_{i*} &= f(t, \mathbf{x}, \mathbf{v}'_{i*}), & f'_j &= f(t, \mathbf{x}, \mathbf{v}'_j) \\ f_i &= f(t, \mathbf{x}, \mathbf{v}_i), & f_{i*} &= f(t, \mathbf{x}, \mathbf{v}_{i*}), & f_j &= f(t, \mathbf{x}, \mathbf{v}_j), \end{aligned} \quad (2.1.6)$$

where $\mathbf{v}_i, \mathbf{v}_{i*}, \mathbf{v}_j$ are the pre-collision velocities and $\mathbf{v}'_i, \mathbf{v}'_{i*}, \mathbf{v}'_j$ are the post-collision velocities. Furthermore, $B_i(\mathbf{v}_i - \mathbf{v}_{i*}, \boldsymbol{\omega})$ and $B_{ij}(\mathbf{v}_i - \mathbf{v}_j, \boldsymbol{\omega})$ with $\boldsymbol{\omega} \in \mathbb{S}^2$ are non-negative functions called the mono-species and bi-species collision kernels, respectively. The mono-species and bi-species collision kernel depends on $|\mathbf{v}_i - \mathbf{v}_{i*}|$ and $|\mathbf{v}_i - \mathbf{v}_j|$, respectively, together with the cosine of the deviation angles. More specifically,

$$B_i(\mathbf{v}_i - \mathbf{v}_{i*}, \boldsymbol{\omega}) = \bar{B}_i(|\mathbf{v}_i - \mathbf{v}_{i*}|, \cos \theta), \quad \text{where} \quad \cos \theta = \left\langle \frac{\mathbf{v}_i - \mathbf{v}_{i*}}{|\mathbf{v}_i - \mathbf{v}_{i*}|}, \boldsymbol{\omega} \right\rangle, \quad (2.1.7)$$

$$B_{ij}(\mathbf{v}_i - \mathbf{v}_j, \boldsymbol{\omega}) = \bar{B}_{ij}(|\mathbf{v}_i - \mathbf{v}_j|, \cos \theta) \quad \text{where} \quad \cos \theta = \left\langle \frac{\mathbf{v}_i - \mathbf{v}_j}{|\mathbf{v}_i - \mathbf{v}_j|}, \boldsymbol{\omega} \right\rangle. \quad (2.1.8)$$

The integrals on the right-hand sides of the mono-species and bi-species collision operators are called the mono-species and bi-species collision integrals, respectively. In addition, notice that the structure of the collision operators reflect the assumptions from which they were derived. In particular, the quadratic nature of the operators is a consequence of assumption (i). The fact that there is no term describing the interactions between the particles and walls of the domain Ω is a consequence of assumption (ii). As we shall see later, the form of the post-collision velocities is a consequence of assumption (iii). The fact that the time and space variables $t, \mathbf{x}$, respectively, appear as parameters is a consequence of assumption (iv). Assumption (v) (i.e., microreversibility) implies the particular structure of the collision kernels. The appearance of the products $f'_i f'_{i*}, f'_i f'_j, f_i f_{i*}$ and $f'_i f'_j$ is a consequence of assumption (vi). Finally, the absence of a force term in the definition of the collision kernels is a consequence of assumption (vii).

The collision operators represent the net rate at which collisions increase or decrease the number of particles entering the phase volume. It can be split into the gain and loss terms. In particular, the mono-species collision operator can be split as follows:

$$Q(f_i, f_{i*}) = Q(f_i, f_{i*})^+ - Q(f_i, f_{i*})^-,$$

where

$$Q(f_i, f_{i*})^+ = \int_{\mathbb{R}^3} \int_{\mathbb{S}^2} f'_i f'_{i*} B_i(\mathbf{v}_i - \mathbf{v}_{i*}, \boldsymbol{\omega}) d\boldsymbol{\omega} d\mathbf{v}_{i*},$$

$$Q(f_i, f_{i*})^- = \int_{\mathbb{R}^3} \int_{\mathbb{S}^2} f_i f_{i*} B_i(\mathbf{v}_i - \mathbf{v}_{i*}, \boldsymbol{\omega}) d\boldsymbol{\omega} d\mathbf{v}_{i*}.$$

The term $Q(f_i, f_{i*})^+$ is a gain term. It measures the number of particles of velocity $\mathbf{v}_i$ which are created due to collision between particles of velocities $\mathbf{v}'_i$ and $\mathbf{v}'_{i*}$. Alternatively, one can think of it as the rate at which particles with velocity $\mathbf{v}_i$ are injected into a volume element $d\mathbf{x} d\mathbf{v}_i$ of phase space about $(\mathbf{x}, \mathbf{v}_i)$ as a result of binary encounters with other particles. The term $Q(f_i, f_{i*})^-$ is a loss term. It counts all collisions in which a given particle of velocity $\mathbf{v}_i$ collides with another particle of velocity $\mathbf{v}_{i*}$, resulting in a change in its velocity, thus leading to a loss of particles of velocity $\mathbf{v}_i$. Alternatively, one can think of it as the rate at which particles with velocity $\mathbf{v}_i$ are ejected from a volume element $d\mathbf{x} d\mathbf{v}_i$ of phase space about $(\mathbf{x}, \mathbf{v}_i)$ as a result of binary encounters with other particles.

Similarly, the bi-species collision operator can be split as follows:

$$Q(f_i, f_j) = Q(f_i, f_j)^+ - Q(f_i, f_j)^-,$$

where

$$Q(f_i, f_j)^+ = \int_{\mathbb{R}^3} \int_{\mathbb{S}^2} f'_i f'_j B_{ij}(\mathbf{v}_i - \mathbf{v}_j, \boldsymbol{\omega}) d\boldsymbol{\omega} d\mathbf{v}_j,$$

$$Q(f_i, f_j)^- = \int_{\mathbb{R}^3} \int_{\mathbb{S}^2} f_i f_j B_{ij}(\mathbf{v}_i - \mathbf{v}_j, \boldsymbol{\omega}) d\boldsymbol{\omega} d\mathbf{v}_j.$$

2.2 Non-Reactive Multi-Species System

This section considers a non-reactive multi-species system composed of a large number of particles. The equations which describe how the distribution functions change as a result of free streaming and collisions, are presented together with some useful properties that are consequences of the form of the collision operators. Furthermore, the macroscopic quantities associated with the distribution functions are given. Finally, the fundamental hydrodynamic or macroscopic equations of continuity, momentum balance, and energy balance associated with these equations will be derived.

2.2.1 Kinetic Equations for Non-Reactive Mixture of Monatomic Gases

Consider a multi-species system composed of $S \geq 2$ different monatomic² gases. For each species A_i with $i = 1, 2, \dots, S$, let m_i be the atomic mass and $f_i = f(t, \mathbf{x}, \mathbf{v}_i) \geq 0$ the distribution function. The functions f_i with $i = 1, 2, \dots, S$ represent the density of particles of the species which at time $t \geq 0$ are located at position $\mathbf{x} \in \mathbb{R}^3$ and have velocity $\mathbf{v}_i \in \mathbb{R}^3$. The equations that describe how the distribution

²Endowed with only translational degrees of freedom. In other words internal energy states of the molecules that are associated with the rotational, vibrational, electronic and nuclei states are not taken into account.

functions f_i change as a result of free streaming and collisions are, obtained by putting together equations (2.1.2) and (2.1.3) to obtain:

$$\frac{\partial f_i}{\partial t} + \mathbf{v}_i \cdot \frac{\partial f_i}{\partial \mathbf{x}} = Q(f_i, f_{i*}) + \sum_{\substack{j=1 \\ j \neq i}}^S Q(f_i, f_j), \quad i = 1, 2, \dots, S. \quad (2.2.1)$$

The equations given in equation (2.2.1) above are mostly called the Boltzmann equation [34, 56, 59, 75, 66, 86, 99]. However, in recognition of the fact that the equation by Boltzmann was a reformulation of the equation by Maxwell, in this thesis, they will be called the Maxwell-Boltzmann equations³ (MBEs).

From assumption (iii) given in section 2.1.2, we have that the conservation laws of linear momentum and kinetic energy for mono-species collisions are respectively, given by the flowing equations:

$$m_i \mathbf{v}_i + m_i \mathbf{v}_{i*} = m_i \mathbf{v}'_i + m_i \mathbf{v}'_{i*}, \quad (2.2.2)$$

$$\frac{1}{2} m_i (\mathbf{v}_i)^2 + \frac{1}{2} m_i (\mathbf{v}_{i*})^2 = \frac{1}{2} m_i (\mathbf{v}'_i)^2 + \frac{1}{2} m_i (\mathbf{v}'_{i*})^2. \quad (2.2.3)$$

Similarly, the conservation laws of linear momentum and kinetic for bi-species collisions are respectively given by:

$$m_i \mathbf{v}_i + m_j \mathbf{v}_j = m_i \mathbf{v}'_i + m_j \mathbf{v}'_j, \quad (2.2.4)$$

$$\frac{1}{2} m_i (\mathbf{v}_i)^2 + \frac{1}{2} m_j (\mathbf{v}_j)^2 = \frac{1}{2} m_i (\mathbf{v}'_i)^2 + \frac{1}{2} m_j (\mathbf{v}'_j)^2, \quad (2.2.5)$$

Now let us show that the form of the post-collision velocities is a consequence of assumption (iii) given in section 2.1.2. More precisely, that the form of the mono-species and bi-species post-collision velocities are consequences of the conservation laws given in equations (2.2.2), (2.2.3) and (2.2.4), (2.2.5), respectively. To obtain the explicit form of the post-collision velocities for mono-species collisions $\mathbf{v}'_i, \mathbf{v}'_{i*}$, observe that dividing both sides of equation (2.2.2) by m_i and multiplying both sides of equation (2.2.3) by $\frac{2}{m_i}$, the conservation laws of linear momentum and kinetic energy reduces to:

$$\mathbf{v}_i + \mathbf{v}_{i*} = \mathbf{v}'_i + \mathbf{v}'_{i*}, \quad (2.2.6)$$

$$(\mathbf{v}_i)^2 + (\mathbf{v}_{i*})^2 = (\mathbf{v}'_i)^2 + (\mathbf{v}'_{i*})^2, \quad (2.2.7)$$

respectively. Equations (2.2.6) and (2.2.7) impose four constraints on the six variables $\mathbf{v}'_i, \mathbf{v}'_{i*}$ (since we are in three dimensional space, i.e., $\mathbb{R}^3$). Consequently, there are two degrees of freedom. If we write

$$\begin{aligned} \mathbf{v}'_i &= \mathbf{v}_i + a(\mathbf{v}_i, \mathbf{v}_{i*}, \boldsymbol{\omega}) \boldsymbol{\omega}, \\ \mathbf{v}'_{i*} &= \mathbf{v}_{i*} - a(\mathbf{v}_i, \mathbf{v}_{i*}, \boldsymbol{\omega}) \boldsymbol{\omega}, \end{aligned} \quad (2.2.8)$$

where $a(\mathbf{v}_i, \mathbf{v}_{i*}, \boldsymbol{\omega})$ is a scalar function to be determined with $|\boldsymbol{\omega}| = 1$, then adding both equations of (2.2.8) gives the conservation of linear momentum (2.2.6). Next we force the conservation of energy as

³Boltzmann [19], equation (12). Maxwell [83], equations (3) and (73). These equations by Maxwell had inferred the equation of transfer (obtained by multiplying the MBEs by an arbitrary function of velocity and integrating over the velocity space) directly from considerations regarding molecular interactions.

in (2.2.7). To do this, observe that from equation (2.2.8), one has that:

$$\begin{aligned} (\mathbf{v}'_i)^2 &= (\mathbf{v}_i)^2 + 2a(\mathbf{v}_i, \mathbf{v}_{i*}, \boldsymbol{\omega})\mathbf{v}_i \cdot \boldsymbol{\omega} + (a(\mathbf{v}_i, \mathbf{v}_{i*}, \boldsymbol{\omega}))^2, \\ (\mathbf{v}'_{i*})^2 &= (\mathbf{v}_{i*})^2 - 2a(\mathbf{v}_i, \mathbf{v}_{i*}, \boldsymbol{\omega})\mathbf{v}_{i*} \cdot \boldsymbol{\omega} + (a(\mathbf{v}_i, \mathbf{v}_{i*}, \boldsymbol{\omega}))^2, \end{aligned}$$

where use have been made of the fact that $\boldsymbol{\omega} \cdot \boldsymbol{\omega} = 1$. Therefore, adding the previous equations gives:

$$(\mathbf{v}'_i)^2 + (\mathbf{v}'_{i*})^2 = (\mathbf{v}_i)^2 + (\mathbf{v}_{i*})^2 + 2(a(\mathbf{v}_i, \mathbf{v}_{i*}, \boldsymbol{\omega}))^2 + 2a(\mathbf{v}_i, \mathbf{v}_{i*}, \boldsymbol{\omega})(\mathbf{v}_i \cdot \boldsymbol{\omega} - \mathbf{v}_{i*} \cdot \boldsymbol{\omega}).$$

From the mono-species conservation of kinetic energy given in equation (2.2.7), we have that the previous equation reduces to:

$$2(a(\mathbf{v}_i, \mathbf{v}_{i*}, \boldsymbol{\omega}))^2 + 2a(\mathbf{v}_i, \mathbf{v}_{i*}, \boldsymbol{\omega})(\mathbf{v}_i \cdot \boldsymbol{\omega} - \mathbf{v}_{i*} \cdot \boldsymbol{\omega}) = 0.$$

Dividing both sides of the previous equation by two and factorising, we obtain:

$$a(\mathbf{v}_i, \mathbf{v}_{i*}, \boldsymbol{\omega})(a(\mathbf{v}_i, \mathbf{v}_{i*}, \boldsymbol{\omega}) + (\mathbf{v}_i - \mathbf{v}_{i*}) \cdot \boldsymbol{\omega}) = 0.$$

Therefore, either $a(\mathbf{v}_i, \mathbf{v}_{i*}, \boldsymbol{\omega}) = 0$ or

$$a(\mathbf{v}_i, \mathbf{v}_{i*}, \boldsymbol{\omega}) + (\mathbf{v}_i - \mathbf{v}_{i*}) \cdot \boldsymbol{\omega} = 0. \quad (2.2.9)$$

Subtracting $(\mathbf{v}_i - \mathbf{v}_{i*}) \cdot \boldsymbol{\omega}$ from both sides of equation (2.2.9), we obtain:

$$a(\mathbf{v}_i, \mathbf{v}_{i*}, \boldsymbol{\omega}) = -(\mathbf{v}_i - \mathbf{v}_{i*}) \cdot \boldsymbol{\omega}.$$

Hence, as long as $a(\mathbf{v}_i, \mathbf{v}_{i*}, \boldsymbol{\omega}) \neq 0$, the mono-species post-collision velocities are given by:

$$\mathbf{v}'_i = \mathbf{v}_i - ((\mathbf{v}_i - \mathbf{v}_{i*}) \cdot \boldsymbol{\omega})\boldsymbol{\omega}, \quad (2.2.10)$$

$$\mathbf{v}'_{i*} = \mathbf{v}_{i*} + ((\mathbf{v}_i - \mathbf{v}_{i*}) \cdot \boldsymbol{\omega})\boldsymbol{\omega}. \quad (2.2.11)$$

Now let us obtain the expressions for the bi-species post-collision velocities $\mathbf{v}'_i$ and $\mathbf{v}'_j$. To do this, observe that the bi-species conservation laws of linear momentum (2.2.4) and kinetic energy (2.2.5) gives a system of four scalar equations in six unknowns (because we are in $\mathbb{R}^3$). Therefore, there are two degrees of freedom. If we write

$$\mathbf{v}'_i = \mathbf{v}_i + \frac{a(\mathbf{v}_i, \mathbf{v}_j, \boldsymbol{\omega})}{m_i}\boldsymbol{\omega}, \quad (2.2.12)$$

$$\mathbf{v}'_j = \mathbf{v}_j - \frac{a(\mathbf{v}_i, \mathbf{v}_j, \boldsymbol{\omega})}{m_j}\boldsymbol{\omega}, \quad (2.2.13)$$

where $a(\mathbf{v}_i, \mathbf{v}_j, \boldsymbol{\omega})$ is a scalar function to be determined with $|\boldsymbol{\omega}| = 1$, then multiplying equation (2.2.12) by m_i , equation (2.2.13) by m_j and adding the resulting two equations, we automatically satisfy the conservation of linear momentum given in equation (2.2.4). Now observe that

$$\begin{aligned}\frac{1}{2}m_i(\mathbf{v}_i')^2 &= \frac{1}{2}m_i(\mathbf{v}_i)^2 + a(\mathbf{v}_i, \mathbf{v}_j, \boldsymbol{\omega})\mathbf{v}_i \cdot \boldsymbol{\omega} + \frac{1}{2m_i}(a(\mathbf{v}_i, \mathbf{v}_j, \boldsymbol{\omega}))^2, \\ \frac{1}{2}m_j(\mathbf{v}_j')^2 &= \frac{1}{2}m_j(\mathbf{v}_j)^2 - a(\mathbf{v}_i, \mathbf{v}_j, \boldsymbol{\omega})\mathbf{v}_j \cdot \boldsymbol{\omega} + \frac{1}{2m_j}(a(\mathbf{v}_i, \mathbf{v}_j, \boldsymbol{\omega}))^2,\end{aligned}$$

where use have been made of the fact that $\boldsymbol{\omega} \cdot \boldsymbol{\omega} = 1$. Therefore, adding the previous equations gives:

$$\begin{aligned}\frac{1}{2}m_i(\mathbf{v}_i')^2 + \frac{1}{2}m_j(\mathbf{v}_j')^2 &= \frac{1}{2}m_i(\mathbf{v}_i)^2 + a(\mathbf{v}_i, \mathbf{v}_j, \boldsymbol{\omega})\mathbf{v}_i \cdot \boldsymbol{\omega} + \frac{1}{2m_i}(a(\mathbf{v}_i, \mathbf{v}_j, \boldsymbol{\omega}))^2 \\ &\quad + \frac{1}{2}m_j(\mathbf{v}_j)^2 - a(\mathbf{v}_i, \mathbf{v}_j, \boldsymbol{\omega})\mathbf{v}_j \cdot \boldsymbol{\omega} + \frac{1}{2m_j}(a(\mathbf{v}_i, \mathbf{v}_j, \boldsymbol{\omega}))^2.\end{aligned}$$

From the bi-species conservation of kinetic energy given in equation (2.2.5), the previous equation reduces to:

$$a(\mathbf{v}_i, \mathbf{v}_j, \boldsymbol{\omega})\mathbf{v}_i \cdot \boldsymbol{\omega} - a(\mathbf{v}_i, \mathbf{v}_j, \boldsymbol{\omega})\mathbf{v}_j \cdot \boldsymbol{\omega} + \frac{1}{2m_i}(a(\mathbf{v}_i, \mathbf{v}_j, \boldsymbol{\omega}))^2 + \frac{1}{2m_j}(a(\mathbf{v}_i, \mathbf{v}_j, \boldsymbol{\omega}))^2 = 0.$$

Multiplying both sides of the previous equation by $2m_im_j$ and factorising gives:

$$a(\mathbf{v}_i, \mathbf{v}_j, \boldsymbol{\omega}) \left(2m_im_j(\mathbf{v}_i - \mathbf{v}_j) \cdot \boldsymbol{\omega} + (a(\mathbf{v}_i, \mathbf{v}_j, \boldsymbol{\omega}))(m_i + m_j) \right) = 0.$$

Therefore, either $a(\mathbf{v}_i, \mathbf{v}_j, \boldsymbol{\omega}) = 0$ or

$$2m_im_j(\mathbf{v}_i - \mathbf{v}_j) \cdot \boldsymbol{\omega} + (a(\mathbf{v}_i, \mathbf{v}_j, \boldsymbol{\omega}))(m_i + m_j) = 0. \quad (2.2.14)$$

Equation (2.2.14) implies that:

$$(a(\mathbf{v}_i, \mathbf{v}_j, \boldsymbol{\omega}))(m_i + m_j) = -2m_im_j(\mathbf{v}_i - \mathbf{v}_j) \cdot \boldsymbol{\omega}.$$

Dividing both sides of the previous equation by $m_i + m_j$, we obtain:

$$(a(\mathbf{v}_i, \mathbf{v}_j, \boldsymbol{\omega})) = -2\mu_{ij}(\mathbf{v}_i - \mathbf{v}_j) \cdot \boldsymbol{\omega}, \quad \text{where} \quad \mu_{ij} = \frac{m_im_j}{m_i + m_j}. \quad (2.2.15)$$

Hence for $a(\mathbf{v}_i, \mathbf{v}_j, \boldsymbol{\omega}) \neq 0$, the bi-species post-collision velocities are given by:

$$\mathbf{v}_i' = \mathbf{v}_i - \frac{2\mu_{ij}}{m_i}((\mathbf{v}_i - \mathbf{v}_j) \cdot \boldsymbol{\omega})\boldsymbol{\omega}, \quad (2.2.16)$$

$$\mathbf{v}_j' = \mathbf{v}_j + \frac{2\mu_{ij}}{m_j}((\mathbf{v}_i - \mathbf{v}_j) \cdot \boldsymbol{\omega})\boldsymbol{\omega}. \quad (2.2.17)$$

2.2.2 Properties of the Mono-Species Collision Operator

In this subsection, the properties of the mono-species collision operator will be presented. Each property is given in the form of a lemma, a proposition, or a corollary. Also, a complete step by step proof of those properties that are consider to be very important for the work developed in this thesis will be given.

Furthermore, for clarity in the computations involving the collision integral, the distribution functions will be written with the velocity argument only. More precisely, the following notations will be used:

$$f(t, \mathbf{x}, \mathbf{v}'_i) = f(\mathbf{v}'_i), f(t, \mathbf{x}, \mathbf{v}'_{i*}) = f(\mathbf{v}'_{i*}), f(t, \mathbf{x}, \mathbf{v}_i) = f(\mathbf{v}_i), f(t, \mathbf{x}, \mathbf{v}_{i*}) = f(\mathbf{v}_{i*}).$$

Lemma 2.2.1. *Let $f(\mathbf{v}_i)$ and $\varphi(\mathbf{v}_i)$ be sufficiently smooth functions which are small at infinity. Then,*

$$\begin{aligned} \int_{\mathbb{R}^3} Q(f_i, f_{i*}) \varphi(\mathbf{v}_i) d\mathbf{v}_i &= \frac{1}{4} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}^2} [f(\mathbf{v}'_i) f(\mathbf{v}'_{i*}) - f(\mathbf{v}_i) f(\mathbf{v}_{i*})] \\ &\quad \times (\varphi(\mathbf{v}_i) + \varphi(\mathbf{v}_{i*}) - \varphi(\mathbf{v}'_i) - \varphi(\mathbf{v}'_{i*})) B_i(\mathbf{v}_i - \mathbf{v}_{i*}, \boldsymbol{\omega}) d\boldsymbol{\omega} d\mathbf{v}_{i*} d\mathbf{v}_i. \end{aligned} \quad (2.2.18)$$

Proof. Multiplying both sides of the mono-species collision operator given in equation (2.1.4) by $\varphi(\mathbf{v}_i)$ and then integrate the resulting equation over $\mathbf{v}_i \in \mathbb{R}^3$, we obtain:

$$\begin{aligned} \int_{\mathbb{R}^3} Q(f_i, f_{i*}) \varphi(\mathbf{v}_i) d\mathbf{v}_i \\ = \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}^2} [f(\mathbf{v}'_i) f(\mathbf{v}'_{i*}) - f(\mathbf{v}_i) f(\mathbf{v}_{i*})] \varphi(\mathbf{v}_i) B_i(\mathbf{v}_i - \mathbf{v}_{i*}, \boldsymbol{\omega}) d\boldsymbol{\omega} d\mathbf{v}_{i*} d\mathbf{v}_i. \end{aligned} \quad (2.2.19)$$

Switch $\mathbf{v}_i$ and $\mathbf{v}_{i*}$ in equation (2.2.19) above. The cross-section or collision kernel is invariant with the switching of $\mathbf{v}_i$ and $\mathbf{v}_{i*}$, that is,

$$B_i(\mathbf{v}_i - \mathbf{v}_{i*}, \boldsymbol{\omega}) = \bar{B}_i(|\mathbf{v}_i - \mathbf{v}_{i*}|, \cos \theta) = \bar{B}_i(|\mathbf{v}_{i*} - \mathbf{v}_i|, \cos \theta) = B_i(\mathbf{v}_{i*} - \mathbf{v}_i, \boldsymbol{\omega}). \quad (2.2.20)$$

Also, the switching of $\mathbf{v}_i$ and $\mathbf{v}_{i*}$ implies:

$$\begin{aligned} \mathbf{v}'_i &= \mathbf{v}_i - ((\mathbf{v}_i - \mathbf{v}_{i*}) \cdot \boldsymbol{\omega}) \boldsymbol{\omega} \rightarrow \mathbf{v}_{i*} - ((\mathbf{v}_{i*} - \mathbf{v}_i) \cdot \boldsymbol{\omega}) \boldsymbol{\omega} = \mathbf{v}_{i*} + ((\mathbf{v}_i - \mathbf{v}_{i*}) \cdot \boldsymbol{\omega}) \boldsymbol{\omega} = \mathbf{v}'_{i*}, \\ \mathbf{v}'_{i*} &= \mathbf{v}_{i*} + ((\mathbf{v}_i - \mathbf{v}_{i*}) \cdot \boldsymbol{\omega}) \boldsymbol{\omega} \rightarrow \mathbf{v}_i + ((\mathbf{v}_{i*} - \mathbf{v}_i) \cdot \boldsymbol{\omega}) \boldsymbol{\omega} = \mathbf{v}_i - ((\mathbf{v}_i - \mathbf{v}_{i*}) \cdot \boldsymbol{\omega}) \boldsymbol{\omega} = \mathbf{v}'_i. \end{aligned} \quad (2.2.21)$$

Therefore, equation (2.2.19) becomes:

$$\begin{aligned} \int_{\mathbb{R}^3} Q(f_i, f_{i*}) \varphi(\mathbf{v}_i) d\mathbf{v}_i \\ = \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}^2} [f(\mathbf{v}'_i) f(\mathbf{v}'_{i*}) - f(\mathbf{v}_i) f(\mathbf{v}_{i*})] \varphi(\mathbf{v}_{i*}) B_i(\mathbf{v}_i - \mathbf{v}_{i*}, \boldsymbol{\omega}) d\boldsymbol{\omega} d\mathbf{v}_{i*} d\mathbf{v}_i. \end{aligned} \quad (2.2.22)$$

Next, we use the change of variables $(\mathbf{v}_i, \mathbf{v}_{i*}) \rightarrow (\mathbf{v}'_i, \mathbf{v}'_{i*})$ in equation (2.2.19) to obtain:

$$\begin{aligned} \int_{\mathbb{R}^3} Q(f_i, f_{i*}) \varphi(\mathbf{v}_i) d\mathbf{v}_i &= \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}^2} [f(\mathbf{v}'_i) f(\mathbf{v}'_{i*}) - f(\mathbf{v}_i(\mathbf{v}'_i, \mathbf{v}'_{i*})) f(\mathbf{v}_{i*}(\mathbf{v}'_i, \mathbf{v}'_{i*}))] \\ &\quad \times \varphi(\mathbf{v}_i(\mathbf{v}'_i, \mathbf{v}'_{i*})) |J| B_i(\mathbf{v}'_i - \mathbf{v}'_{i*}, \boldsymbol{\omega}) d\boldsymbol{\omega} d\mathbf{v}'_{i*} d\mathbf{v}'_i, \end{aligned} \quad (2.2.23)$$

where $|J|$ is the Jacobian determinant of the transformation $(\mathbf{v}_i, \mathbf{v}_{i*}) \rightarrow (\mathbf{v}'_i, \mathbf{v}'_{i*})$. In the sequel, it will be shown that the absolute value of $|J|$ is unity. Furthermore, observe that

$$|\mathbf{v}_i - \mathbf{v}_{i*}|^2 = 2|\mathbf{v}_i|^2 + 2|\mathbf{v}_{i*}|^2 - |\mathbf{v}_i + \mathbf{v}_{i*}|^2 = |\mathbf{v}'_i - \mathbf{v}'_{i*}|^2,$$

where use have been made of the conservation laws of linear momentum and kinetic energy given in equations (2.2.6) and (2.2.7) in the first equality to obtain the last equality. Therefore, the collision kernel is invariant under the change of variables, i.e.,

$$B(\mathbf{v}_i - \mathbf{v}_{i*}, \boldsymbol{\omega}) = B(|\mathbf{v}_i - \mathbf{v}_{i*}|, \cos \theta) = B(|\mathbf{v}'_i - \mathbf{v}'_{i*}|, \cos \theta) = B_i(\mathbf{v}'_i - \mathbf{v}'_{i*}, \boldsymbol{\omega}). \quad (2.2.24)$$

Hence we can rewrite equation (2.2.23) as given below:

$$\begin{aligned} \int_{\mathbb{R}^3} Q(f_i, f_{i*}) \varphi(\mathbf{v}_i) d\mathbf{v}_i &= \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}^2} [f(\mathbf{v}'_i) f(\mathbf{v}'_{i*}) - f(\mathbf{v}_i(\mathbf{v}'_i, \mathbf{v}'_{i*})) f(\mathbf{v}_{i*}(\mathbf{v}'_i, \mathbf{v}'_{i*}))] \\ &\quad \times \varphi(\mathbf{v}_i(\mathbf{v}'_i, \mathbf{v}'_{i*})) B_i(\mathbf{v}_i - \mathbf{v}_{i*}, \boldsymbol{\omega}) d\boldsymbol{\omega} d\mathbf{v}'_{i*} d\mathbf{v}'_i. \end{aligned} \quad (2.2.25)$$

Observe that subtracting equation (2.2.11) from equation (2.2.10) and then take the scalar product of the resulting equation with $\boldsymbol{\omega}$, we obtain:

$$(\mathbf{v}'_i - \mathbf{v}'_{i*}) \cdot \boldsymbol{\omega} = (\mathbf{v}_i - \mathbf{v}_{i*}) \cdot \boldsymbol{\omega} - 2((\mathbf{v}_i - \mathbf{v}_{i*}) \cdot \boldsymbol{\omega}) \boldsymbol{\omega} \cdot \boldsymbol{\omega} = -(\mathbf{v}_i - \mathbf{v}_{i*}) \cdot \boldsymbol{\omega}, \quad (2.2.26)$$

where $\boldsymbol{\omega} \cdot \boldsymbol{\omega} = 1$ was used in the first equality to obtain the last equality of the previous equation. Also, inverting equations (2.2.10) and (2.2.11) yield:

$$\begin{aligned} \mathbf{v}_i &= \mathbf{v}'_i + ((\mathbf{v}_i - \mathbf{v}_{i*}) \cdot \boldsymbol{\omega}) \boldsymbol{\omega}, \\ \mathbf{v}_{i*} &= \mathbf{v}'_{i*} - ((\mathbf{v}_i - \mathbf{v}_{i*}) \cdot \boldsymbol{\omega}) \boldsymbol{\omega}. \end{aligned} \quad (2.2.27)$$

Using equation (2.2.26) we can write equation (2.2.27) as follows:

$$\begin{aligned} \mathbf{v}_i &= \mathbf{v}'_i + ((\mathbf{v}_i - \mathbf{v}_{i*}) \cdot \boldsymbol{\omega}) \boldsymbol{\omega} = \mathbf{v}'_i - ((\mathbf{v}'_i - \mathbf{v}'_{i*}) \cdot \boldsymbol{\omega}) \boldsymbol{\omega} \equiv \mathbf{v}_i(\mathbf{v}'_i, \mathbf{v}'_{i*}). \\ \mathbf{v}_{i*} &= \mathbf{v}'_{i*} - ((\mathbf{v}_i - \mathbf{v}_{i*}) \cdot \boldsymbol{\omega}) \boldsymbol{\omega} = \mathbf{v}'_{i*} + ((\mathbf{v}'_i - \mathbf{v}'_{i*}) \cdot \boldsymbol{\omega}) \boldsymbol{\omega} \equiv \mathbf{v}_{i*}(\mathbf{v}'_i, \mathbf{v}'_{i*}). \end{aligned} \quad (2.2.28)$$

Substituting the expressions for $\mathbf{v}_i(\mathbf{v}'_i, \mathbf{v}'_{i*})$ and $\mathbf{v}_{i*}(\mathbf{v}'_i, \mathbf{v}'_{i*})$ above into equation (2.2.25) and rename $(\mathbf{v}'_i, \mathbf{v}'_{i*})$ to $(\mathbf{v}_i, \mathbf{v}_{i*})$, we obtain:

$$\begin{aligned} \int_{\mathbb{R}^3} Q(f_i, f_{i*}) \varphi(\mathbf{v}_i) d\mathbf{v}_i &= \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}^2} [f(\mathbf{v}_i) f(\mathbf{v}_{i*}) - f(\mathbf{v}_i - ((\mathbf{v}_i - \mathbf{v}_{i*}) \cdot \boldsymbol{\omega}) \boldsymbol{\omega}) f(\mathbf{v}_{i*} + ((\mathbf{v}_i - \mathbf{v}_{i*}) \cdot \boldsymbol{\omega}) \boldsymbol{\omega})] \\ &\quad \times \varphi(\mathbf{v}_i - ((\mathbf{v}_i - \mathbf{v}_{i*}) \cdot \boldsymbol{\omega}) \boldsymbol{\omega}) B_i(\mathbf{v}_i - \mathbf{v}_{i*}, \boldsymbol{\omega}) d\boldsymbol{\omega} d\mathbf{v}_{i*} d\mathbf{v}_i. \end{aligned}$$

Using equations (2.2.10) and (2.2.11), we can rewrite the previous equation as:

$$\begin{aligned} \int_{\mathbb{R}^3} Q(f_i, f_{i*}) \varphi(\mathbf{v}_i) d\mathbf{v}_i &= - \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}^2} [f(\mathbf{v}'_i) f(\mathbf{v}'_{i*}) - f(\mathbf{v}_i) f(\mathbf{v}_{i*})] \varphi(\mathbf{v}'_i) B_i(\mathbf{v}_i - \mathbf{v}_{i*}, \boldsymbol{\omega}) d\boldsymbol{\omega} d\mathbf{v}_{i*} d\mathbf{v}_i. \end{aligned} \quad (2.2.29)$$

Finally, switching $\mathbf{v}_i$ and $\mathbf{v}_{i*}$ in equation (2.2.29) above and then use equation (2.2.21) in the resulting equation gives:

$$\begin{aligned} & \int_{\mathbb{R}^3} Q(f_i, f_{i*}) \varphi(\mathbf{v}_i) d\mathbf{v}_i \\ &= - \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}^2} [f(\mathbf{v}'_i) f(\mathbf{v}'_{i*}) - f(\mathbf{v}_i) f(\mathbf{v}_{i*})] \varphi(\mathbf{v}'_{i*}) B_i(\mathbf{v}_i - \mathbf{v}_{i*}, \boldsymbol{\omega}) d\boldsymbol{\omega} d\mathbf{v}_{i*} d\mathbf{v}_i. \end{aligned} \quad (2.2.30)$$

Summing equations (2.2.19), (2.2.22), (2.2.29) and (2.2.29), then divide both sides of the resulting equation by 4 gives equation (2.2.18). $\square$

Lemma 2.2.2. *The Jacobian matrix J of the transformation $(\mathbf{v}_i, \mathbf{v}_{i*}) \rightarrow (\mathbf{v}'_i, \mathbf{v}'_{i*})$ is such that its determinant, denoted by $|J|$, satisfies $|J| = 1$.*

Proof. The Jacobian matrix J is a 6×6 matrix which can be given in terms of four 3×3 blocks as follows:

$$J = \begin{bmatrix} \frac{\partial \mathbf{v}'_i}{\partial \mathbf{v}_i} & \frac{\partial \mathbf{v}'_{i*}}{\partial \mathbf{v}_i} \\ \frac{\partial \mathbf{v}'_i}{\partial \mathbf{v}_{i*}} & \frac{\partial \mathbf{v}'_{i*}}{\partial \mathbf{v}_{i*}} \end{bmatrix} = \begin{bmatrix} I - \boldsymbol{\omega} \otimes \boldsymbol{\omega} & \boldsymbol{\omega} \otimes \boldsymbol{\omega} \\ -\boldsymbol{\omega} \otimes \boldsymbol{\omega} & I + \boldsymbol{\omega} \otimes \boldsymbol{\omega} \end{bmatrix},$$

where $\mathbf{v}'_i = \mathbf{v}_i - ((\mathbf{v}_i - \mathbf{v}_{i*}) \cdot \boldsymbol{\omega}) \boldsymbol{\omega}$, $\mathbf{v}'_{i*} = \mathbf{v}_{i*} + ((\mathbf{v}_i - \mathbf{v}_{i*}) \cdot \boldsymbol{\omega}) \boldsymbol{\omega}$, I is a 3×3 identity matrix and $\otimes$ is the tensor product. In order to evaluate $\det(J)$, we add the fourth column to the first column, add the fifth column to the second column, and add the sixth column to the third column to obtain:

$$|J| = \det \begin{bmatrix} I & \boldsymbol{\omega} \otimes \boldsymbol{\omega} \\ I & I + \boldsymbol{\omega} \otimes \boldsymbol{\omega} \end{bmatrix}.$$

Next subtract the first row from the fourth row, the second row from the fifth row, and the third row from the sixth row to obtain:

$$|J| = \det \begin{bmatrix} I & \boldsymbol{\omega} \otimes \boldsymbol{\omega} \\ 0 & I \end{bmatrix}.$$

Thus the determinant of the previous matrix is

$$|J| = \det \begin{bmatrix} I & \boldsymbol{\omega} \otimes \boldsymbol{\omega} \\ 0 & I \end{bmatrix} = 1.$$

$\square$

Lemma 2.2.3. *Let $f(\mathbf{v}_i)$ and $\varphi(\mathbf{v}_i)$ be sufficiently smooth functions which are small at infinity. Then*

$$\int_{\mathbb{R}^3} Q(f_i, f_{i*}) \varphi(\mathbf{v}_i) d\mathbf{v}_i$$

$$\begin{aligned}
&= \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{S^2} [f(\mathbf{v}'_i) f(\mathbf{v}'_{i*}) - f(\mathbf{v}_i) f(\mathbf{v}_{i*})] \varphi(\mathbf{v}_i) B_i(\mathbf{v}_i - \mathbf{v}_{i*}, \boldsymbol{\omega}) d\boldsymbol{\omega} d\mathbf{v}_{i*} d\mathbf{v}_i \\
&= \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{S^2} f(\mathbf{v}_i) f(\mathbf{v}_{i*}) (\varphi(\mathbf{v}'_i) - \varphi(\mathbf{v}_i)) B_i(\mathbf{v}_i - \mathbf{v}_{i*}, \boldsymbol{\omega}) d\boldsymbol{\omega} d\mathbf{v}_{i*} d\mathbf{v}_i \quad (2.2.31) \\
&= \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{S^2} f(\mathbf{v}_i) f(\mathbf{v}_{i*}) (\varphi(\mathbf{v}'_i) + \varphi(\mathbf{v}'_{i*}) - \varphi(\mathbf{v}_i) - \varphi(\mathbf{v}_{i*})) \\
&\quad \times B_i(\mathbf{v}_i - \mathbf{v}_{i*}, \boldsymbol{\omega}) d\boldsymbol{\omega} d\mathbf{v}_{i*} d\mathbf{v}_i.
\end{aligned}$$

Proof. The first equation of (2.2.31) is the definition. It is obtained by multiplying both sides of equation (2.1.4) by $\varphi(\mathbf{v}_i)$ and integrating the resulting equation over $\mathbf{v}_i \in \mathbb{R}^3$. Observe that it can be rewritten as given below:

$$\begin{aligned}
\int_{\mathbb{R}^3} Q(f_i, f_{i*}) \varphi(\mathbf{v}_i) d\mathbf{v}_i &= \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{S^2} f(\mathbf{v}'_i) f(\mathbf{v}'_{i*}) \varphi(\mathbf{v}_i) B_i(\mathbf{v}_i - \mathbf{v}_{i*}, \boldsymbol{\omega}) d\boldsymbol{\omega} d\mathbf{v}_{i*} d\mathbf{v}_i \\
&\quad - \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{S^2} f(\mathbf{v}_i) f(\mathbf{v}_{i*}) \varphi(\mathbf{v}_i) B_i(\mathbf{v}_i - \mathbf{v}_{i*}, \boldsymbol{\omega}) d\boldsymbol{\omega} d\mathbf{v}_{i*} d\mathbf{v}_i. \quad (2.2.32)
\end{aligned}$$

Using the change the variables $(\mathbf{v}_i, \mathbf{v}_{i*}) \rightarrow (\mathbf{v}'_i, \mathbf{v}'_{i*})$ together with the fact that the Jacobian of the transformation is unity (see Lemma 2.2.2), we can write the first term on the right-hand side of equation (2.2.32) as given below:

$$\int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{S^2} f(\mathbf{v}'_i) f(\mathbf{v}'_{i*}) \varphi(\mathbf{v}_i(\mathbf{v}'_i, \mathbf{v}'_{i*})) B_i(\mathbf{v}'_i - \mathbf{v}'_{i*}, \boldsymbol{\omega}) d\boldsymbol{\omega} d\mathbf{v}'_{i*} d\mathbf{v}'_i.$$

Using the expression for $\mathbf{v}_i(\mathbf{v}'_i, \mathbf{v}'_{i*})$ given in equation (2.2.28)₁ and equation (2.2.24), we can rewrite the previous equation as given below:

$$\int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{S^2} f(\mathbf{v}'_i) f(\mathbf{v}'_{i*}) \varphi(\mathbf{v}'_i - ((\mathbf{v}'_i - \mathbf{v}'_{i*}) \cdot \boldsymbol{\omega}) \boldsymbol{\omega}) B_i(\mathbf{v}_i - \mathbf{v}_{i*}, \boldsymbol{\omega}) d\boldsymbol{\omega} d\mathbf{v}'_{i*} d\mathbf{v}'_i.$$

Renaming $(\mathbf{v}'_i, \mathbf{v}'_{i*})$ to $(\mathbf{v}_i, \mathbf{v}_{i*})$ in the previous equation, we obtain:

$$\int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{S^2} f(\mathbf{v}_i) f(\mathbf{v}_{i*}) \varphi(\mathbf{v}_i - ((\mathbf{v}_i - \mathbf{v}_{i*}) \cdot \boldsymbol{\omega}) \boldsymbol{\omega}) B_i(\mathbf{v}_i - \mathbf{v}_{i*}, \boldsymbol{\omega}) d\boldsymbol{\omega} d\mathbf{v}_{i*} d\mathbf{v}_i.$$

Using (2.2.10), we obtain that:

$$\varphi(\mathbf{v} - ((\mathbf{v} - \mathbf{v}_*) \cdot \boldsymbol{\omega}) \boldsymbol{\omega}) = \varphi(\mathbf{v}').$$

Thus the previous integral becomes:

$$\int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{S^2} f(\mathbf{v}_i) f(\mathbf{v}_{i*}) \varphi(\mathbf{v}'_i) B_i(\mathbf{v}_i - \mathbf{v}_{i*}, \boldsymbol{\omega}) d\boldsymbol{\omega} d\mathbf{v}_{i*} d\mathbf{v}_i. \quad (2.2.33)$$

Replacing the first term on the right-hand side of equation (2.2.32) with equation (2.2.33) and summing the two terms on the right-hand side of the resulting equation gives the second equation of (2.2.31).

Finally, switching $\mathbf{v}_i$ and $\mathbf{v}_{i*}$ in the second equation of (2.2.31) and then use equations (2.2.21)₁,

(2.2.20), we obtain:

$$\int_{\mathbb{R}^3} Q(f_i, f_{i*}) \varphi(\mathbf{v}_i) d\mathbf{v}_i = \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{S^2} f(\mathbf{v}_i) f(\mathbf{v}_{i*}) (\varphi(\mathbf{v}'_{i*}) - \varphi(\mathbf{v}_{i*})) B_i(\mathbf{v}_i - \mathbf{v}_{i*}, \boldsymbol{\omega}) d\boldsymbol{\omega} d\mathbf{v}_{i*} d\mathbf{v}_i. \quad (2.2.34)$$

Adding equation (2.2.34) to the second equation of (2.2.31) and then divide both sides of the resulting equation by 2 gives the last equation of (2.2.31). This completes the proof. $\square$

Corollary 2.2.4. *Let $f(\mathbf{v}_i)$ and $\varphi(\mathbf{v}_i)$ be sufficiently smooth functions which are small at infinity. Then,*

$$\begin{aligned} \int_{\mathbb{R}^3} Q(f_i, f_{i*}) m_i d\mathbf{v}_i &= 0, \\ \int_{\mathbb{R}^3} Q(f_i, f_{i*}) m_i \mathbf{v}_i d\mathbf{v}_i &= 0, \\ \int_{\mathbb{R}^3} Q(f_i, f_{i*}) \frac{1}{2} m_i (\mathbf{v}_i)^2 d\mathbf{v}_i &= 0. \end{aligned} \quad (2.2.35)$$

Proof. Setting $\varphi(\mathbf{v}_i) = m_i$, $\varphi(\mathbf{v}_i) = m_i \mathbf{v}_i$ and $\varphi(\mathbf{v}_i) = \frac{1}{2} m_i (\mathbf{v}_i)^2$, respectively, in (2.2.18), one has that

$$\varphi(\mathbf{v}_i) + \varphi(\mathbf{v}_{i*}) - \varphi(\mathbf{v}'_i) - \varphi(\mathbf{v}'_{i*}) = 0 \quad (2.2.36)$$

by virtue of the conservation laws of mass, linear momentum and kinetic energy, respectively. More precisely,

$$\begin{aligned} m_i + m_{i*} - m_i - m_{i*} &= 0, \\ m_i \mathbf{v}_i + m_{i*} \mathbf{v}_{i*} - m_i \mathbf{v}'_i - m_{i*} \mathbf{v}'_{i*} &= 0, \\ \frac{1}{2} m_i (\mathbf{v}_i)^2 + \frac{1}{2} m_{i*} (\mathbf{v}_{i*})^2 - \frac{1}{2} m_i (\mathbf{v}'_i)^2 - \frac{1}{2} m_{i*} (\mathbf{v}'_{i*})^2 &= 0. \end{aligned} \quad (2.2.37)$$

$\square$

Definition 2.2.5. *A measurable function $\varphi(\mathbf{v}_i)$ defined almost everywhere in $\mathbb{R}^3$ that satisfies equation (2.2.36), where $\mathbf{v}'_i(\mathbf{v}_i, \mathbf{v}_{i*}, \boldsymbol{\omega})$ and $\mathbf{v}'_{i*}(\mathbf{v}_i, \mathbf{v}_{i*}, \boldsymbol{\omega})$ are as defined in equations (2.2.10) and (2.2.11), respectively, is called a collision (summation) invariant.*

Since mass m_i , linear momentum $m_i \mathbf{v}_i$ and kinetic energy $\frac{1}{2} m_i (\mathbf{v}_i)^2$ satisfy equation (2.2.36) as shown in equation (2.2.37), they are collision invariants.

Remark 2.2.6. *The term on the right-hand side of equation (2.2.18) and those on the right-hand side of the equation (2.2.31) are often referred to as the weak formulation (or weak form) of the collision integral. These weak forms allow the manipulation of the collision integral in problems of basic character despite its complicated form. From the mathematical point of view, these weak formulations are very interesting because they may be well defined in situations where the collision integral itself is not.*

Proposition 2.2.7. A continuous function $\varphi(\mathbf{v}_i)$ is a collision invariant if and only if there exist scalar functions $a, c \in \mathbb{R}$ and a vector function $\mathbf{b} \in \mathbb{R}^3$ such that

$$\varphi(\mathbf{v}_i) = a + \mathbf{b} \cdot \mathbf{v}_i + c(\mathbf{v}_i)^2. \quad (2.2.38)$$

Proof. See, for example, [8, 35, 37, 60] for the proof of the above proposition. $\square$

Proposition 2.2.8. Let the distribution function $f(\mathbf{v}_i)$ be positive and rapidly decaying at infinity. If we assume that the collision kernel $B_i(\mathbf{v}_i - \mathbf{v}_{i*}, \boldsymbol{\omega})$ is strictly positive almost everywhere, then

$$\int_{\mathbb{R}^3} Q(f_i, f_{i*}) \log f(\mathbf{v}_i) d\mathbf{v}_i \leq 0.$$

Moreover, the following three properties are equivalent:

(i)

$$\int_{\mathbb{R}^3} Q(f_i, f_{i*}) \log f_i(\mathbf{v}_i) d\mathbf{v}_i = 0,$$

for all $\mathbf{v}_i \in \mathbb{R}^3$,

(ii)

$$Q(f_i, f_{i*}) = 0,$$

(iii) $f(\mathbf{v}_i)$ is a Maxwellian distribution, that is, there exist $n_i(t, \mathbf{x}) > 0$, $T_i(t, \mathbf{x}) > 0$ and $\mathbf{u}_i(t, \mathbf{x}) \in \mathbb{R}^3$ such that

$$f(\mathbf{v}_i) = n_i \left(\frac{m_i}{2\pi k_B T_i} \right)^{\frac{3}{2}} \exp \left(- \frac{m_i(\mathbf{v}_i - \mathbf{u}_i)^2}{2k_B T_i} \right). \quad (2.2.39)$$

Proof. The proof of this proposition is standard. It can be found for example, in [58] $\square$

2.2.3 Properties of the Bi-Species Collision Operator

In this subsection, the properties of the bi-species collision operator will be presented. Each property will be given in the form of a lemma, a proposition or a corollary. Also, because of the importance of these properties especially in relation to hydrodynamics, a complete step by step proof of these properties will be given. Furthermore, for clarity in the computations involving the collision integral, the distribution functions will be written with the velocity argument only. More precisely, for $i, j = 1, 2, \dots, S$ with $i \neq j$, the following notations for the distribution functions will be used:

$$f(t, \mathbf{x}, \mathbf{v}'_i) = f(\mathbf{v}'_i), f(t, \mathbf{x}, \mathbf{v}'_j) = f(\mathbf{v}'_j), f(t, \mathbf{x}, \mathbf{v}_i) = f(\mathbf{v}_i), f(t, \mathbf{x}, \mathbf{v}_j) = f(\mathbf{v}_j).$$

Lemma 2.2.9. Let $f(\mathbf{v}_i)$ and $\varphi(\mathbf{v}_i)$ be sufficiently smooth functions which are small at infinity. Then

$$\int_{\mathbb{R}^3} Q(f_i, f_j) \varphi(\mathbf{v}_i) d\mathbf{v}_i = \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}^2} [f(\mathbf{v}'_i) f(\mathbf{v}'_j) - f(\mathbf{v}_i) f(\mathbf{v}_j)] \times (\varphi(\mathbf{v}_i) - \varphi(\mathbf{v}'_i)) B_{ij}(\mathbf{v}_i - \mathbf{v}_j, \boldsymbol{\omega}) d\boldsymbol{\omega} d\mathbf{v}_j d\mathbf{v}_i. \quad (2.2.40)$$

Proof. Multiplying both sides of equation (2.1.5) by $\varphi(\mathbf{v}_i)$ and then integrate the resulting equation over $\mathbf{v}_i \in \mathbb{R}^3$ gives:

$$\begin{aligned} \int_{\mathbb{R}^3} Q(f_i, f_j) \varphi(\mathbf{v}_i) d\mathbf{v}_i \\ = \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}^2} [f(\mathbf{v}'_i) f(\mathbf{v}'_j) - f(\mathbf{v}_i) f(\mathbf{v}_j)] \varphi(\mathbf{v}_i) B_{ij}(\mathbf{v}_i - \mathbf{v}_j, \boldsymbol{\omega}) d\boldsymbol{\omega} d\mathbf{v}_j d\mathbf{v}_i. \end{aligned} \quad (2.2.41)$$

Using the change the variables $(\mathbf{v}_i, \mathbf{v}_j) \rightarrow (\mathbf{v}'_i, \mathbf{v}'_j)$ together with the fact that the determinant of the Jacobian of this transformation is one (see Lemma 2.2.2 with i^* replaced by j), we can write equation (2.2.41) as follows:

$$\begin{aligned} \int_{\mathbb{R}^3} Q(f_i, f_j) \varphi(\mathbf{v}_i) d\mathbf{v}_i = \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}^2} [f(\mathbf{v}'_i) f(\mathbf{v}'_j) - f(\mathbf{v}_i(\mathbf{v}'_i, \mathbf{v}'_j)) f(\mathbf{v}_j(\mathbf{v}'_i, \mathbf{v}'_j))] \\ \times \varphi(\mathbf{v}_i(\mathbf{v}'_i, \mathbf{v}'_j)) B_{ij}(\mathbf{v}'_i - \mathbf{v}'_j, \boldsymbol{\omega}) d\boldsymbol{\omega} d\mathbf{v}'_j d\mathbf{v}'_i. \end{aligned} \quad (2.2.42)$$

Moreover, subtracting equation (2.2.17) from equation (2.2.16) gives:

$$\begin{aligned} \mathbf{v}'_i - \mathbf{v}'_j &= \mathbf{v}_i - \mathbf{v}_j - \left(\frac{2m_i m_j}{(m_i + m_j)m_i} + \frac{2m_i m_j}{(m_i + m_j)m_j} \right) ((\mathbf{v}_i - \mathbf{v}_j) \cdot \boldsymbol{\omega}) \boldsymbol{\omega} \\ &= \mathbf{v}_i - \mathbf{v}_j - 2((\mathbf{v}_i - \mathbf{v}_j) \cdot \boldsymbol{\omega}) \boldsymbol{\omega}. \end{aligned}$$

Taking the inner product with $\boldsymbol{\omega}$, we obtain:

$$(\mathbf{v}'_i - \mathbf{v}'_j) \cdot \boldsymbol{\omega} = -(\mathbf{v}_i - \mathbf{v}_j) \cdot \boldsymbol{\omega}. \quad (2.2.43)$$

Therefore,

$$(\mathbf{v}'_i - \mathbf{v}'_j) = -(\mathbf{v}_i - \mathbf{v}_j) \implies |\mathbf{v}'_i - \mathbf{v}'_j| = |\mathbf{v}_i - \mathbf{v}_j|.$$

Thus,

$$B_{ij}(\mathbf{v}_i - \mathbf{v}_j, \boldsymbol{\omega}) = \bar{B}_{ij}(|\mathbf{v}_i - \mathbf{v}_j|, \cos \theta) = \bar{B}_{ij}(|\mathbf{v}'_i - \mathbf{v}'_j|, \cos \theta) = B_{ij}(\mathbf{v}'_i - \mathbf{v}'_j, \boldsymbol{\omega}). \quad (2.2.44)$$

Thus we can rewrite equation (2.2.42) as follows:

$$\begin{aligned} \int_{\mathbb{R}^3} Q(f_i, f_j) \varphi(\mathbf{v}_i) d\mathbf{v}_i = \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}^2} [f(\mathbf{v}'_i) f(\mathbf{v}'_j) - f(\mathbf{v}_i(\mathbf{v}'_i, \mathbf{v}'_j)) f(\mathbf{v}_j(\mathbf{v}'_i, \mathbf{v}'_j))] \\ \times \varphi(\mathbf{v}_i(\mathbf{v}'_i, \mathbf{v}'_j)) B_{ij}(\mathbf{v}_i - \mathbf{v}_j, \boldsymbol{\omega}) d\boldsymbol{\omega} d\mathbf{v}'_j d\mathbf{v}'_i. \end{aligned} \quad (2.2.45)$$

Inverting equations (2.2.16) and (2.2.17), we obtain:

$$\begin{aligned}
\mathbf{v}_i &= \mathbf{v}'_i + \frac{2\mu_{ij}}{m_i} ((\mathbf{v}_i - \mathbf{v}_j) \cdot \boldsymbol{\omega}) \boldsymbol{\omega}, \\
\mathbf{v}_j &= \mathbf{v}'_j - \frac{2\mu_{ij}}{m_j} ((\mathbf{v}_i - \mathbf{v}_j) \cdot \boldsymbol{\omega}) \boldsymbol{\omega}.
\end{aligned} \tag{2.2.46}$$

Using equation (2.2.43), we can write equation (2.2.46) as follows:

$$\begin{aligned}
\mathbf{v}_i &= \mathbf{v}'_i + \frac{2\mu_{ij}}{m_i} ((\mathbf{v}_i - \mathbf{v}_j) \cdot \boldsymbol{\omega}) \boldsymbol{\omega} = \mathbf{v}'_i - \frac{2\mu_{ij}}{m_i} ((\mathbf{v}'_i - \mathbf{v}'_j) \cdot \boldsymbol{\omega}) \boldsymbol{\omega} \equiv \mathbf{v}_i(\mathbf{v}'_i, \mathbf{v}'_j), \\
\mathbf{v}_j &= \mathbf{v}'_j - \frac{2\mu_{ij}}{m_j} ((\mathbf{v}_i - \mathbf{v}_j) \cdot \boldsymbol{\omega}) \boldsymbol{\omega} = \mathbf{v}'_j + \frac{2\mu_{ij}}{m_j} ((\mathbf{v}'_i - \mathbf{v}'_j) \cdot \boldsymbol{\omega}) \boldsymbol{\omega} \equiv \mathbf{v}_j(\mathbf{v}'_i, \mathbf{v}'_j).
\end{aligned} \tag{2.2.47}$$

Substituting the expressions for $\mathbf{v}_i(\mathbf{v}'_i, \mathbf{v}'_j)$ and $\mathbf{v}_j(\mathbf{v}'_i, \mathbf{v}'_j)$ given in equation (2.2.47) above into equation (2.2.45), we obtain:

$$\begin{aligned}
&\int_{\mathbb{R}^3} Q(f_i, f_j) \varphi(\mathbf{v}_i) d\mathbf{v}_i \\
&= \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{S^2} \left[f(\mathbf{v}'_i) f(\mathbf{v}'_j) - f\left(\mathbf{v}'_i - \frac{2\mu_{ij}}{m_i} ((\mathbf{v}'_i - \mathbf{v}'_j) \cdot \boldsymbol{\omega}) \boldsymbol{\omega}\right) f\left(\mathbf{v}'_j + \frac{2\mu_{ij}}{m_j} ((\mathbf{v}'_i - \mathbf{v}'_j) \cdot \boldsymbol{\omega}) \boldsymbol{\omega}\right) \right] \\
&\quad \times \varphi\left(\left(\mathbf{v}'_i - \frac{2\mu_{ij}}{m_i} ((\mathbf{v}'_i - \mathbf{v}'_j) \cdot \boldsymbol{\omega}) \boldsymbol{\omega}\right)\right) B_{ij}(\mathbf{v}_i - \mathbf{v}_j, \boldsymbol{\omega}) d\boldsymbol{\omega} d\mathbf{v}'_j d\mathbf{v}'_i.
\end{aligned} \tag{2.2.48}$$

Now rename $(\mathbf{v}'_i, \mathbf{v}'_j)$ to $(\mathbf{v}_i, \mathbf{v}_j)$ in equation (2.2.48) to obtain:

$$\begin{aligned}
&\int_{\mathbb{R}^3} Q(f_i, f_j) \varphi(\mathbf{v}_i) d\mathbf{v}_i \\
&= \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{S^2} \left[f(\mathbf{v}_i) f(\mathbf{v}_j) - f\left(\mathbf{v}_i - \frac{2\mu_{ij}}{m_i} ((\mathbf{v}_i - \mathbf{v}_j) \cdot \boldsymbol{\omega}) \boldsymbol{\omega}\right) f\left(\mathbf{v}_j + \frac{2\mu_{ij}}{m_j} ((\mathbf{v}_i - \mathbf{v}_j) \cdot \boldsymbol{\omega}) \boldsymbol{\omega}\right) \right] \\
&\quad \times \varphi\left(\left(\mathbf{v}_i - \frac{2\mu_{ij}}{m_i} ((\mathbf{v}_i - \mathbf{v}_j) \cdot \boldsymbol{\omega}) \boldsymbol{\omega}\right)\right) B_{ij}(\mathbf{v}_i - \mathbf{v}_j, \boldsymbol{\omega}) d\boldsymbol{\omega} d\mathbf{v}_j d\mathbf{v}_i.
\end{aligned} \tag{2.2.49}$$

Using equations (2.2.16) and (2.2.17), we can rewrite equation (2.2.49) as follows:

$$\begin{aligned}
&\int_{\mathbb{R}^3} Q(f_i, f_j) \varphi(\mathbf{v}_i) d\mathbf{v}_i \\
&= - \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{S^2} [f(\mathbf{v}'_i) f(\mathbf{v}'_j) - f(\mathbf{v}_i) f(\mathbf{v}_j)] \varphi(\mathbf{v}'_i) B_{ij}(\mathbf{v}_i - \mathbf{v}_j, \boldsymbol{\omega}) d\boldsymbol{\omega} d\mathbf{v}_j d\mathbf{v}_i.
\end{aligned} \tag{2.2.50}$$

Adding equations (2.2.41), (2.2.50) and then divide the resulting equation by 2 gives equation (2.2.40).

Therefore, the proof is complete. $\square$

Lemma 2.2.10. *Let $f(\mathbf{v}_j)$ and $\varphi(\mathbf{v}_j)$ be sufficiently smooth functions which are small at infinity. Then*

$$\begin{aligned}
\int_{\mathbb{R}^3} Q(f_j, f_i) \varphi(\mathbf{v}_j) d\mathbf{v}_j &= \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{S^2} [f(\mathbf{v}'_i) f(\mathbf{v}'_j) - f(\mathbf{v}_i) f(\mathbf{v}_j)] \\
&\quad \times (\varphi(\mathbf{v}_j) - \varphi(\mathbf{v}'_j)) B_{ij}(\mathbf{v}_i - \mathbf{v}_j, \boldsymbol{\omega}) d\boldsymbol{\omega} d\mathbf{v}_j d\mathbf{v}_i
\end{aligned} \tag{2.2.51}$$

Proof. Switch i and j in equation (2.1.5), then multiply the resulting equation by $\varphi(\mathbf{v}_j)$ and integrate over $\mathbf{v}_j \in \mathbb{R}^3$ to obtain:

$$\begin{aligned} \int_{\mathbb{R}^3} Q(f_j, f_i) \varphi(\mathbf{v}_j) d\mathbf{v}_j \\ = \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{S^2} [f(\mathbf{v}'_j) f(\mathbf{v}'_i) - f(\mathbf{v}_j) f(\mathbf{v}_i)] \varphi(\mathbf{v}_j) B(\mathbf{v}_j - \mathbf{v}_i, \boldsymbol{\omega}) d\boldsymbol{\omega} d\mathbf{v}_i d\mathbf{v}_j \end{aligned} \quad (2.2.52)$$

Observe that:

$$B_{ij}(\mathbf{v}_j - \mathbf{v}_i, \boldsymbol{\omega}) = \bar{B}_{ij}(|\mathbf{v}_j - \mathbf{v}_i|, \cos \theta) = \bar{B}_{ij}(|\mathbf{v}_i - \mathbf{v}_j|, \cos \theta) = B_{ij}(\mathbf{v}_i - \mathbf{v}_j, \boldsymbol{\omega}).$$

Therefore, we can rewrite equation (2.2.52) as given below:

$$\begin{aligned} \int_{\mathbb{R}^3} Q(f_j, f_i) \varphi(\mathbf{v}_j) d\mathbf{v}_j \\ = \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{S^2} [f(\mathbf{v}'_i) f(\mathbf{v}'_j) - f(\mathbf{v}_i) f(\mathbf{v}_j)] \varphi(\mathbf{v}_j) B_{ij}(\mathbf{v}_i - \mathbf{v}_j, \boldsymbol{\omega}) d\boldsymbol{\omega} d\mathbf{v}_j d\mathbf{v}_i. \end{aligned} \quad (2.2.53)$$

Using the change of variables $(\mathbf{v}_i, \mathbf{v}_j) \rightarrow (\mathbf{v}'_i, \mathbf{v}'_j)$ together with the fact that the determinant of the Jacobian of this transformation is unity (see Lemma 2.2.2 with i^* replaced by j), we can rewrite equation (2.2.53) as follows:

$$\begin{aligned} \int_{\mathbb{R}^3} Q(f_j, f_i) \varphi(\mathbf{v}_j) d\mathbf{v}_j = \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{S^2} [f(\mathbf{v}'_i) f(\mathbf{v}'_j) - f(\mathbf{v}_i(\mathbf{v}'_i, \mathbf{v}'_j)) f(\mathbf{v}_j(\mathbf{v}'_i, \mathbf{v}'_j))] \\ \times \varphi(\mathbf{v}_j(\mathbf{v}'_i, \mathbf{v}'_j)) B_{ij}(\mathbf{v}'_i - \mathbf{v}'_j, \boldsymbol{\omega}) d\boldsymbol{\omega} d\mathbf{v}'_j d\mathbf{v}'_i. \end{aligned}$$

Using equation (2.2.44) for the collision kernel and the expressions for $\mathbf{v}_i(\mathbf{v}'_i, \mathbf{v}'_j)$, $\mathbf{v}_j(\mathbf{v}'_i, \mathbf{v}'_j)$ given in equation (2.2.47), the previous equation becomes:

$$\begin{aligned} \int_{\mathbb{R}^3} Q(f_j, f_i) \varphi(\mathbf{v}_j) d\mathbf{v}_j \\ = \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{S^2} \left[f(\mathbf{v}'_i) f(\mathbf{v}'_j) - f\left(\mathbf{v}'_i - \frac{2\mu_{ij}}{m_i} ((\mathbf{v}'_i - \mathbf{v}'_j) \cdot \boldsymbol{\omega}) \boldsymbol{\omega}\right) f\left(\mathbf{v}'_j + \frac{2\mu_{ij}}{m_j} ((\mathbf{v}'_i - \mathbf{v}'_j) \cdot \boldsymbol{\omega}) \boldsymbol{\omega}\right) \right] \\ \times \varphi\left(\left(\mathbf{v}'_j + \frac{2\mu_{ij}}{m_j} ((\mathbf{v}'_i - \mathbf{v}'_j) \cdot \boldsymbol{\omega}) \boldsymbol{\omega}\right)\right) B_{ij}(\mathbf{v}'_i - \mathbf{v}'_j, \boldsymbol{\omega}) d\boldsymbol{\omega} d\mathbf{v}'_j d\mathbf{v}'_i. \end{aligned} \quad (2.2.54)$$

Now rename $(\mathbf{v}'_i, \mathbf{v}'_j)$ to $(\mathbf{v}_i, \mathbf{v}_j)$ in equation (2.2.54) above to obtain:

$$\begin{aligned} \int_{\mathbb{R}^3} Q(f_j, f_i) \varphi(\mathbf{v}_j) d\mathbf{v}_j \\ = \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{S^2} \left[f(\mathbf{v}_i) f(\mathbf{v}_j) - f\left(\mathbf{v}_i - \frac{2\mu_{ij}}{m_i} ((\mathbf{v}_i - \mathbf{v}_j) \cdot \boldsymbol{\omega}) \boldsymbol{\omega}\right) f\left(\mathbf{v}_j + \frac{2\mu_{ij}}{m_j} ((\mathbf{v}_i - \mathbf{v}_j) \cdot \boldsymbol{\omega}) \boldsymbol{\omega}\right) \right] \\ \times \varphi\left(\left(\mathbf{v}_j + \frac{2\mu_{ij}}{m_j} ((\mathbf{v}_i - \mathbf{v}_j) \cdot \boldsymbol{\omega}) \boldsymbol{\omega}\right)\right) B_{ij}(\mathbf{v}_i - \mathbf{v}_j, \boldsymbol{\omega}) d\boldsymbol{\omega} d\mathbf{v}_j d\mathbf{v}_i. \end{aligned} \quad (2.2.55)$$

Using equations (2.2.16) and (2.2.17), we can rewrite equation (2.2.55) as given below:

$$\begin{aligned} & \int_{\mathbb{R}^3} Q(f_j, f_i) \varphi(\mathbf{v}_j) d\mathbf{v}_j \\ &= - \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}^2} [f(\mathbf{v}'_i) f(\mathbf{v}'_j) - f(\mathbf{v}_i) f(\mathbf{v}_j)] \varphi(\mathbf{v}'_j) B_{ij}(\mathbf{v}_i - \mathbf{v}_j, \boldsymbol{\omega}) d\boldsymbol{\omega} d\mathbf{v}_j d\mathbf{v}_i. \end{aligned} \quad (2.2.56)$$

Adding equations (2.2.53), (2.2.56) and then divide the resulting equation by 2 gives equation (2.2.51). Therefore, the proof is complete. $\square$

Corollary 2.2.11. *Let $\varphi(\mathbf{v}_i)$ and $\varphi(\mathbf{v}_j)$ with $i, j = 1, 2, \dots, S$, $i \neq j$, be functions such that*

$$\int_{\mathbb{R}^3} Q(f_i, f_j) \varphi(\mathbf{v}_i) d\mathbf{v}_i \quad \text{and} \quad \int_{\mathbb{R}^3} Q(f_j, f_i) \varphi(\mathbf{v}_j) d\mathbf{v}_j$$

make sense. Then

$$\begin{aligned} & \int_{\mathbb{R}^3} Q(f_i, f_j) \varphi(\mathbf{v}_i) d\mathbf{v}_i + \int_{\mathbb{R}^3} Q(f_j, f_i) \varphi(\mathbf{v}_j) d\mathbf{v}_j \\ &= -\frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}^2} [f(\mathbf{v}'_i) f(\mathbf{v}'_j) - f(\mathbf{v}_i) f(\mathbf{v}_j)] (\varphi(\mathbf{v}'_i) + \varphi(\mathbf{v}'_j) - \varphi(\mathbf{v}_i) - \varphi(\mathbf{v}_j)) \\ & \quad \times B_{ij}(\mathbf{v}_i - \mathbf{v}_j, \boldsymbol{\omega}) d\boldsymbol{\omega} d\mathbf{v}_j d\mathbf{v}_i. \end{aligned} \quad (2.2.57)$$

Proof. It is enough to add equations (2.2.40) and (2.2.51) of Lemmas 2.2.9 and 2.2.10. $\square$

Corollary 2.2.12. *Let $f(\mathbf{v}_i)$, $f(\mathbf{v}_j)$, $\varphi(\mathbf{v}_i)$ and $\varphi(\mathbf{v}_j)$ be sufficiently smooth functions which are small at infinity. Then*

$$\int_{\mathbb{R}^3} Q(f_i, f_j) m_i d\mathbf{v}_i = 0, \quad (2.2.58)$$

$$\int_{\mathbb{R}^3} Q(f_i, f_j) m_i \mathbf{v}_i d\mathbf{v}_i + \int_{\mathbb{R}^3} Q(f_j, f_i) m_j \mathbf{v}_j d\mathbf{v}_j = 0 \quad (2.2.59)$$

$$\int_{\mathbb{R}^3} Q(f_i, f_j) \frac{1}{2} m_i (\mathbf{v}_i)^2 d\mathbf{v}_i + \int_{\mathbb{R}^3} Q(f_j, f_i) \frac{1}{2} m_j (\mathbf{v}_j)^2 d\mathbf{v}_j = 0. \quad (2.2.60)$$

Proof. Setting $\varphi(\mathbf{v}_i) = m_i$ in equation (2.2.40) gives (2.2.58). Setting $\varphi(\mathbf{v}_i) = m_i \mathbf{v}_i$, $\varphi(\mathbf{v}_j) = m_j \mathbf{v}_j$ and $\varphi(\mathbf{v}_i) = \frac{1}{2} m_i (\mathbf{v}_i)^2$, $\varphi(\mathbf{v}_j) = \frac{1}{2} m_j (\mathbf{v}_j)^2$, in equation (2.2.57), we obtain equations (2.2.59) and (2.2.60), respectively, by virtue of the conservation laws of linear momentum (2.2.4) and kinetic energy (2.2.5), respectively. $\square$

Proposition 2.2.13. *Let the distribution functions $f(\mathbf{v}_i)$ with $i = 1, 2, \dots, S$ be positive and rapidly decaying at infinity. If one assumes that the collision kernels $B_{ij}(\mathbf{v}_i - \mathbf{v}_j, \boldsymbol{\omega})$ with $i, j = 1, 2, \dots, S$, $i \neq j$, are strictly positive almost everywhere, then*

$$\sum_{i=1}^S \sum_{\substack{j=1 \\ j \neq i}}^S \int_{\mathbb{R}^3} Q(f_i, f_j) \log f_i(\mathbf{v}_i) d\mathbf{v}_i \leq 0.$$

Moreover, the following three properties are equivalent:

(i) for all $\mathbf{v}_i \in \mathbb{R}^3$

$$\sum_{i=1}^S \sum_{\substack{j=1 \\ j \neq i}}^S \int_{\mathbb{R}^3} Q(f_i, f_j) \log f(\mathbf{v}_i) d\mathbf{v}_i = 0,$$

(ii) for $i, j = 1, 2, \dots, S$ with $i \neq j$

$$Q(f_i, f_j) = 0,$$

(iii) there exist $n_i(t, \mathbf{x}) \geq 0$ with $i = 1, 2, \dots, S$, $\mathbf{u}(t, \mathbf{x}) \in \mathbb{R}^3$ and $T(t, \mathbf{x}) > 0$ such that

$$f(\mathbf{v}_i) = n_i \left(\frac{m_i}{2\pi k_B T} \right)^{\frac{3}{2}} \exp \left(- \frac{m_i (\mathbf{v}_i - \mathbf{u})^2}{2k_B T} \right). \quad (2.2.61)$$

Proof. Using equation (2.2.57) with $\varphi(\mathbf{v}_i) = \log f(\mathbf{v}_i)$, $\varphi(\mathbf{v}_j) = \log f(\mathbf{v}_j)$, we obtain:

$$\begin{aligned} \sum_{i=1}^S \sum_{\substack{j=1 \\ j \neq i}}^S \int_{\mathbb{R}^3} Q(f_i, f_j) \log f(\mathbf{v}_i) d\mathbf{v}_i &= -\frac{1}{2} \sum_{i=1}^S \sum_{\substack{j=1 \\ j \neq i}}^S \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{S^2} [f(\mathbf{v}'_i) f(\mathbf{v}'_j) - f(\mathbf{v}_i) f(\mathbf{v}_j)] \\ &\quad \times \log \left(\frac{f(\mathbf{v}'_i) f(\mathbf{v}'_j)}{f(\mathbf{v}_i) f(\mathbf{v}_j)} \right) B_{ij}(\mathbf{v}_i - \mathbf{v}_j, \boldsymbol{\omega}) d\boldsymbol{\omega} d\mathbf{v}_j d\mathbf{v}_i. \end{aligned} \quad (2.2.62)$$

Observe that each of the integrand in the summation of integrals in the previous equation is of the form

$$(a - b) \log \frac{a}{b} \bar{B}, \quad (2.2.63)$$

where in each case

$$a = f(\mathbf{v}'_i) f(\mathbf{v}'_j), \quad b = f(\mathbf{v}_i) f(\mathbf{v}_j) \quad \text{and} \quad \bar{B} = B_{ij}(\mathbf{v}_i - \mathbf{v}_j, \boldsymbol{\omega}).$$

If $a > b$, then both $(a - b)$ and $\log \frac{a}{b}$ are positive. If $a < b$, then both $(a - b)$ and $\log \frac{a}{b}$ are negative. Observe that, in both cases (i.e., $a > b$ and $a < b$), equation (2.2.63) is positive, since by assumption $B_{ij}(\mathbf{v}_i - \mathbf{v}_j, \boldsymbol{\omega})$ is strictly positive almost everywhere. Therefore, the integrand of each of the integral in summation of integrals given in equation (2.2.62) is always positive. Thus

$$\sum_{i=1}^S \sum_{\substack{j=1 \\ j \neq i}}^S \int_{\mathbb{R}^3} Q(f_i, f_j) \log f_i(\mathbf{v}_i) d\mathbf{v}_i \leq 0,$$

as required. Furthermore, observe that since equation (2.2.63) is positive, equation (2.2.62) reduces to:

$$\sum_{i=1}^S \sum_{\substack{j=1 \\ j \neq i}}^S \int_{\mathbb{R}^3} Q(f_i, f_j) \log f_i(\mathbf{v}_i) d\mathbf{v}_i = 0 \quad (2.2.64)$$

if and only if

$$f(\mathbf{v}'_i) f(\mathbf{v}'_j) = f(\mathbf{v}_i) f(\mathbf{v}_j).$$

The previous equation accounts for the the equivalence between (i) and (ii).

Now let us prove that (i) implies (iii). Suppose that (i) holds, this implies that $f(\mathbf{v}'_i)f(\mathbf{v}'_j) = f(\mathbf{v}_i)f(\mathbf{v}_j)$. Therefore, there exist $n_i(t, \mathbf{x}) \geq 0$ with $i = 1, 2, \dots, S$, $\mathbf{u}_i(t, \mathbf{x}) \in \mathbb{R}^3$ and $T_i(t, \mathbf{x}) > 0$ such that

$$f(\mathbf{v}_i) = n_i \left(\frac{m_i}{2\pi k_B T_i} \right)^{\frac{3}{2}} \exp \left(- \frac{m_i(\mathbf{v}_i - \mathbf{u}_i)^2}{2k_B T_i} \right),$$

see Lemma 3.4 of [58]. It remains to show that $\mathbf{u}_i = \mathbf{u}_j = \mathbf{u}$ and $T_i = T_j = T$. To do this, observe that $f(\mathbf{v}'_i)f(\mathbf{v}'_j) = f(\mathbf{v}_i)f(\mathbf{v}_j)$ implies that:

$$\frac{m_i(\mathbf{v}'_i - \mathbf{u}_i)^2}{2k_B T_i} + \frac{m_j(\mathbf{v}'_j - \mathbf{u}_j)^2}{2k_B T_j} = \frac{m_i(\mathbf{v}_i - \mathbf{u}_i)^2}{2k_B T_i} + \frac{m_j(\mathbf{v}_j - \mathbf{u}_j)^2}{2k_B T_j}.$$

Using equations (2.2.16) and (2.2.17), we can rewrite the previous equation as follows:

$$\begin{aligned} \frac{m_i}{2k_B T_i} \left(\mathbf{v}_i - \frac{2\mu_{ij}}{m_i} ((\mathbf{v}_i - \mathbf{v}_j) \cdot \boldsymbol{\omega}) \boldsymbol{\omega} - \mathbf{u}_i \right)^2 + \frac{m_j}{2k_B T_j} \left(\mathbf{v}_j + \frac{2\mu_{ij}}{m_j} ((\mathbf{v}_i - \mathbf{v}_j) \cdot \boldsymbol{\omega}) \boldsymbol{\omega} - \mathbf{u}_j \right)^2 \\ = \frac{m_i(\mathbf{v}_i - \mathbf{u}_i)^2}{2k_B T_i} + \frac{m_j(\mathbf{v}_j - \mathbf{u}_j)^2}{2k_B T_j}. \end{aligned} \quad (2.2.65)$$

Observe that

$$\begin{aligned} \frac{m_i}{2k_B T_i} \left(\mathbf{v}_i - \frac{2\mu_{ij}}{m_i} ((\mathbf{v}_i - \mathbf{v}_j) \cdot \boldsymbol{\omega}) \boldsymbol{\omega} - \mathbf{u}_i \right)^2 \\ = \frac{m_i(\mathbf{v}_i)^2}{2k_B T_i} - \frac{2\mu_{ij}}{k_B T_i} (\boldsymbol{\omega} \cdot \mathbf{v}_i)^2 + \frac{2\mu_{ij}}{k_B T_i} (\boldsymbol{\omega} \cdot \mathbf{v}_j)(\boldsymbol{\omega} \cdot \mathbf{v}_i) - \frac{m_i}{k_B T_i} (\mathbf{u}_i \cdot \mathbf{v}_i) \\ + \frac{m_i}{2k_B T_i} \left(\frac{2\mu_{ij}}{m_i} ((\mathbf{v}_i - \mathbf{v}_j) \cdot \boldsymbol{\omega}) \right)^2 + \frac{2\mu_{ij}}{k_B T_i} (\boldsymbol{\omega} \cdot \mathbf{v}_i)(\boldsymbol{\omega} \cdot \mathbf{u}_i) - \frac{2\mu_{ij}}{k_B T_i} (\boldsymbol{\omega} \cdot \mathbf{v}_j)(\boldsymbol{\omega} \cdot \mathbf{u}_i) + \frac{m_i(\mathbf{u}_i)^2}{2k_B T_i}, \end{aligned} \quad (2.2.66)$$

$$\begin{aligned} \frac{m_j}{2k_B T_j} \left(\mathbf{v}_j + \frac{2\mu_{ij}}{m_j} ((\mathbf{v}_i - \mathbf{v}_j) \cdot \boldsymbol{\omega}) \boldsymbol{\omega} - \mathbf{u}_j \right)^2 \\ = \frac{m_j(\mathbf{v}_j)^2}{2k_B T_j} + \frac{2\mu_{ij}}{k_B T_j} (\boldsymbol{\omega} \cdot \mathbf{v}_i)(\boldsymbol{\omega} \cdot \mathbf{v}_j) - \frac{2\mu_{ij}}{k_B T_j} (\boldsymbol{\omega} \cdot \mathbf{v}_j)^2 - \frac{m_j}{k_B T_j} (\mathbf{u}_j \cdot \mathbf{v}_j) \\ + \frac{m_j}{2k_B T_j} \left(\frac{2\mu_{ij}}{m_j} ((\mathbf{v}_i - \mathbf{v}_j) \cdot \boldsymbol{\omega}) \right)^2 - \frac{2\mu_{ij}}{k_B T_j} (\boldsymbol{\omega} \cdot \mathbf{v}_i)(\boldsymbol{\omega} \cdot \mathbf{u}_j) + \frac{2\mu_{ij}}{k_B T_j} (\boldsymbol{\omega} \cdot \mathbf{v}_j)(\boldsymbol{\omega} \cdot \mathbf{u}_j) + \frac{m_j(\mathbf{u}_j)^2}{2k_B T_j}, \end{aligned} \quad (2.2.67)$$

and

$$\begin{aligned} \frac{m_i(\mathbf{v}_i - \mathbf{u}_i)^2}{2k_B T_i} + \frac{m_j(\mathbf{v}_j - \mathbf{u}_j)^2}{2k_B T_j} \\ = \frac{m_i(\mathbf{v}_i)^2}{2k_B T_i} - \frac{m_i}{k_B T_i} (\mathbf{u}_i \cdot \mathbf{v}_i) + \frac{m_i(\mathbf{u}_i)^2}{2k_B T_i} + \frac{m_j(\mathbf{v}_j)^2}{2k_B T_j} - \frac{m_j}{k_B T_j} (\mathbf{u}_j \cdot \mathbf{v}_j) + \frac{m_j(\mathbf{u}_j)^2}{2k_B T_j}. \end{aligned} \quad (2.2.68)$$

Therefore, substituting Eqs. (2.2.66), (2.2.67) and (2.2.68) into Eq. (2.2.65) gives:

$$\frac{m_i(\mathbf{v}_i)^2}{2k_B T_i} - \frac{2\mu_{ij}}{k_B T_i} (\boldsymbol{\omega} \cdot \mathbf{v}_i)^2 + \frac{2\mu_{ij}}{k_B} (\boldsymbol{\omega} \cdot \mathbf{v}_j) \left(\frac{(\boldsymbol{\omega} \cdot \mathbf{v}_i)}{T_i} + \frac{(\boldsymbol{\omega} \cdot \mathbf{v}_i)}{T_j} \right) - \frac{m_i}{k_B T_i} (\mathbf{u}_i \cdot \mathbf{v}_i)$$

$$\begin{aligned}
& + \frac{m_i}{2k_B T_i} \left(\frac{2\mu_{ij}}{m_i} ((\mathbf{v}_i - \mathbf{v}_j) \cdot \boldsymbol{\omega}) \right)^2 + \frac{2\mu_{ij}}{k_B} (\boldsymbol{\omega} \cdot \mathbf{v}_i) \left(\frac{(\boldsymbol{\omega} \cdot \mathbf{u}_i)}{T_i} - \frac{(\boldsymbol{\omega} \cdot \mathbf{u}_j)}{T_j} \right) \\
& - \frac{2\mu_{ij}}{k_B T_i} (\boldsymbol{\omega} \cdot \mathbf{v}_j) (\boldsymbol{\omega} \cdot \mathbf{u}_i) + \frac{m_i (\mathbf{u}_i)^2}{2k_B T_i} + \frac{m_j (\mathbf{v}_j)^2}{2k_B T_j} - \frac{2\mu_{ij}}{k_B T_j} (\boldsymbol{\omega} \cdot \mathbf{v}_j)^2 - \frac{m_j}{k_B T_j} (\mathbf{u}_j \cdot \mathbf{v}_j) \\
& + \frac{m_j}{2k_B T_j} \left(\frac{2\mu_{ij}}{m_j} ((\mathbf{v}_i - \mathbf{v}_j) \cdot \boldsymbol{\omega}) \right)^2 + \frac{2\mu_{ij}}{k_B T_j} (\boldsymbol{\omega} \cdot \mathbf{v}_j) (\boldsymbol{\omega} \cdot \mathbf{u}_j) + \frac{m_j (\mathbf{u}_j)^2}{2k_B T_j} \\
& = \frac{m_i (\mathbf{v}_i)^2}{2k_B T_i} - \frac{m_i}{k_B T_i} (\mathbf{u}_i \cdot \mathbf{v}_i) + \frac{m_i (\mathbf{u}_i)^2}{2k_B T_i} + \frac{m_j (\mathbf{v}_j)^2}{2k_B T_j} - \frac{m_j}{k_B T_j} (\mathbf{u}_j \cdot \mathbf{v}_j) + \frac{m_j (\mathbf{u}_j)^2}{2k_B T_j}.
\end{aligned}$$

Equating terms with coefficients $\frac{2\mu_{ij}}{k_B} (\boldsymbol{\omega} \cdot \mathbf{v}_i)$, we obtain

$$\frac{\boldsymbol{\omega} \cdot \mathbf{u}_i}{T_i} - \frac{\boldsymbol{\omega} \cdot \mathbf{u}_j}{T_j} = \boldsymbol{\omega} \cdot \left(\frac{\mathbf{u}_i}{T_i} - \frac{\mathbf{u}_j}{T_j} \right) = 0,$$

which is only possible if $\mathbf{u}_i = \mathbf{u}_j$ and $T_i = T_j$ since $\boldsymbol{\omega} \neq 0$.

Finally, let us prove that (iii) implies (i). This can be done by inspection: for instance one can observe that if f_i is a Maxwellian distribution, then $\log(f_i)$, is a linear combination of 1, $\mathbf{v}_i$ and $(\mathbf{v}_i)^2$, so that

$$\log f(\mathbf{v}'_i) + \log f(\mathbf{v}'_j) - \log f(\mathbf{v}_i) - \log f(\mathbf{v}_j) = 0.$$

Therefore, as a consequence of Proposition 2.2.7, there exists constants a, b_1, b_2, b_3 and c such that the following equation holds:

$$f(\mathbf{v}_i) = \exp(a + b^1 v_i^1 + b^2 v_i^2 + b^3 v_i^3 + c(\mathbf{v}_i)^2).$$

Setting

$$a = \log \left(n_i \left(\frac{m_i}{2\pi k_B T_i} \right)^{\frac{3}{2}} \right) - \frac{m_i (\mathbf{u}_i)^2}{2k_B T_i} \quad b^l = \frac{m_i u_i^l}{k_B T_i}, \quad l = 1, 2, 3, \quad c = -\frac{m_i}{2k_B T_i},$$

for $n_i > 0$, $T_i > 0$ and $\mathbf{u}_i \in \mathbb{R}^3$ gives equation (2.2.39). This completes the proof. $\square$

2.2.4 Macroscopic Quantities

Here, the macroscopic quantities associated with the distribution functions will be given.

2.2.4.1 Number Density

The number density of the species is denoted by $n_i(t, \mathbf{x})$. It is obtained by integrating the distribution functions over all possible velocities. More specifically,

$$n_i(t, \mathbf{x}) = \int_{\mathbb{R}^3} f_i d\mathbf{v}_i, \quad i = 1, 2, \dots, S. \quad (2.2.69)$$

2.2.4.2 Mass Density

The mass density of the species is denoted by $\varrho_i(t, \mathbf{x})$. It is obtained by multiplying the distribution functions by m_i and integrating over all possible velocities. More specifically,

$$\varrho_i(t, \mathbf{x}) = \int_{\mathbb{R}^3} m_i f_i d\mathbf{v}_i, \quad i = 1, 2, \dots, S. \quad (2.2.70)$$

Because of the probabilistic meaning of the distribution function, the mass density is the expected mass per unit volume at $(t, \mathbf{x})$ or the product of the molecular mass m_i by the probability density of finding a molecule at $(t, \mathbf{x})$.

2.2.4.3 Bulk Velocity

The bulk velocity of the species is what can be directly perceived of the molecular motion by means of macroscopic observations. It is denoted by $\mathbf{u}_i(t, \mathbf{x})$ and is defined as given below:

$$\mathbf{u}_i(t, \mathbf{x}) = \frac{\int_{\mathbb{R}^3} m_i \mathbf{v}_i f_i d\mathbf{v}_i}{\int_{\mathbb{R}^3} m_i f_i d\mathbf{v}_i} = \frac{1}{\varrho_i(t, \mathbf{x})} \int_{\mathbb{R}^3} m_i \mathbf{v}_i f_i d\mathbf{v}_i, \quad i = 1, 2, \dots, S, \quad (2.2.71)$$

2.2.4.4 Momentum Density

The momentum density of the species is also referred to as the mass flow. It is obtained by multiplying the bulk velocity $\mathbf{u}_i$ by the mass density ϱ_i . More precisely,

$$\varrho_i(t, \mathbf{x}) \mathbf{u}_i(t, \mathbf{x}) = \int_{\mathbb{R}^3} m_i \mathbf{v}_i f_i d\mathbf{v}_i, \quad i = 1, 2, \dots, S. \quad (2.2.72)$$

Remark 2.2.14. The velocity of each molecule $\mathbf{v}_i(t, \mathbf{x})$ can be split into the sum of the bulk velocity $\mathbf{u}_i(t, \mathbf{x})$ and a velocity which we shall denote with $\boldsymbol{\xi}_i(t, \mathbf{x})$, that is,

$$\mathbf{v}_i = \mathbf{u}_i + \boldsymbol{\xi}_i \quad \Rightarrow \quad d\boldsymbol{\xi}_i = d\mathbf{v}_i. \quad (2.2.73)$$

The velocity $\boldsymbol{\xi}_i$ describes the random deviation of the molecular velocity from the ordered motion with the bulk velocity. It is usually called the peculiar velocity or random velocity and is equal to the velocity of each molecule $\mathbf{v}_i$ when the bulk velocity $\mathbf{u}_i = 0$. Furthermore, observe that

$$\int_{\mathbb{R}^3} m_i \boldsymbol{\xi}_i f_i d\boldsymbol{\xi}_i = \mathbf{0}, \quad (2.2.74)$$

where use has been made of equations (2.2.70) and (2.2.72).

2.2.4.5 Momentum Flow

The momentum flow of the species is given by:

$$\int_{\mathbb{R}^3} m_i \mathbf{v}_i (\mathbf{v}_i f_i) d\mathbf{v}_i = \int_{\mathbb{R}^3} m_i (\mathbf{v}_i \otimes \mathbf{v}_i) f_i d\mathbf{v}_i, \quad i = 1, 2, \dots, S.$$

Using equation (2.2.73), we can rewrite the previous equation as given below:

$$\int_{\mathbb{R}^3} m_i (\mathbf{v}_i \otimes \mathbf{v}_i) f_i d\mathbf{v}_i = (\mathbf{u}_i \otimes \mathbf{u}_i) \int_{\mathbb{R}^3} m_i f_i d\mathbf{v}_i + 2\mathbf{u}_i \otimes \int_{\mathbb{R}^3} m_i \boldsymbol{\xi}_i f_i d\mathbf{v}_i + \int_{\mathbb{R}^3} m_i (\boldsymbol{\xi}_i \otimes \boldsymbol{\xi}_i) f_i d\boldsymbol{\xi}_i.$$

Using equation (2.2.70) for the first term and equation (2.2.74) for the second term on the right-hand side of the previous equation, we obtain:

$$\int_{\mathbb{R}^3} m_i (\mathbf{v}_i \otimes \mathbf{v}_i) f_i d\mathbf{v}_i = \varrho_i (\mathbf{u}_i \otimes \mathbf{u}_i) + \underbrace{\int_{\mathbb{R}^3} m_i (\boldsymbol{\xi}_i \otimes \boldsymbol{\xi}_i) f_i d\boldsymbol{\xi}_i}_{\mathbf{P}_i}. \quad (2.2.75)$$

Thus the momentum flow decomposes into two components. The first term on the right-hand side of equation (2.2.75) is the macroscopic momentum flow and the second term is the pressure tensor. Furthermore, when the pressure tensor is expressed with a minus sign, it is referred to as the stress tensor.

2.2.4.6 Energy Density

The energy density of the species is obtained by multiplying the distribution functions by the kinetic energy $\frac{1}{2}m_i(\mathbf{v}_i)$ and then integrate the resulting expression over all possible velocities to obtain:

$$\int_{\mathbb{R}^3} \frac{1}{2} m_i (\mathbf{v}_i)^2 f_i d\mathbf{v}_i = \frac{1}{2} \int_{\mathbb{R}^3} m_i (\mathbf{v}_i)^2 f_i d\mathbf{v}_i, \quad i = 1, 2, \dots, S.$$

Using equation (2.2.73), we can rewrite the energy density as given below:

$$\frac{1}{2} \int_{\mathbb{R}^3} m_i (\mathbf{v}_i)^2 f_i d\boldsymbol{\xi}_i = \frac{1}{2} (\mathbf{u}_i)^2 \int_{\mathbb{R}^3} m_i f_i d\boldsymbol{\xi}_i + \mathbf{u}_i \cdot \int_{\mathbb{R}^3} m_i \boldsymbol{\xi}_i f_i d\mathbf{v}_i + \frac{1}{2} \int_{\mathbb{R}^3} m_i (\boldsymbol{\xi}_i)^2 f_i d\boldsymbol{\xi}_i.$$

Using equation (2.2.70) for the first term and equation (2.2.74) for the second term on the right-hand side of the previous equation, we obtain:

$$\frac{1}{2} \int_{\mathbb{R}^3} m_i (\mathbf{v}_i)^2 f_i d\mathbf{v}_i = \frac{1}{2} (\mathbf{u}_i)^2 \varrho_i + \frac{1}{2} \int_{\mathbb{R}^3} m_i (\boldsymbol{\xi}_i)^2 f_i d\boldsymbol{\xi}_i. \quad (2.2.76)$$

The first term on the right-hand side of equation (2.2.76) is the kinetic energy density. The second term is ascribed to the internal energy density and is denoted by $\varrho_i e_i$. Therefore, equation (2.2.76) can be rewritten as:

$$\frac{1}{2} \int_{\mathbb{R}^3} m_i (\mathbf{v}_i)^2 f_i d\mathbf{v}_i = \frac{1}{2} \varrho_i (\mathbf{u}_i)^2 + \varrho_i e_i, \quad \text{where} \quad \varrho_i e_i = \frac{1}{2} \int_{\mathbb{R}^3} m_i (\boldsymbol{\xi}_i)^2 f_i d\boldsymbol{\xi}_i. \quad (2.2.77)$$

Remark 2.2.15. Comparing the internal energy density (i.e., $\varrho_i e_i$ defined in equation (2.2.77) above) and the pressure tensor $\mathbf{P}_i$ given in equation (2.2.75), we see that the internal energy

density is related to the trace or spur of the pressure tensor. More precisely, we obtain:

$$\varrho_i e_i = \frac{1}{2} \text{tr} \mathbf{P}_i$$

Furthermore, the trace of the pressure tensor divided by 3 is usually associated with the pressure of a gas. Therefore, if we denoted the pressure of a gas by p_i , we obtain:

$$p_i(t, \mathbf{x}) = \frac{1}{3} \text{tr} \mathbf{P}_i = \frac{2}{3} \varrho_i e_i. \quad (2.2.78)$$

2.2.4.7 Temperature

The temperature of the species is denoted by T_i . It can be obtained using the fact that the equation of state of an ideal gas is given by $p_i = \varrho_i k_B T_i$, where k_B is the Boltzmann constant. From the equation of state, one has that the expression for temperature can be obtained in terms of the distribution function as follows:

$$T_i(t, \mathbf{x}) = \frac{p_i}{\varrho_i k_B} = \frac{2}{3} \varrho_i e_i \frac{1}{\varrho_i k_B} = \frac{1}{3 \varrho_i k_B} \int_{\mathbb{R}^3} m_i(\boldsymbol{\xi}_i)^2 f_i d\boldsymbol{\xi}_i, \quad i = 1, 2, \dots, S. \quad (2.2.79)$$

2.2.4.8 Energy Flow

The energy flow of the species is obtained by multiplying the distribution functions by $\mathbf{v}_i \left(\frac{1}{2} m_i(\mathbf{v}_i)^2 \right)$ and integrating the resulting expression over all possible velocities, i.e.,

$$\int_{\mathbb{R}^3} \mathbf{v}_i \left(\frac{1}{2} m_i(\mathbf{v}_i)^2 f_i \right) d\mathbf{v}_i = \frac{1}{2} \int_{\mathbb{R}^3} m_i(\mathbf{v}_i)^2 \mathbf{v}_i f_i d\mathbf{v}_i, \quad i = 1, 2, \dots, S.$$

Using equation (2.2.73), we obtain:

$$\begin{aligned} & \frac{1}{2} \int_{\mathbb{R}^3} m_i(\mathbf{v}_i)^2 \mathbf{v}_i f_i d\mathbf{v}_i \\ &= \frac{1}{2} \mathbf{u}_i(\mathbf{u}_i)^2 \underbrace{\int_{\mathbb{R}^3} m_i f_i d\boldsymbol{\xi}_i}_{\varrho_i} + \mathbf{u}_i \left(\mathbf{u}_i \cdot \underbrace{\int_{\mathbb{R}^3} m_i \boldsymbol{\xi}_i f_i d\boldsymbol{\xi}_i}_{\mathbf{0}} \right) + \mathbf{u}_i \underbrace{\frac{1}{2} \int_{\mathbb{R}^3} m_i(\boldsymbol{\xi}_i)^2 f_i d\boldsymbol{\xi}_i}_{\varrho_i e_i} \\ &+ \frac{1}{2} (\mathbf{u}_i)^2 \underbrace{\int_{\mathbb{R}^3} m_i \boldsymbol{\xi}_i f_i d\boldsymbol{\xi}_i}_{\mathbf{0}} + \mathbf{u}_i \cdot \underbrace{\int_{\mathbb{R}^3} m_i(\boldsymbol{\xi}_i \otimes \boldsymbol{\xi}_i) f_i d\boldsymbol{\xi}_i}_{\mathbf{P}_i} + \frac{1}{2} \int_{\mathbb{R}^3} m_i \boldsymbol{\xi}_i (\boldsymbol{\xi}_i)^2 f_i d\boldsymbol{\xi}_i. \end{aligned}$$

where use have been made of equations (2.2.70), (2.2.74), (2.2.77) and (2.2.75). Therefore,

$$\frac{1}{2} \int_{\mathbb{R}^3} m_i(\mathbf{v}_i)^2 \mathbf{v}_i f_i d\mathbf{v}_i = \frac{1}{2} \varrho_i \mathbf{u}_i(\mathbf{u}_i)^2 + \mathbf{u}_i \varrho_i e_i + \mathbf{u}_i \cdot \mathbf{P}_i + \frac{1}{2} \int_{\mathbb{R}^3} m_i \boldsymbol{\xi}_i (\boldsymbol{\xi}_i)^2 f_i d\boldsymbol{\xi}_i. \quad (2.2.80)$$

The first two terms on the right-hand side of the previous equation is the energy flow due to macroscopic convection. The third term can be interpreted macroscopically as the work done by the pressure tensor in unit time. The last term is the heat flux vector and will be denoted by $\mathbf{q}_i$. Thus equation (2.2.80) can be rewritten as:

$$\frac{1}{2} \int_{\mathbb{R}^3} m_i(\mathbf{v}_i)^2 \mathbf{v}_i f_i d\mathbf{v}_i = \left(\frac{1}{2}(\mathbf{u}_i)^2 + e_i \right) \rho_i \mathbf{u}_i + \mathbf{u}_i \cdot \mathbf{P}_i + \mathbf{q}_i. \quad (2.2.81)$$

2.2.5 Macroscopic Equations for the Multi-Species System

Macroscopic equations like the equations of continuity, motion and energy balance for the species can be derived from the MBEs (2.2.1) without determining the actual form of the distribution functions. To see this, we multiply the MBEs given in equation (2.2.1) by an arbitrary function of the microscopic state of the particles, say $\varphi(\mathbf{v}_i)$ and integrate the resulting equations over all possible values of the velocity component, to obtain:

$$\begin{aligned} \int_{\mathbb{R}^3} \frac{\partial f_i}{\partial t} \varphi(\mathbf{v}_i) d\mathbf{v}_i + \int_{\mathbb{R}^3} \mathbf{v}_i \cdot \frac{\partial f_i}{\partial \mathbf{x}} \varphi(\mathbf{v}_i) d\mathbf{v}_i \\ = \int_{\mathbb{R}^3} Q(f_i, f_{i*}) \varphi(\mathbf{v}_i) d\mathbf{v}_i + \sum_{\substack{j=1 \\ j \neq i}}^S \int_{\mathbb{R}^3} Q(f_i, f_j) \varphi(\mathbf{v}_i) d\mathbf{v}_i, \quad i = 1, 2, \dots, S. \end{aligned} \quad (2.2.82)$$

Equation (2.2.82) above is called the transfer equation or equation of transfer⁴. Using Leibniz integral rule, more precisely, the Leibniz rule for differentiation under the integral sign, we can rewrite the first and second terms of the left-hand side of equation (2.2.82) as follows:

$$\int_{\mathbb{R}^3} \frac{\partial f_i}{\partial t} \varphi(\mathbf{v}_i) d\mathbf{v}_i = \frac{\partial}{\partial t} \int_{\mathbb{R}^3} f_i \varphi(\mathbf{v}_i) d\mathbf{v}_i \quad (2.2.83)$$

$$\int_{\mathbb{R}^3} \mathbf{v}_i \cdot \frac{\partial f_i}{\partial \mathbf{x}} \varphi(\mathbf{v}_i) d\mathbf{v}_i = \frac{\partial}{\partial \mathbf{x}} \int_{\mathbb{R}^3} \mathbf{v}_i f_i \varphi(\mathbf{v}_i) d\mathbf{v}_i. \quad (2.2.84)$$

Therefore, equation (2.2.82) can be rewritten as given below:

$$\begin{aligned} \frac{\partial}{\partial t} \int_{\mathbb{R}^3} f_i \varphi(\mathbf{v}_i) d\mathbf{v}_i + \frac{\partial}{\partial \mathbf{x}} \int_{\mathbb{R}^3} \mathbf{v}_i f_i \varphi(\mathbf{v}_i) d\mathbf{v}_i \\ = \int_{\mathbb{R}^3} Q(f_i, f_{i*}) \varphi(\mathbf{v}_i) d\mathbf{v}_i + \sum_{\substack{j=1 \\ j \neq i}}^S \int_{\mathbb{R}^3} Q(f_i, f_j) \varphi(\mathbf{v}_i) d\mathbf{v}_i \end{aligned} \quad (2.2.85)$$

Setting $\varphi(\mathbf{v}_i) = m_i$ in equation (2.2.85), we obtain for $i = 1, 2, \dots, S$:

$$\frac{\partial}{\partial t} \int_{\mathbb{R}^3} m_i f_i d\mathbf{v}_i + \frac{\partial}{\partial \mathbf{x}} \int_{\mathbb{R}^3} m_i \mathbf{v}_i f_i d\mathbf{v}_i = \int_{\mathbb{R}^3} m_i Q(f_i, f_{i*}) d\mathbf{v}_i + \sum_{\substack{j=1 \\ j \neq i}}^S \int_{\mathbb{R}^3} m_i Q(f_i, f_j) d\mathbf{v}_i$$

⁴Indeed, it was the equation of transfer rather than the MBEs, that Maxwell inferred, for an arbitrary function of the velocity variable alone. The requirement that the distribution functions f_i shall satisfy the equation of transfer for this arbitrary function of the velocity variable may be weaker mathematically than the condition that it satisfies the MBEs itself. Furthermore, a more general relation known as the Enskog's equation of transfer is obtained when the arbitrary function is not a function of the velocity variable alone.

Using equations (2.2.70) and (2.2.72), respectively, for the first and second integrals on the left-hand side of the previous equation, we obtain:

$$\frac{\partial \varrho_i}{\partial t} + \frac{\partial}{\partial \mathbf{x}}(\varrho_i \mathbf{u}_i) = \int_{\mathbb{R}^3} m_i Q(f_i, f_{i*}) d\mathbf{v}_i + \sum_{\substack{j=1 \\ j \neq i}}^S \int_{\mathbb{R}^3} m_i Q(f_i, f_j) d\mathbf{v}_i, \quad i = 1, 2, \dots, S. \quad (2.2.86)$$

Setting $\varphi(\mathbf{v}_i) = m_i \mathbf{v}_i$ in equation (2.2.85), we obtain for $i = 1, 2, \dots, S$:

$$\frac{\partial}{\partial t} \int_{\mathbb{R}^3} m_i \mathbf{v}_i f_i d\mathbf{v}_i + \frac{\partial}{\partial \mathbf{x}} \int_{\mathbb{R}^3} m_i (\mathbf{v}_i \otimes \mathbf{v}_i) f_i d\mathbf{v}_i = \int_{\mathbb{R}^3} m_i \mathbf{v}_i Q(f_i, f_{i*}) d\mathbf{v}_i + \sum_{\substack{j=1 \\ j \neq i}}^S \int_{\mathbb{R}^3} m_i \mathbf{v}_i Q(f_i, f_j) d\mathbf{v}_i.$$

Using equations (2.2.72) and (2.2.75), respectively, for the first and second integrals on the left-hand side of the previous equation, we obtain for $i = 1, 2, \dots, S$:

$$\frac{\partial}{\partial t}(\varrho_i \mathbf{u}_i) + \frac{\partial}{\partial \mathbf{x}}(\varrho_i (\mathbf{u}_i \otimes \mathbf{u}_i) + \mathbf{P}_i) = \int_{\mathbb{R}^3} m_i \mathbf{v}_i Q(f_i, f_{i*}) d\mathbf{v}_i + \sum_{\substack{j=1 \\ j \neq i}}^S \int_{\mathbb{R}^3} m_i \mathbf{v}_i Q(f_i, f_j) d\mathbf{v}_i. \quad (2.2.87)$$

Setting $\varphi(\mathbf{v}_i) = \frac{1}{2} m_i (\mathbf{v}_i)^2$ in equation (2.2.85), we obtain for $i = 1, 2, \dots, S$:

$$\begin{aligned} \frac{\partial}{\partial t} \frac{1}{2} \int_{\mathbb{R}^3} m_i (\mathbf{v}_i)^2 f_i d\mathbf{v}_i + \frac{\partial}{\partial \mathbf{x}} \frac{1}{2} \int_{\mathbb{R}^3} m_i \mathbf{v}_i (\mathbf{v}_i)^2 f_i d\mathbf{v}_i \\ = \frac{1}{2} \int_{\mathbb{R}^3} m_i (\mathbf{v}_i)^2 Q(f_i, f_{i*}) d\mathbf{v}_i + \frac{1}{2} \sum_{\substack{j=1 \\ j \neq i}}^S \int_{\mathbb{R}^3} m_i (\mathbf{v}_i)^2 Q(f_i, f_j) d\mathbf{v}_i. \end{aligned}$$

Using equations (2.2.77) and (2.2.81), respectively, for the first and second integrals on the left-hand side of the previous equation, we obtain:

$$\begin{aligned} \frac{\partial}{\partial t} \left(\frac{1}{2} \varrho_i (\mathbf{u}_i)^2 + \varrho_i e_i \right) + \frac{\partial}{\partial \mathbf{x}} \left[\left(\frac{1}{2} (\mathbf{u}_i)^2 + e_i \right) \varrho_i \mathbf{u}_i + \mathbf{u}_i \cdot \mathbf{P}_i + \mathbf{q}_i \right] \\ = \frac{1}{2} \int_{\mathbb{R}^3} m_i (\mathbf{v}_i)^2 Q(f_i, f_{i*}) d\mathbf{v}_i + \frac{1}{2} \sum_{\substack{j=1 \\ j \neq i}}^S \int_{\mathbb{R}^3} m_i (\mathbf{v}_i)^2 Q(f_i, f_j) d\mathbf{v}_i, \quad i = 1, 2, \dots, S. \quad (2.2.88) \end{aligned}$$

The Equations given in (2.2.86), (2.2.87) and (2.2.88) are the continuity, momentum balance and energy balance equations, respectively.

Proposition 2.2.16. *Let f_i with $i = 1, 2, \dots, S$ be solutions of the MBEs (2.2.1) that are continuous almost everywhere in $(t, \mathbf{x}) \in \mathbb{R}_+ \times \mathbb{R}^3$ and with compact support on $\mathbb{R}_{\mathbf{v}_i}^3$. Then the local conservation of mass, momentum and energy hold and they are, respectively, given by:*

$$\begin{aligned}
\frac{\partial \varrho_i}{\partial t} + \frac{\partial}{\partial \mathbf{x}}(\varrho_i \mathbf{u}_i) &= 0, \quad i = 1, 2, \dots, S, \\
\sum_{i=1}^S \frac{\partial}{\partial t}(\varrho_i \mathbf{u}_i) + \sum_{i=1}^S \frac{\partial}{\partial \mathbf{x}}(\varrho_i (\mathbf{u}_i \otimes \mathbf{u}_i) + \mathbf{P}_i) &= 0, \\
\sum_{i=1}^S \frac{\partial}{\partial t} \left(\frac{1}{2} \varrho_i (\mathbf{u}_i)^2 + \varrho_i e_i \right) + \sum_{i=1}^S \frac{\partial}{\partial \mathbf{x}} \left[\left(\frac{1}{2} (\mathbf{u}_i)^2 + e_i \right) \varrho_i \mathbf{u}_i + \mathbf{u}_i \cdot \mathbf{P}_i + \mathbf{q}_i \right] &= 0,
\end{aligned} \tag{2.2.89}$$

Proof. The conservation of mass (i.e., the first equation of (2.2.89)) is obtained by using the first equation of (2.2.35) and equation (2.2.58), respectively for the first and second integrals on the right-hand side of equation (2.2.86).

The conservation of linear momentum for the mixture (i.e., the second equation of (2.2.89)) is obtained by using the second equation of (2.2.35) and equation (2.2.59), respectively, for the first and second integrals on the right-hand side of equation (2.2.87), and then sum the resulting equation over i .

The conservation of energy for the mixture (i.e., the third equation of (2.2.89)) is obtained by using the third equation of (2.2.35) and equation (2.2.60), respectively, for the first and second integrals on the right-hand side of equation (2.2.88), and then sum the resulting equation over i . $\square$

2.3 Reactive System of Monatomic Gases

This section studies a chemically reactive multi-species system of monatomic gases. A kinetic model that describe how the species distribution functions change due to free streaming and collisions is presented. This kinetic model is known in the literature as the “Simple Reacting Sphere” (SRS) kinetic model and it is one of the two kinetic models whose hydrodynamic limits will be studied.

2.3.1 The Simple Reacting Sphere Kinetic Model

The SRS kinetic model is based on the kinetic theory of simple reacting spheres proposed by Marron in [82], but was developed by Xystris, Dahler and Qin in [42, 96, 112]. Some aspects of the mathematical analysis of the SRS kinetic model have been investigated, see, for example, [33, 61, 92, 93]. Here, we introduce the model and briefly describe some of its properties that will be needed for the analysis developed in this thesis. The presentation of the kinetic model in this chapter follows [5]. Other details about the SRS kinetic model can be found in the references quoted above.

To describe the SRS kinetic model, we consider a mixture of four monatomic like gases: A_1, A_2, A_3 and A_4 . These gases participate in a bi-molecular reversible chemical reaction of type:



Equation (2.3.1) above means that species A_1, A_2 react to produce species A_3, A_4 and conversely, species A_3, A_4 also react to produce species A_1, A_2 . More specifically, species A_1, A_2 are reactants, while species A_3, A_4 are products of the forward chemical reaction and vice versa for the backward or reverse chemical reaction. The species A_1, A_2 and A_3, A_4 are called the reactive species or the reactive

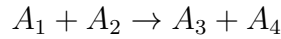
pairs. Furthermore, let m_i be the mass, d_i the diameter, E_i the formation or chemical binding energy and ζ_i the activation energy of the species A_i with $i = 1, 2, 3, 4$. Conservation of mass holds for the chemical reaction (2.3.1) and is given by:

$$m_1 + m_2 = m_3 + m_4 = M_*. \quad (2.3.2)$$

The reaction heat denoted by Q_R , is given by the difference between the formation energies of the products of the forward reaction and those of the reactants. More specifically, the reaction heat can be written mathematically as:

$$Q_R = E_3 + E_4 - E_1 - E_2. \quad (2.3.3)$$

This means that the forward reaction



is exothermic if $Q_R < 0$, otherwise, it is endothermic. In addition, ζ_i is such that

$$\zeta_1 = \zeta_2, \quad \zeta_3 = \zeta_4 \quad \text{and} \quad \zeta_3 = \zeta_1 - Q_R. \quad (2.3.4)$$

2.3.1.1 Collision Dynamics

Particles in the mixture undergo binary elastic and reactive collisions, both of which are of hard sphere type and obeying the chemical law described by equation (2.3.1). Elastic collisions take place between particles of the same species, as well as between particles of different species. These elastic collisions result in changes in the velocities of the colliding pair. The cross-sections of an elastic collision between particles of species A_i and A_s is defined as:

$$\sigma_{is}^2 = \frac{1}{4}(d_i + d_s)^2, \quad i, s = 1, 2, 3, 4. \quad (2.3.5)$$

Now let $\mathbf{v}_i$ and $\mathbf{v}_s$ be the pre-collision velocities, while $\mathbf{v}'_i$ and $\mathbf{v}'_s$ are the post-collision velocities. The conservation laws of linear momentum and kinetic energy for elastic collisions between particles of different species are, respectively, given by:

$$m_i \mathbf{v}_i + m_s \mathbf{v}_s = m_i \mathbf{v}'_i + m_s \mathbf{v}'_s, \quad (2.3.6)$$

$$\frac{1}{2} m_i (\mathbf{v}_i)^2 + \frac{1}{2} m_s (\mathbf{v}_s)^2 = \frac{1}{2} m_i (\mathbf{v}'_i)^2 + \frac{1}{2} m_s (\mathbf{v}'_s)^2, \quad (2.3.7)$$

while that of same species collisions are given in equations (2.2.2) and (2.2.3), respectively. Using equations (2.3.6) and (2.3.7) above and following the steps used to obtain equations (2.2.16) and (2.2.17), we obtain the post-collision velocities in terms of the pre-collision velocities as given below:

$$\mathbf{v}'_i = \mathbf{v}_i - 2 \frac{\mu_{is}}{m_i} \boldsymbol{\epsilon} \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_s \rangle, \quad (2.3.8)$$

$$\mathbf{v}'_s = \mathbf{v}_s + 2 \frac{\mu_{is}}{m_s} \boldsymbol{\epsilon} \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_s \rangle. \quad (2.3.9)$$

In equations (2.3.8) and (2.3.9), μ_{is} is the reduced mass defined in equation (2.2.15), but with j replaced by s . The term ϵ is a unit vector directed along the line joining the centre of the two spheres at the moment of impact, i.e., $\epsilon \in \mathbb{S}_+ = \{\bar{\epsilon} \in \mathbb{R}^3 : \|\bar{\epsilon}\| = 1, \langle \bar{\epsilon}, \mathbf{v}_i - \mathbf{v}_s \rangle > 0\}$. Moreover, $\langle \cdot, \cdot \rangle$ represents the inner product in $\mathbb{R}^3$ and $\|\cdot\|$ is the norm induced by this inner product.

Remark 2.3.1. Note that if we use spherical coordinates with $\theta \in [0, \pi/2]$ as the polar angle between $\mathbf{v}_i - \mathbf{v}_s$ and ϵ , while $\phi \in [0, 2\pi[$ is the azimuth angle in the plane orthogonal to $\mathbf{v}_i - \mathbf{v}_s$, then ϵ is such that: $\epsilon = (\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta)$. Also, $\langle \epsilon, \mathbf{v}_i - \mathbf{v}_s \rangle = V_* \cos \theta$, where $V_* = \|\mathbf{v}_i - \mathbf{v}_s\| = |\mathbf{v}_i - \mathbf{v}_s|$ is the norm of the relative velocity before collision.

Concerning reactive collisions, a collision between the particles of species A_i and A_j with pre-collision velocities $\mathbf{v}_i$ and $\mathbf{v}_j$, respectively, will result in a chemical reaction if the kinetic energy associated with the relative motion of the colliding pair, along the line of their centres is greater than or equal to the activation energy, that is,

$$\frac{1}{2}\mu_{ij} \langle \epsilon, \mathbf{v}_i - \mathbf{v}_j \rangle^2 \geq \zeta_i. \quad (2.3.10)$$

These reactive collisions result in: changes in the velocities of the colliding pair, rearrangement of masses, redistribution of formation energies and transformation of the reactants into products. If A_k and A_l represent the products of the forward chemical reaction with post-collision velocities $\mathbf{v}_k^\circ$ and $\mathbf{v}_l^\circ$, respectively, then the conservation laws of linear momentum and total energy (kinetic plus binding) for reactive collisions are, respectively, given by

$$m_i \mathbf{v}_i + m_j \mathbf{v}_j = m_k \mathbf{v}_k^\circ + m_l \mathbf{v}_l^\circ, \quad (2.3.11)$$

$$E_i + \frac{1}{2}m_i(\mathbf{v}_i)^2 + E_j + \frac{1}{2}m_j(\mathbf{v}_j)^2 = E_k + \frac{1}{2}m_k(\mathbf{v}_k^\circ)^2 + E_l + \frac{1}{2}m_l(\mathbf{v}_l^\circ)^2, \quad (2.3.12)$$

where the indices are such that $(i, j, k, l) \in \{(1, 2, 3, 4), (2, 1, 4, 3), (3, 4, 1, 2), (4, 3, 2, 1)\}$. From now on, if nothing is said about the indices or subscripts (i, j, k, l) , we assume that they are as introduced above.

Remark 2.3.2. From the condition for a reactive collision to occur (2.3.10), we have that

$$\langle \epsilon, \mathbf{v}_i - \mathbf{v}_j \rangle \geq \sqrt{\frac{2\zeta_i}{\mu_{ij}}}.$$

Using the definitions of the unit vector ϵ and relative velocity norm $V^* = \|\mathbf{v}_i - \mathbf{v}_j\|$ before the collision, we obtain

$$V^* \geq \sqrt{\frac{2\zeta_i}{\mu_{ij}}} = \Xi_{ij}, \quad (2.3.13)$$

where Ξ_{ij} is the threshold relative velocity required to assure that the collision will be of reactive type. $\square$

The reactive cross-sections for the forward and reverse chemical reactions is defined in terms of their

threshold relative velocities by:

$$\sigma_{12}^2 = \begin{cases} \beta_{12}\sigma_{12}^2, & \langle \epsilon, \mathbf{v}_1 - \mathbf{v}_2 \rangle \geq \Xi_{12}, \\ 0, & \langle \epsilon, \mathbf{v}_1 - \mathbf{v}_2 \rangle < \Xi_{12}, \end{cases} \quad \sigma_{34}^2 = \begin{cases} \beta_{34}\sigma_{34}^2, & \langle \epsilon, \mathbf{v}_3 - \mathbf{v}_4 \rangle \geq \Xi_{34}, \\ 0, & \langle \epsilon, \mathbf{v}_3 - \mathbf{v}_4 \rangle < \Xi_{34}, \end{cases} \quad (2.3.14)$$

where the coefficients β_{12} and β_{34} play the role of steric factors. These steric factors are such that $0 \leq \beta_{12}, \beta_{34} \leq 1$.

The post-collision velocities for the forward chemical reaction $A_1 + A_2 \rightarrow A_3 + A_4$ are given by:

$$\begin{aligned} \mathbf{v}_3^\circ &= \frac{1}{M_*} \left[m_1 \mathbf{v}_1 + m_2 \mathbf{v}_2 + m_4 \sqrt{\frac{\mu_{12}}{\mu_{34}}} \left\{ (\mathbf{v}_1 - \mathbf{v}_2) - \epsilon \langle \epsilon, (\mathbf{v}_1 - \mathbf{v}_2) \rangle + \epsilon \omega^- \right\} \right], \\ \mathbf{v}_4^\circ &= \frac{1}{M_*} \left[m_1 \mathbf{v}_1 + m_2 \mathbf{v}_2 - m_3 \sqrt{\frac{\mu_{12}}{\mu_{34}}} \left\{ (\mathbf{v}_1 - \mathbf{v}_2) - \epsilon \langle \epsilon, (\mathbf{v}_1 - \mathbf{v}_2) \rangle + \epsilon \omega^- \right\} \right], \end{aligned} \quad (2.3.15)$$

where $\omega^- = \sqrt{(\langle \epsilon, (\mathbf{v}_1 - \mathbf{v}_2) \rangle)^2 - 2Q_R/\mu_{12}}$.

Analogously, the post-collision velocities for the reverse chemical reaction $A_3 + A_4 \rightarrow A_1 + A_2$ are given by:

$$\begin{aligned} \mathbf{v}_1^\circ &= \frac{1}{M_*} \left[m_3 \mathbf{v}_3 + m_4 \mathbf{v}_4 + m_2 \sqrt{\frac{\mu_{34}}{\mu_{12}}} \left\{ (\mathbf{v}_3 - \mathbf{v}_4) - \epsilon \langle \epsilon, (\mathbf{v}_3 - \mathbf{v}_4) \rangle + \epsilon \omega^+ \right\} \right], \\ \mathbf{v}_2^\circ &= \frac{1}{M_*} \left[m_3 \mathbf{v}_3 + m_4 \mathbf{v}_4 - m_1 \sqrt{\frac{\mu_{34}}{\mu_{12}}} \left\{ (\mathbf{v}_3 - \mathbf{v}_4) - \epsilon \langle \epsilon, (\mathbf{v}_3 - \mathbf{v}_4) \rangle + \epsilon \omega^+ \right\} \right], \end{aligned} \quad (2.3.16)$$

where $\omega^+ = \sqrt{(\langle \epsilon, (\mathbf{v}_3 - \mathbf{v}_4) \rangle)^2 + 2Q_R/\mu_{34}}$.

To conclude this subsection, let me recall some properties about the dynamics of the reactive collisions. These properties are given in the form of lemmas.

Lemma 2.3.3. *For a reactive collision, the following properties hold:*

$$\frac{1}{2}\mu_{ij}(\mathbf{v}_i - \mathbf{v}_j)^2 = \frac{1}{2}\mu_{kl}(\mathbf{v}_k^\circ - \mathbf{v}_l^\circ)^2 + Q_R, \quad (2.3.17)$$

$$\mu_{ij}(\langle \epsilon, \mathbf{v}_i - \mathbf{v}_j \rangle)^2 = \mu_{kl}(\langle \epsilon, \mathbf{v}_k^\circ - \mathbf{v}_l^\circ \rangle)^2 + 2Q_R, \quad (2.3.18)$$

$$\frac{1}{2}\mu_{ij}(\langle \epsilon, \mathbf{v}_i - \mathbf{v}_j \rangle)^2 - \zeta_i = \frac{1}{2}\mu_{kl}(\langle \epsilon, \mathbf{v}_k^\circ - \mathbf{v}_l^\circ \rangle)^2 - \zeta_k, \quad (2.3.19)$$

$$\langle \epsilon, \mathbf{v}_i - \mathbf{v}_j \rangle = \left(\frac{\mu_{kl}}{\mu_{ij}} \right)^{\frac{1}{2}} \omega^+. \quad (2.3.20)$$

Proof. To prove equation (2.3.17), we use the conservation of total energy for reactive collisions given in equation (2.3.12), but written in a slightly different form as follow:

$$\frac{1}{2}m_i(\mathbf{v}_i)^2 + \frac{1}{2}m_j(\mathbf{v}_j)^2 = \frac{1}{2}m_k(\mathbf{v}_k^\circ)^2 + \frac{1}{2}m_l(\mathbf{v}_l^\circ)^2 + E_k + E_l - E_i - E_j.$$

Using equation (2.3.3), we can rewrite the previous equation as:

$$\frac{1}{2}m_i(\mathbf{v}_i)^2 + \frac{1}{2}m_j(\mathbf{v}_j)^2 = \frac{1}{2}m_k(\mathbf{v}_k^\circ)^2 + \frac{1}{2}m_l(\mathbf{v}_l^\circ)^2 + Q_R.$$

Multiplying both sides of the previous equation by $m_i + m_j = m_k + m_l = M$, we obtain:

$$\left(\frac{1}{2}m_i(\mathbf{v}_i)^2 + \frac{1}{2}m_j(\mathbf{v}_j)^2\right)(m_i + m_j) = \left(\frac{1}{2}m_k(\mathbf{v}_k^\circ)^2 + \frac{1}{2}m_l(\mathbf{v}_l^\circ)^2\right)(m_k + m_l) + MQ_R.$$

Expanding, we obtain:

$$\begin{aligned} \frac{1}{2}m_i^2(\mathbf{v}_i)^2 + \frac{1}{2}m_i m_j(\mathbf{v}_i)^2 + \frac{1}{2}m_i m_j(\mathbf{v}_j)^2 + \frac{1}{2}m_j^2(\mathbf{v}_j)^2 \\ = \frac{1}{2}m_k^2(\mathbf{v}_k^\circ)^2 + \frac{1}{2}m_k m_l(\mathbf{v}_k^\circ)^2 + \frac{1}{2}m_k m_l(\mathbf{v}_l^\circ)^2 + \frac{1}{2}m_l^2(\mathbf{v}_l^\circ)^2 + MQ_R. \end{aligned}$$

The previous equation can equivalently be written as

$$\begin{aligned} \frac{1}{2}(m_i \mathbf{v}_i + m_j \mathbf{v}_j)^2 - m_i m_j(\mathbf{v}_i \cdot \mathbf{v}_j) + \frac{1}{2}m_i m_j(\mathbf{v}_i)^2 + \frac{1}{2}m_i m_j(\mathbf{v}_j)^2 \\ = \frac{1}{2}(m_k \mathbf{v}_k^\circ + m_l \mathbf{v}_l^\circ)^2 - m_k m_l(\mathbf{v}_k^\circ \cdot \mathbf{v}_l^\circ) + \frac{1}{2}m_k m_l(\mathbf{v}_k^\circ)^2 + \frac{1}{2}m_k m_l(\mathbf{v}_l^\circ)^2 + MQ_R. \end{aligned}$$

Applying the conservation of momentum given in equation (2.3.11) and then factorising, we obtain that the previous equation reduces to:

$$m_i m_j \left(\frac{1}{2}(\mathbf{v}_i)^2 - (\mathbf{v}_i \cdot \mathbf{v}_j) + \frac{1}{2}(\mathbf{v}_j)^2 \right) = m_k m_l \left(\frac{1}{2}(\mathbf{v}_k^\circ)^2 - (\mathbf{v}_k^\circ \cdot \mathbf{v}_l^\circ) + \frac{1}{2}(\mathbf{v}_l^\circ)^2 \right) + MQ_R.$$

The previous equation can be rewritten as:

$$\frac{1}{2}m_i m_j (\mathbf{v}_i - \mathbf{v}_j)^2 = \frac{1}{2}m_k m_l (\mathbf{v}_k^\circ - \mathbf{v}_l^\circ)^2 + MQ_R.$$

Dividing both sides of the previous equation by M and using the definition of reduced mass given in equation (2.2.15), we obtain equation (2.3.17).

To prove equation (2.3.18), we use the fact that the pre-collision and post-collision relative velocities can be split into the tangential and normal components as given below

$$\mathbf{v}_i - \mathbf{v}_j = \langle \boldsymbol{\epsilon}', \mathbf{v}_i - \mathbf{v}_j \rangle \boldsymbol{\epsilon}' + \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_j \rangle \boldsymbol{\epsilon}, \quad \mathbf{v}_k^\circ - \mathbf{v}_l^\circ = \langle \boldsymbol{\epsilon}', \mathbf{v}_k^\circ - \mathbf{v}_l^\circ \rangle \boldsymbol{\epsilon}' + \langle \boldsymbol{\epsilon}, \mathbf{v}_k^\circ - \mathbf{v}_l^\circ \rangle \boldsymbol{\epsilon}, \quad (2.3.21)$$

where $\boldsymbol{\epsilon}'$ is the unit tangent vector perpendicular to the unit normal vector $\boldsymbol{\epsilon}$. Substituting equation (2.3.21) into equation (2.3.17) and multiplying the resulting equation by 2, we obtain:

$$\mu_{ij}(\langle \boldsymbol{\epsilon}', \mathbf{v}_i - \mathbf{v}_j \rangle \boldsymbol{\epsilon}' + \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_j \rangle \boldsymbol{\epsilon})^2 = \mu_{kl}(\langle \boldsymbol{\epsilon}', \mathbf{v}_k^\circ - \mathbf{v}_l^\circ \rangle \boldsymbol{\epsilon}' + \langle \boldsymbol{\epsilon}, \mathbf{v}_k^\circ - \mathbf{v}_l^\circ \rangle \boldsymbol{\epsilon})^2 + 2Q_R.$$

Expanding, we obtain:

$$\begin{aligned} \mu_{ij} \left((\langle \boldsymbol{\epsilon}', \mathbf{v}_i - \mathbf{v}_j \rangle)^2 + 2 \langle \boldsymbol{\epsilon}', \mathbf{v}_i - \mathbf{v}_j \rangle \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_j \rangle \boldsymbol{\epsilon}' \cdot \boldsymbol{\epsilon} + (\langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_j \rangle)^2 \right) \\ = \mu_{kl} \left((\langle \boldsymbol{\epsilon}', \mathbf{v}_k^\circ - \mathbf{v}_l^\circ \rangle)^2 + 2 \langle \boldsymbol{\epsilon}', \mathbf{v}_k^\circ - \mathbf{v}_l^\circ \rangle \langle \boldsymbol{\epsilon}, \mathbf{v}_k^\circ - \mathbf{v}_l^\circ \rangle \boldsymbol{\epsilon}' \cdot \boldsymbol{\epsilon} + (\langle \boldsymbol{\epsilon}, \mathbf{v}_k^\circ - \mathbf{v}_l^\circ \rangle)^2 \right) + 2Q_R. \end{aligned}$$

since ϵ' is perpendicular to ϵ (i.e., $\epsilon' \cdot \epsilon = 0$), we have that the above equation reduces to:

$$\mu_{ij} \left((\langle \epsilon', \mathbf{v}_i - \mathbf{v}_j \rangle)^2 + (\langle \epsilon, \mathbf{v}_i - \mathbf{v}_j \rangle)^2 \right) = \mu_{kl} \left((\langle \epsilon', \mathbf{v}_k^\circ - \mathbf{v}_l^\circ \rangle)^2 + (\langle \epsilon, \mathbf{v}_k^\circ - \mathbf{v}_l^\circ \rangle)^2 \right) + 2Q_R.$$

Expanding the previous equation, we obtain:

$$\mu_{ij} (\langle \epsilon', \mathbf{v}_i - \mathbf{v}_j \rangle)^2 + \mu_{ij} (\langle \epsilon, \mathbf{v}_i - \mathbf{v}_j \rangle)^2 = \mu_{kl} (\langle \epsilon', \mathbf{v}_k^\circ - \mathbf{v}_l^\circ \rangle)^2 + \mu_{kl} (\langle \epsilon, \mathbf{v}_k^\circ - \mathbf{v}_l^\circ \rangle)^2 + 2Q_R. \quad (2.3.22)$$

Using the fact that in a hard sphere collision, the tangential component of the relative velocity remains unchanged, see [36] page 2, we obtain:

$$\mu_{ij} (\langle \epsilon', \mathbf{v}_i - \mathbf{v}_j \rangle)^2 = \mu_{kl} (\langle \epsilon', \mathbf{v}_k^\circ - \mathbf{v}_l^\circ \rangle)^2.$$

Therefore, equation (2.3.22) reduces to equation (2.3.18).

To prove equation (2.3.19), we substitute equation (2.3.4)₃ rewritten as $Q_R = \zeta_i - \zeta_k$ into equation (2.3.18) and then divide the resulting equation by 2 to obtain:

$$\frac{1}{2} \mu_{ij} (\langle \epsilon, \mathbf{v}_i - \mathbf{v}_j \rangle)^2 = \frac{1}{2} \mu_{kl} (\langle \epsilon, \mathbf{v}_k^\circ - \mathbf{v}_l^\circ \rangle)^2 + \zeta_i - \zeta_k.$$

Subtracting ζ_i from both sides of the previous equation gives equation (2.3.19).

To prove equation (2.3.20), we divide both sides of equation (2.3.18) by μ_{ij} to obtain:

$$\begin{aligned} (\langle \epsilon, \mathbf{v}_i - \mathbf{v}_j \rangle)^2 &= \frac{\mu_{kl}}{\mu_{ij}} (\langle \epsilon, \mathbf{v}_k^\circ - \mathbf{v}_l^\circ \rangle)^2 + \frac{2Q_R}{\mu_{ij}} \\ &= \frac{\mu_{kl}}{\mu_{ij}} \left((\langle \epsilon, \mathbf{v}_k^\circ - \mathbf{v}_l^\circ \rangle)^2 + \frac{2Q_R}{\mu_{kl}} \right). \end{aligned}$$

Taking square root of both sides gives the desired result. Thus the proof is complete. $\square$

Lemma 2.3.4. *For a fixed vector ϵ , the Jacobians of the transformations $(\mathbf{v}_i, \mathbf{v}_j) \mapsto (\mathbf{v}_k^\circ, \mathbf{v}_l^\circ)$ and $(\mathbf{v}_k, \mathbf{v}_l) \mapsto (\mathbf{v}_i^\circ, \mathbf{v}_j^\circ)$ are, respectively, given by*

$$\left(\frac{\mu_{kl}}{\mu_{ij}} \right)^{\frac{3}{2}} \frac{\langle \epsilon, \mathbf{v}_k^\circ - \mathbf{v}_l^\circ \rangle}{\omega^+} \quad \text{and} \quad \left(\frac{\mu_{ij}}{\mu_{kl}} \right)^{\frac{3}{2}} \frac{\langle \epsilon, \mathbf{v}_i - \mathbf{v}_j \rangle}{\omega^-}. \quad (2.3.23)$$

Proof. For the proof of this lemma, see Lemma 4.2.3 pages 93 to 94 of [33]. $\square$

2.3.1.2 SRS Kinetic Equations

The state of the reactive mixture is described by the distribution functions $f_i(t, \mathbf{x}, \mathbf{v}_i)$, with $i = 1, 2, 3, 4$ and $(t, \mathbf{x}, \mathbf{v}_i) \in \mathbb{R}_+ \times \Omega \times \mathbb{R}^3$. These distribution functions represent the density of particles of species A_i , expressed in moles, which at time t are located at position $\mathbf{x}$ and have velocity $\mathbf{v}_i$. The functions f_i are related to the molar concentrations c_i as given below:

$$c_i(t, \mathbf{x}) = \int_{\mathbb{R}^3} f_i(t, \mathbf{x}, \mathbf{v}_i) d\mathbf{v}_i, \quad t \geq 0, \quad \mathbf{x} \in \Omega, \quad i = 1, 2, 3, 4. \quad (2.3.24)$$

In absence of external forces, the SRS kinetic equations, that is, the Maxwell-Boltzmann type equations for a reactive multi-species mixture of monatomic like gases are given by

$$\frac{\partial f_i}{\partial t} + \mathbf{v}_i \cdot \frac{\partial f_i}{\partial \mathbf{x}} = J_i^E + J_i^R, \quad \text{in } \mathbb{R}_+ \times \Omega \times \mathbb{R}^3, \quad \text{for } i = 1, 2, 3, 4, \quad (2.3.25)$$

where J_i^E is the elastic collision operator and J_i^R is the reactive collision operator. These collision operators are defined as follows:

$$\begin{aligned} J_i^E = & \sigma_{ii}^2 \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} [f_i' f_{i_*}' - f_i f_{i_*}] \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_{i_*} \rangle d\boldsymbol{\epsilon} d\mathbf{v}_{i_*} \\ & + \sum_{\substack{s=1 \\ s \neq i}}^4 \sigma_{is}^2 \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} [f_i' f_s' - f_i f_s] \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_s \rangle d\boldsymbol{\epsilon} d\mathbf{v}_s \end{aligned} \quad (2.3.26)$$

$$- \beta_{ij} \sigma_{ij}^2 \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} [f_i' f_j' - f_i f_j] \Theta(\langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_j \rangle - \Xi_{ij}) \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_j \rangle d\boldsymbol{\epsilon} d\mathbf{v}_j,$$

$$J_i^R = \beta_{ij} \sigma_{ij}^2 \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} \left[\left(\frac{\mu_{ij}}{\mu_{kl}} \right)^2 f_k^\circ f_l^\circ - f_i f_j \right] \Theta(\langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_j \rangle - \Xi_{ij}) \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_j \rangle d\boldsymbol{\epsilon} d\mathbf{v}_j. \quad (2.3.27)$$

In Eqs. (2.3.26) and (2.3.27) above, $f_i, f_{i_*}, f_i', f_{i_*}'$ are as given in Eq. (2.1.6), while

$$f_j = f(t, \mathbf{x}, \mathbf{v}_j), f_s = f(t, \mathbf{x}, \mathbf{v}_s), f_j' = f(t, \mathbf{x}, \mathbf{v}_j'), f_s' = f(t, \mathbf{x}, \mathbf{v}_s'), f_k^\circ = f(t, \mathbf{x}, \mathbf{v}_k^\circ), f_l^\circ = f(t, \mathbf{x}, \mathbf{v}_l^\circ).$$

Furthermore, Θ is a Heaviside step function, defined at $x \in \mathbb{R}$ by:

$$\Theta(x) = \begin{cases} 1, & x \geq 0, \\ 0, & x < 0. \end{cases} \quad (2.3.28)$$

Equations (2.3.25) together with (2.3.26) and (2.3.27) constitute the SRS kinetic system.

In equation (2.3.26), the first term on the right-hand side represent collisions involving particles of the same species and the indices i and i_* are used to distinguish their velocities. This term is the standard collision integral for a single gas (mono-species). It will be denoted by J_i^{mE} . The second term on the right-hand side of equation (2.3.26) describes elastic collisions between particles of different species (bi-species) and it will be denoted by J_i^{bE} . The last term on the right-hand side of equation (2.3.26) singles out those pre-collision states that are energetic enough to result in chemical reaction. This term prevents the double counting of these collisions in the elastic and reactive operators. It will be denoted by J_{ij}^{b*E} . Accordingly, in what follows, for $i = 1, 2, 3, 4$, we will sometimes write

$$J_i^E = J_i^{mE} + J_i^{bE} - J_{ij}^{b*E}, \quad (2.3.29)$$

with the following notations:

$$J_i^{mE} = \sigma_{ii}^2 \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} [f_i' f_{i_*}' - f_i f_{i_*}] \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_{i_*} \rangle d\boldsymbol{\epsilon} d\mathbf{v}_{i_*}, \quad (2.3.30)$$

$$J_i^{bE} = \sum_{\substack{s=1 \\ s \neq i}}^4 \sigma_{is}^2 \underbrace{\int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} [f_i' f_s' - f_i f_s] \langle \epsilon, \mathbf{v}_i - \mathbf{v}_s \rangle d\epsilon d\mathbf{v}_s}_{Q_{is}}, \quad (2.3.31)$$

$$J_{ij}^{b*E} = \beta_{ij} \sigma_{ij}^2 \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} [f_i' f_j' - f_i f_j] \Theta(\langle \epsilon, \mathbf{v}_i - \mathbf{v}_j \rangle - \Xi_{ij}) \langle \epsilon, \mathbf{v}_i - \mathbf{v}_j \rangle d\epsilon d\mathbf{v}_j. \quad (2.3.32)$$

The following proposition provides an alternative form of writing the sum of the elastic collision operator J_i^E and the reactive collision operator J_i^R , which is very useful to interpret the collision dynamics of the model, in particular, the role of the operator J_{ij}^{b*E} .

Proposition 2.3.5. *The sum of the elastic collision operator given in equation (2.3.29) and reactive collision operator given in equation (2.3.27) can be written as:*

$$\begin{aligned} J_i^E + J_i^R = & \sigma_{ii}^2 \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} [f_i' f_{i*}' - f_i f_{i*}] \langle \epsilon, \mathbf{v}_i - \mathbf{v}_{i*} \rangle d\epsilon d\mathbf{v}_{i*} \\ & + \sigma_{ik}^2 \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} [f_i' f_k' - f_i f_k] \langle \epsilon, \mathbf{v}_i - \mathbf{v}_k \rangle d\epsilon d\mathbf{v}_k \\ & + \sigma_{il}^2 \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} [f_i' f_l' - f_i f_l] \langle \epsilon, \mathbf{v}_i - \mathbf{v}_l \rangle d\epsilon d\mathbf{v}_l \\ & + \sigma_{ij}^2 \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} [f_i' f_j' - f_i f_j] \Theta(\Xi_{ij} - \langle \epsilon, \mathbf{v}_i - \mathbf{v}_j \rangle) \langle \epsilon, \mathbf{v}_i - \mathbf{v}_j \rangle d\epsilon d\mathbf{v}_j \\ & + (1 - \beta_{ij}) \sigma_{ij}^2 \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} [f_i' f_j' - f_i f_j] \Theta(\langle \epsilon, \mathbf{v}_i - \mathbf{v}_j \rangle - \Xi_{ij}) \langle \epsilon, \mathbf{v}_i - \mathbf{v}_j \rangle d\epsilon d\mathbf{v}_j \\ & + \beta_{ij} \sigma_{ij}^2 \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} \left[\left(\frac{\mu_{ij}}{\mu_{kl}} \right)^2 f_k^\circ f_l^\circ - f_i f_j \right] \Theta(\langle \epsilon, \mathbf{v}_i - \mathbf{v}_j \rangle - \Xi_{ij}) \langle \epsilon, \mathbf{v}_i - \mathbf{v}_j \rangle d\epsilon d\mathbf{v}_j, \end{aligned} \quad (2.3.33)$$

where $(i, j, k, l) \in \{(1, 2, 3, 4), (2, 1, 4, 3), (3, 4, 1, 2), (4, 3, 2, 1)\}$.

Proof. Setting $i = 1$ in equations (2.3.29) and (2.3.27), respectively and then take the sum of the resulting equations, we obtain:

$$\begin{aligned} J_1^E + J_1^R = & \sigma_{11}^2 \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} [f_1' f_{1*}' - f_1 f_{1*}] \langle \epsilon, \mathbf{v}_1 - \mathbf{v}_{1*} \rangle d\epsilon d\mathbf{v}_{1*} \\ & + \sigma_{12}^2 \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} [f_1' f_2' - f_1 f_2] \langle \epsilon, \mathbf{v}_1 - \mathbf{v}_2 \rangle d\epsilon d\mathbf{v}_2 \\ & + \sigma_{13}^2 \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} [f_1' f_3' - f_1 f_3] \langle \epsilon, \mathbf{v}_1 - \mathbf{v}_3 \rangle d\epsilon d\mathbf{v}_3 \\ & + \sigma_{14}^2 \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} [f_1' f_4' - f_1 f_4] \langle \epsilon, \mathbf{v}_1 - \mathbf{v}_4 \rangle d\epsilon d\mathbf{v}_4 \\ & - \beta_{12} \sigma_{12}^2 \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} [f_1' f_2' - f_1 f_2] \Theta(\langle \epsilon, \mathbf{v}_1 - \mathbf{v}_2 \rangle - \Xi_{12}) \langle \epsilon, \mathbf{v}_1 - \mathbf{v}_2 \rangle d\epsilon d\mathbf{v}_2 \\ & + \beta_{12} \sigma_{12}^2 \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} \left[\left(\frac{\mu_{12}}{\mu_{34}} \right)^2 f_3^\circ f_4^\circ - f_1 f_2 \right] \Theta(\langle \epsilon, \mathbf{v}_1 - \mathbf{v}_2 \rangle - \Xi_{12}) \langle \epsilon, \mathbf{v}_1 - \mathbf{v}_2 \rangle d\epsilon d\mathbf{v}_2 \end{aligned}$$

$$\times \Theta(\langle \epsilon, \mathbf{v}_1 - \mathbf{v}_2 \rangle - \Xi_{12}) \langle \epsilon, \mathbf{v}_1 - \mathbf{v}_2 \rangle d\epsilon d\mathbf{v}_2. \quad (2.3.34)$$

The second and fifth terms on the right-hand side of equation (2.3.34) above can be combined to give:

$$\sigma_{12}^2 \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} [f_1' f_2' - f_1 f_2] \langle \epsilon, \mathbf{v}_1 - \mathbf{v}_2 \rangle (1 - \beta_{12} \Theta(\langle \epsilon, \mathbf{v}_1 - \mathbf{v}_2 \rangle - \Xi_{12})) d\epsilon d\mathbf{v}_2. \quad (2.3.35)$$

Using the identity $\Theta(x) + \Theta(-x) = 1$, we can rewrite expression (2.3.35) as:

$$\begin{aligned} \sigma_{12}^2 \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} & \left(\Theta(\langle \epsilon, \mathbf{v}_1 - \mathbf{v}_2 \rangle - \Xi_{12}) + \Theta(\Xi_{12} - \langle \epsilon, \mathbf{v}_1 - \mathbf{v}_2 \rangle) - \beta_{12} \Theta(\langle \epsilon, \mathbf{v}_1 - \mathbf{v}_2 \rangle - \Xi_{12}) \right) \\ & \times [f_1' f_2' - f_1 f_2] \langle \epsilon, \mathbf{v}_1 - \mathbf{v}_2 \rangle d\epsilon d\mathbf{v}_2. \end{aligned}$$

Factorising the previous expression, we obtain:

$$\begin{aligned} \sigma_{12}^2 \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} & \left(\Theta(\Xi_{12} - \langle \epsilon, \mathbf{v}_1 - \mathbf{v}_2 \rangle) + (1 - \beta_{12}) \Theta(\langle \epsilon, \mathbf{v}_1 - \mathbf{v}_2 \rangle - \Xi_{12}) \right) \\ & \times [f_1' f_2' - f_1 f_2] \langle \epsilon, \mathbf{v}_1 - \mathbf{v}_2 \rangle d\epsilon d\mathbf{v}_2. \end{aligned}$$

Expanding the previous expression, we obtain:

$$\begin{aligned} \sigma_{12}^2 \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} & [f_1' f_2' - f_1 f_2] \Theta(\Xi_{12} - \langle \epsilon, \mathbf{v}_1 - \mathbf{v}_2 \rangle) \langle \epsilon, \mathbf{v}_1 - \mathbf{v}_2 \rangle d\epsilon d\mathbf{v}_2 \\ & + \sigma_{12}^2 (1 - \beta_{12}) \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} [f_1' f_2' - f_1 f_2] \Theta(\langle \epsilon, \mathbf{v}_1 - \mathbf{v}_2 \rangle - \Xi_{12}) \langle \epsilon, \mathbf{v}_1 - \mathbf{v}_2 \rangle d\epsilon d\mathbf{v}_2. \end{aligned} \quad (2.3.36)$$

Substituting expression (2.3.36) into equation (2.3.34) and rearranging gives:

$$\begin{aligned} J_1^E + J_1^R = & \sigma_{11}^2 \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} [f_1' f_{1*}' - f_1 f_{1*}] \langle \epsilon, \mathbf{v}_1 - \mathbf{v}_{1*} \rangle d\epsilon d\mathbf{v}_{1*} \\ & + \sigma_{13}^2 \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} [f_1' f_3' - f_1 f_3] \langle \epsilon, \mathbf{v}_1 - \mathbf{v}_3 \rangle d\epsilon d\mathbf{v}_3 \\ & + \sigma_{14}^2 \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} [f_1' f_4' - f_1 f_4] \langle \epsilon, \mathbf{v}_1 - \mathbf{v}_4 \rangle d\epsilon d\mathbf{v}_4 \\ & + \sigma_{12}^2 \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} [f_1' f_2' - f_1 f_2] \Theta(\Xi_{12} - \langle \epsilon, \mathbf{v}_1 - \mathbf{v}_2 \rangle) \langle \epsilon, \mathbf{v}_1 - \mathbf{v}_2 \rangle d\epsilon d\mathbf{v}_2 \\ & + \sigma_{12}^2 (1 - \beta_{12}) \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} [f_1' f_2' - f_1 f_2] \Theta(\langle \epsilon, \mathbf{v}_1 - \mathbf{v}_2 \rangle - \Xi_{12}) \langle \epsilon, \mathbf{v}_1 - \mathbf{v}_2 \rangle d\epsilon d\mathbf{v}_2 \\ & + \beta_{12} \sigma_{12}^2 \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} \left[\left(\frac{\mu_{12}}{\mu_{34}} \right)^2 f_3^\circ f_4^\circ - f_1 f_2 \right] \Theta(\langle \epsilon, \mathbf{v}_1 - \mathbf{v}_2 \rangle - \Xi_{12}) \langle \epsilon, \mathbf{v}_1 - \mathbf{v}_2 \rangle d\epsilon d\mathbf{v}_2. \end{aligned}$$

Similar computations can be done for $i = 2, 3, 4$, respectively. $\square$

The last three terms on the right-hand side of equation (2.3.33) are associated to collisions between the reactive species A_i and A_j . The first of these terms with σ_{ij}^2 in front of it is related to collisions between species A_i and A_j with insufficient amount of energy to produce a chemical reaction. Therefore, it is governed by elastic collision dynamics. The last two terms correspond to collisions between species A_i and A_j with sufficient amount of energy to produce a chemical reaction. However, only a fraction β_{ij} of such collisions results in a chemical reaction (last term) and produces species A_k and A_l . The remaining fraction $(1 - \beta_{ij})$ corresponds to collisions that are also governed by elastic collision dynamics (second to the last term).

Remark 2.3.6. *Observe that by setting β_{ij} equal to zero, the collision operators J_{ij}^{b*E} and J_i^R vanish, see equations (2.3.27) and (2.3.32). This corresponds to a situation in which the chemical reaction is turned off and we recover from the SRS model the hard-spheres model for a non-reactive mixture. Moreover, by setting β_{ij} equal to one in J_{ij}^{b*E} and J_i^R , all collisions with sufficient amount of energy to produce a chemical reaction will result, in a reactive collision. However, this is not the case in general because it is well known in chemistry [116] that besides the activation energy barrier, the relative orientation of the molecules at the instant of collision is very important for the occurrence of a chemical reaction. This means that only collisions with sufficient amount of energy and correct orientation will result in a chemical reaction. Accordingly, in this thesis the case in which $\beta_{ij} \in]0, 1[$ will be considered. This guarantee that chemical reaction occur (i.e., $\beta_{ij} > 0$), but some collisions between the reactive species will not result in a chemical reaction due to improper collision orientation (i.e., $\beta_{ij} < 1$), even if they have enough energy to react chemically. $\square$*

2.3.2 Properties of the Collision Operators for the SRS Model

In this subsection, a review of some of the properties of the elastic and reactive collision integrals of SRS kinetic model will be given. These properties will be presented in form of lemmas, corollaries and propositions. Furthermore, for clarity in the manipulations that follow, the distribution functions will be written with the velocity arguments only.

Lemma 2.3.7. *Given the mono-species elastic collision operator J_i^{mE} defined in equation (2.3.30), let $\varphi(\mathbf{v}_i)$ be a sufficiently smooth test function. Then, the weak form of J_i^{mE} for each of the species in the reactive mixture is given by:*

$$\begin{aligned} \int_{\mathbb{R}^3} J_i^{mE} \varphi(\mathbf{v}_i) d\mathbf{v}_i &= \frac{1}{4} \sigma_{ii}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} [f(\mathbf{v}'_i) f(\mathbf{v}'_{i*}) - f(\mathbf{v}_i) f(\mathbf{v}_{i*})] \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_{i*} \rangle \\ &\quad \times [\varphi(\mathbf{v}_i) + \varphi(\mathbf{v}_{i*}) - \varphi(\mathbf{v}'_i) - \varphi(\mathbf{v}'_{i*})] d\boldsymbol{\epsilon} d\mathbf{v}_{i*} d\mathbf{v}_i. \end{aligned} \quad (2.3.37)$$

Proof. The proof of this lemma is similar or equivalent to that of Lemma 2.2.1 with $d\boldsymbol{\omega}$ and $B(\mathbf{v}_i - \mathbf{v}_{i*}, \boldsymbol{\omega})$ replaced by $d\boldsymbol{\epsilon}$ and $\sigma_{ii}^2 \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_{i*} \rangle$, respectively. $\square$

Lemma 2.3.8. Given the bi-species elastic collision operator J_i^{bE} defined in equation (2.3.31) as a sum of several contributions of $\mathcal{Q}_{is}$, let $\varphi(\mathbf{v}_i)$ be a sufficiently smooth test function. Then, for each $i, s = 1, 2, 3, 4$ with $i \neq s$, we have that:

$$\int_{\mathbb{R}^3} \mathcal{Q}_{is} \varphi(\mathbf{v}_i) d\mathbf{v}_i = \sigma_{is}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} f(\mathbf{v}_i) f(\mathbf{v}_s) [\varphi(\mathbf{v}_i') - \varphi(\mathbf{v}_i)] \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_s \rangle d\boldsymbol{\epsilon} d\mathbf{v}_s d\mathbf{v}_i. \quad (2.3.38)$$

Proof. Multiplying $\mathcal{Q}_{is}$ given in Eq. (2.3.31) by $\varphi(\mathbf{v}_i)$ and integrating over $\mathbf{v}_i \in \mathbb{R}^3$ gives:

$$\int_{\mathbb{R}^3} \mathcal{Q}_{is} \varphi(\mathbf{v}_i) d\mathbf{v}_i = \sigma_{is}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} [f(\mathbf{v}_i') f(\mathbf{v}_s') - f(\mathbf{v}_i) f(\mathbf{v}_s)] \varphi(\mathbf{v}_i) \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_s \rangle d\boldsymbol{\epsilon} d\mathbf{v}_s d\mathbf{v}_i.$$

The previous equation can be rewritten as given below:

$$\begin{aligned} \int_{\mathbb{R}^3} \mathcal{Q}_{is} \varphi(\mathbf{v}_i) d\mathbf{v}_i &= \sigma_{is}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} f(\mathbf{v}_i') f(\mathbf{v}_s') \varphi(\mathbf{v}_i) \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_s \rangle d\boldsymbol{\epsilon} d\mathbf{v}_s d\mathbf{v}_i \\ &\quad - \sigma_{is}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} f(\mathbf{v}_i) f(\mathbf{v}_s) \varphi(\mathbf{v}_i) \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_s \rangle d\boldsymbol{\epsilon} d\mathbf{v}_s d\mathbf{v}_i. \end{aligned} \quad (2.3.39)$$

Using the change the variables $(\mathbf{v}_i, \mathbf{v}_s) \rightarrow (\mathbf{v}_i', \mathbf{v}_s')$ together with the fact that the Jacobian of this transformation is unity (this can be shown following similar steps as those used to prove Lemma 2.2.2), we can write the first term on the right-hand side of equation (2.3.39) as given below:

$$\sigma_{is}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} f(\mathbf{v}_i') f(\mathbf{v}_s') \varphi(\mathbf{v}_i(\mathbf{v}_i', \mathbf{v}_s')) \langle \boldsymbol{\epsilon}, \mathbf{v}_i' - \mathbf{v}_s' \rangle d\boldsymbol{\epsilon} d\mathbf{v}_s' d\mathbf{v}_i'. \quad (2.3.40)$$

Observe that subtracting equation (2.3.9) from equation (2.3.8) gives:

$$\begin{aligned} \mathbf{v}_i' - \mathbf{v}_s' &= \mathbf{v}_i - \mathbf{v}_s - \left(2 \frac{m_i m_s}{(m_i + m_s) m_i} + 2 \frac{m_i m_s}{(m_i + m_s) m_s} \right) \boldsymbol{\epsilon} \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_s \rangle \\ &= \mathbf{v}_i - \mathbf{v}_s - 2\boldsymbol{\epsilon} \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_s \rangle. \end{aligned}$$

Taking the inner product with $\boldsymbol{\epsilon}$, we obtain:

$$(\mathbf{v}_i' - \mathbf{v}_s') \cdot \boldsymbol{\epsilon} = (\mathbf{v}_i - \mathbf{v}_s) \cdot \boldsymbol{\epsilon} - 2 \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_s \rangle \boldsymbol{\epsilon} \cdot \boldsymbol{\epsilon} = -(\mathbf{v}_i - \mathbf{v}_s) \cdot \boldsymbol{\epsilon}, \quad (2.3.41)$$

where use have been made of the facts that $\boldsymbol{\epsilon} \cdot \boldsymbol{\epsilon} = 1$ and $2 \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_s \rangle = 2(\mathbf{v}_i - \mathbf{v}_s) \cdot \boldsymbol{\epsilon}$ in the first equality of the previous equation to obtain the last equality. Therefore,

$$\mathbf{v}_i' - \mathbf{v}_s' = -(\mathbf{v}_i - \mathbf{v}_s) \iff |\mathbf{v}_i' - \mathbf{v}_s'| = |\mathbf{v}_i - \mathbf{v}_s| \quad (2.3.42)$$

Furthermore, inverting equations (2.3.8) and (2.3.9), we obtain:

$$\begin{aligned} \mathbf{v}_i &= \mathbf{v}_i' + 2 \frac{\mu_{is}}{m_i} \boldsymbol{\epsilon} \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_s \rangle \\ \mathbf{v}_s &= \mathbf{v}_s' - 2 \frac{\mu_{is}}{m_s} \boldsymbol{\epsilon} \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_s \rangle. \end{aligned} \quad (2.3.43)$$

Observe that equation (2.3.41) can be rewritten as given below:

$$\langle \epsilon, \mathbf{v}'_i - \mathbf{v}'_s \rangle = -\langle \epsilon, \mathbf{v}_i - \mathbf{v}_s \rangle.$$

Thus, we can write equation (2.3.43) as given below:

$$\mathbf{v}_i = \mathbf{v}'_i + 2\frac{\mu_{is}}{m_i}\epsilon \langle \epsilon, \mathbf{v}_i - \mathbf{v}_s \rangle = \mathbf{v}'_i - 2\frac{\mu_{is}}{m_i}\epsilon \langle \epsilon, \mathbf{v}'_i - \mathbf{v}'_s \rangle \equiv \mathbf{v}_i(\mathbf{v}'_i, \mathbf{v}'_s) \quad (2.3.44)$$

$$\mathbf{v}_s = \mathbf{v}'_s - 2\frac{\mu_{is}}{m_s}\epsilon \langle \epsilon, \mathbf{v}_i - \mathbf{v}_s \rangle = \mathbf{v}'_s + 2\frac{\mu_{is}}{m_s}\epsilon \langle \epsilon, \mathbf{v}'_i - \mathbf{v}'_s \rangle \equiv \mathbf{v}_s(\mathbf{v}'_i, \mathbf{v}'_s). \quad (2.3.45)$$

Using equations (2.3.42) and (2.3.44), we can rewrite expression (2.3.40) as follows:

$$\sigma_{is}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} f(\mathbf{v}'_i) f(\mathbf{v}'_s) \varphi \left(\mathbf{v}'_i - 2\frac{\mu_{is}}{m_i}\epsilon \langle \epsilon, \mathbf{v}'_i - \mathbf{v}'_s \rangle \right) \langle \epsilon, \mathbf{v}_i - \mathbf{v}_s \rangle d\epsilon d\mathbf{v}'_s d\mathbf{v}'_i.$$

Renaming $(\mathbf{v}'_i, \mathbf{v}'_s)$ to $(\mathbf{v}_i, \mathbf{v}_s)$ in the previous integral, we obtain:

$$\sigma_{is}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} f(\mathbf{v}_i) f(\mathbf{v}_s) \varphi \left(\mathbf{v}_i - 2\frac{\mu_{is}}{m_i}\epsilon \langle \epsilon, \mathbf{v}_i - \mathbf{v}_s \rangle \right) \langle \epsilon, \mathbf{v}_i - \mathbf{v}_s \rangle d\epsilon d\mathbf{v}_s d\mathbf{v}_i. \quad (2.3.46)$$

Using equation (2.3.8), we obtain that

$$\varphi \left(\mathbf{v}_i - 2\frac{\mu_{is}}{m_i}\epsilon \langle \epsilon, \mathbf{v}_i - \mathbf{v}_s \rangle \right) = \varphi(\mathbf{v}'_i).$$

Therefore, the integral given in (2.3.46) becomes:

$$\sigma_{is}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} f(\mathbf{v}_i) f(\mathbf{v}_s) \varphi(\mathbf{v}'_i) \langle \epsilon, \mathbf{v}_i - \mathbf{v}_s \rangle d\epsilon d\mathbf{v}_s d\mathbf{v}_i. \quad (2.3.47)$$

Replacing the first term on the right-hand side of equation (2.3.39) with expression (2.3.47) and then, take the sum of the two terms on the right-hand side of the resulting equation gives equation (2.3.38). Therefore, the proof is complete. $\square$

Remark 2.3.9. Interchanging i and s in the definition of $\mathcal{Q}_{is}$ given in equation (2.3.31) for the bi-species elastic collision operator J_i^{bE} and following the steps used in the proof of Lemma 2.3.8 above, one obtains:

$$\int_{\mathbb{R}^3} \mathcal{Q}_{si} \varphi(\mathbf{v}_s) d\mathbf{v}_s = \sigma_{is}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} f(\mathbf{v}_i) f(\mathbf{v}_s) [\varphi(\mathbf{v}'_s) - \varphi(\mathbf{v}_s)] \langle \epsilon, \mathbf{v}_i - \mathbf{v}_s \rangle d\epsilon d\mathbf{v}_s d\mathbf{v}_i. \quad (2.3.48)$$

Lemma 2.3.10. Given the bi-species elastic collision operator J_{ij}^{b*E} defined in equation (2.3.32), let $\varphi(\mathbf{v}_i)$ be a sufficiently smooth test function. If we assume that $\beta_{ij} = \beta_{ji}$, then for $(i, j) \in \{(1, 2), (2, 1), (3, 4), (4, 3)\}$, we have that:

$$\int_{\mathbb{R}^3} J_{ij}^{b*E} \varphi(\mathbf{v}_i) d\mathbf{v}_i = \beta_{ij} \sigma_{ij}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} f(\mathbf{v}_i) f(\mathbf{v}_j) [\varphi(\mathbf{v}'_i) - \varphi(\mathbf{v}_i)]$$

$$\times \Theta(\langle \epsilon, \mathbf{v}_i - \mathbf{v}_j \rangle - \Xi_{ij}) \langle \epsilon, \mathbf{v}_i - \mathbf{v}_j \rangle d\epsilon d\mathbf{v}_j d\mathbf{v}_i. \quad (2.3.49)$$

Proof. Multiplying both sides of equation (2.3.32) by $\varphi(\mathbf{v}_i)$ and integrating the resulting equation over $\mathbf{v}_i \in \mathbb{R}^3$ gives:

$$\begin{aligned} \int_{\mathbb{R}^3} J_{ij}^{b*E} \varphi(\mathbf{v}_i) d\mathbf{v}_i &= \beta_{ij} \sigma_{ij}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} [f(\mathbf{v}'_i) f(\mathbf{v}'_j) - f(\mathbf{v}_i) f(\mathbf{v}_j)] \varphi(\mathbf{v}_i) \\ &\quad \times \Theta(\langle \epsilon, \mathbf{v}_i - \mathbf{v}_j \rangle - \Xi_{ij}) \langle \epsilon, \mathbf{v}_i - \mathbf{v}_j \rangle d\epsilon d\mathbf{v}_j d\mathbf{v}_i. \end{aligned}$$

The previous equation can be rewritten as given below:

$$\begin{aligned} \int_{\mathbb{R}^3} J_{ij}^{b*E} \varphi(\mathbf{v}_i) d\mathbf{v}_i &= \beta_{ij} \sigma_{ij}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} f(\mathbf{v}'_i) f(\mathbf{v}'_j) \varphi(\mathbf{v}_i) \Theta(\langle \epsilon, \mathbf{v}_i - \mathbf{v}_j \rangle - \Xi_{ij}) \langle \epsilon, \mathbf{v}_i - \mathbf{v}_j \rangle d\epsilon d\mathbf{v}_j d\mathbf{v}_i \\ &\quad - \beta_{ij} \sigma_{ij}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} f(\mathbf{v}_i) f(\mathbf{v}_j) \varphi(\mathbf{v}_i) \Theta(\langle \epsilon, \mathbf{v}_i - \mathbf{v}_j \rangle - \Xi_{ij}) \langle \epsilon, \mathbf{v}_i - \mathbf{v}_j \rangle d\epsilon d\mathbf{v}_j d\mathbf{v}_i. \end{aligned} \quad (2.3.50)$$

Using the change the variables $(\mathbf{v}_i, \mathbf{v}_j) \rightarrow (\mathbf{v}'_i, \mathbf{v}'_j)$ together with the fact that the Jacobian of the transformation is unity (this can be shown following similar steps as those used to prove Lemma 2.2.2), we can write the first term on the right-hand side of the previous equation as given below:

$$\beta_{ij} \sigma_{ij}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} f(\mathbf{v}'_i) f(\mathbf{v}'_j) \varphi(\mathbf{v}_i(\mathbf{v}'_i, \mathbf{v}'_j)) \Theta(\langle \epsilon, \mathbf{v}'_i - \mathbf{v}'_j \rangle - \Xi_{ij}) \langle \epsilon, \mathbf{v}'_i - \mathbf{v}'_j \rangle d\epsilon d\mathbf{v}'_j d\mathbf{v}'_i.$$

Using equations (2.3.42) and (2.3.44) with s replaced by j , we can rewrite the previous equation as:

$$\begin{aligned} \beta_{ij} \sigma_{ij}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} f(\mathbf{v}'_i) f(\mathbf{v}'_j) \varphi\left(\mathbf{v}'_i - 2 \frac{\mu_{ij}}{m_i} \epsilon \langle \epsilon, \mathbf{v}'_i - \mathbf{v}'_j \rangle\right) \\ \times \Theta(\langle \epsilon, \mathbf{v}_i - \mathbf{v}_j \rangle - \Xi_{ij}) \langle \epsilon, \mathbf{v}_i - \mathbf{v}_j \rangle d\epsilon d\mathbf{v}'_j d\mathbf{v}'_i. \end{aligned}$$

Renaming $(\mathbf{v}'_i, \mathbf{v}'_j)$ to $(\mathbf{v}_i, \mathbf{v}_j)$ in the previous integral, we obtain:

$$\begin{aligned} \beta_{ij} \sigma_{ij}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} f(\mathbf{v}_i) f(\mathbf{v}_j) \varphi\left(\mathbf{v}_i - 2 \frac{\mu_{ij}}{m_i} \epsilon \langle \epsilon, \mathbf{v}_i - \mathbf{v}_j \rangle\right) \\ \times \Theta(\langle \epsilon, \mathbf{v}_i - \mathbf{v}_j \rangle - \Xi_{ij}) \langle \epsilon, \mathbf{v}_i - \mathbf{v}_j \rangle d\epsilon d\mathbf{v}_j d\mathbf{v}_i. \end{aligned}$$

Using equation (2.3.8) with s replaced by j , we obtain that

$$\varphi\left(\mathbf{v}_i - 2 \frac{\mu_{ij}}{m_i} \epsilon \langle \epsilon, \mathbf{v}_i - \mathbf{v}_j \rangle\right) = \varphi(\mathbf{v}'_i).$$

Therefore, the previous integral becomes:

$$\beta_{ij} \sigma_{ij}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} f(\mathbf{v}_i) f(\mathbf{v}_j) \varphi(\mathbf{v}'_i) \Theta(\langle \epsilon, \mathbf{v}_i - \mathbf{v}_j \rangle - \Xi_{ij}) \langle \epsilon, \mathbf{v}_i - \mathbf{v}_j \rangle d\epsilon d\mathbf{v}_j d\mathbf{v}_i. \quad (2.3.51)$$

Replacing the first term on the right-hand side of equation (2.3.50) with expression (2.3.51) and then, take the sum of the two terms on the right-hand side of the resulting equation gives equation (2.3.49). This completes the the proof. $\square$

Remark 2.3.11. *Interchanging i and j in the definition of the bi-species elastic collision operator J_{ij}^{b*E} given in equation (2.3.32) and following the steps used in the proof of Lemma 2.3.10 above, one obtains:*

$$\begin{aligned} \int_{\mathbb{R}^3} J_{ji}^{b*E} \varphi(\mathbf{v}_j) d\mathbf{v}_j &= \beta_{ij} \sigma_{ij}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} f(\mathbf{v}_i) f(\mathbf{v}_j) [\varphi(\mathbf{v}'_j) - \varphi(\mathbf{v}_j)] \\ &\quad \times \Theta(\langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_j \rangle - \Xi_{ij}) \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_j \rangle d\boldsymbol{\epsilon} d\mathbf{v}_j d\mathbf{v}_i. \end{aligned} \quad (2.3.52)$$

Lemma 2.3.12. *Given the reactive collision operator J_i^R defined in equation (2.3.27), let $\varphi(\mathbf{v}_i)$ be a sufficiently smooth test function. If we assume that*

$$\beta_{ij} = \beta_{ji} \quad \text{and} \quad \beta_{12} \sigma_{12}^2 = \beta_{34} \sigma_{34}^2,$$

then

$$\begin{aligned} \sum_{i=1}^4 \int_{\mathbb{R}^3} J_i^R \varphi_i(\mathbf{v}_i) d\mathbf{v}_i &= \beta_{12} \sigma_{12}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} \left[\left(\frac{\mu_{12}}{\mu_{34}} \right)^2 f_3^\circ f_4^\circ - f_1 f_2 \right] [\varphi_1 + \varphi_2 - \varphi_3^\circ - \varphi_4^\circ] \\ &\quad \times \Theta(\langle \boldsymbol{\epsilon}, \mathbf{v}_1 - \mathbf{v}_2 \rangle - \Xi_{12}) \langle \boldsymbol{\epsilon}, \mathbf{v}_1 - \mathbf{v}_2 \rangle d\boldsymbol{\epsilon} d\mathbf{v}_2 d\mathbf{v}_1 \\ &= \beta_{34} \sigma_{34}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} \left[\left(\frac{\mu_{34}}{\mu_{12}} \right)^2 f_1^\circ f_2^\circ - f_3 f_4 \right] [\varphi_3 + \varphi_4 - \varphi_1^\circ - \varphi_2^\circ] \\ &\quad \times \Theta(\langle \boldsymbol{\epsilon}, \mathbf{v}_3 - \mathbf{v}_4 \rangle - \Xi_{34}) \langle \boldsymbol{\epsilon}, \mathbf{v}_3 - \mathbf{v}_4 \rangle d\boldsymbol{\epsilon} d\mathbf{v}_4 d\mathbf{v}_3. \end{aligned} \quad (2.3.53)$$

Proof. The proof of this lemma is given in Proposition 4.3.2 page 100 of [33]. $\square$

2.3.3 Conservation Equations

The conservation equations of the SRS model are obtained by using the properties of the collision operators stated in subsection 2.3.2. Their proofs are rather standard and follow the same line as in [33, 61, 92, 93].

Corollary 2.3.13. *The mono-species elastic collision operator given in equation (2.3.30) is such that*

$$\int_{\mathbb{R}^3} J_i^{mE} \begin{pmatrix} m_i \\ m_i \mathbf{v}_i \\ \frac{1}{2} m_i (\mathbf{v}_i)^2 \end{pmatrix} d\mathbf{v}_i = 0, \quad i = 1, 2, 3, 4. \quad (2.3.54)$$

Proof. Setting $\varphi(\mathbf{v}_i) = m_i$, $\varphi(\mathbf{v}_i) = m_i \mathbf{v}_i$ and $\varphi(\mathbf{v}_i) = \frac{1}{2} m_i (\mathbf{v}_i)^2$, respectively, in equation (2.3.37), one has that

$$\varphi(\mathbf{v}_i) + \varphi(\mathbf{v}_{i*}) - \varphi(\mathbf{v}'_i) - \varphi(\mathbf{v}'_{i*}) = 0,$$

by virtue of the conservation laws of mass, linear momentum and kinetic energy, see the first second and third equations of (2.2.37), respectively. $\square$

Corollary 2.3.14. *Let $\mathcal{Q}_{is}$ and J_{ij}^{b*E} be as defined in equations (2.3.31) and (2.3.32), respectively. Then*

$$\int_{\mathbb{R}^3} m_i \mathcal{Q}_{is} d\mathbf{v}_i = 0, \quad (2.3.55)$$

$$\int_{\mathbb{R}^3} m_i J_{ij}^{b*E} d\mathbf{v}_i = 0, \quad (2.3.56)$$

$$\int_{\mathbb{R}^3} \mathcal{Q}_{is} \left(\begin{matrix} m_i \mathbf{v}_i \\ \frac{1}{2} m_i (\mathbf{v}_i)^2 \end{matrix} \right) d\mathbf{v}_i + \int_{\mathbb{R}^3} \mathcal{Q}_{si} \left(\begin{matrix} m_s \mathbf{v}_s \\ \frac{1}{2} m_s (\mathbf{v}_s)^2 \end{matrix} \right) d\mathbf{v}_s = 0, \quad (2.3.57)$$

$$\int_{\mathbb{R}^3} J_{ij}^{b*E} \left(\begin{matrix} m_i \mathbf{v}_i \\ \frac{1}{2} m_i (\mathbf{v}_i)^2 \end{matrix} \right) d\mathbf{v}_i + \int_{\mathbb{R}^3} J_{ji}^{b*E} \left(\begin{matrix} m_j \mathbf{v}_j \\ \frac{1}{2} m_j (\mathbf{v}_j)^2 \end{matrix} \right) d\mathbf{v}_j = 0. \quad (2.3.58)$$

Proof. Setting $\varphi(\mathbf{v}_i) = m_i$ in equations (2.3.38) and (2.3.49), respectively, one has that

$$\varphi(\mathbf{v}'_i) - \varphi(\mathbf{v}_i) = 0$$

by virtue of the fact that $m_i - m_i = 0$. Thus equations (2.3.55) and (2.3.56) are proven.

To prove equation (2.3.57), we add equations (2.3.38) and (2.3.48) to obtain:

$$\begin{aligned} & \int_{\mathbb{R}^3} \mathcal{Q}_{is} \varphi(\mathbf{v}_i) d\mathbf{v}_i + \int_{\mathbb{R}^3} \mathcal{Q}_{si} \varphi(\mathbf{v}_s) d\mathbf{v}_s \\ &= \sigma_{is}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} f(\mathbf{v}_i) f(\mathbf{v}_s) [\varphi(\mathbf{v}'_i) + \varphi(\mathbf{v}'_s) - \varphi(\mathbf{v}_i) - \varphi(\mathbf{v}_s)] \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_s \rangle d\boldsymbol{\epsilon} d\mathbf{v}_s d\mathbf{v}_i. \end{aligned}$$

Setting $\varphi(\mathbf{v}_i) = m_i \mathbf{v}_i$, $\varphi(\mathbf{v}_s) = m_s \mathbf{v}_s$ and $\varphi(\mathbf{v}_i) = \frac{1}{2} m_i (\mathbf{v}_i)^2$, $\varphi(\mathbf{v}_s) = \frac{1}{2} m_s (\mathbf{v}_s)^2$, respectively, in the previous equation one has that

$$\varphi(\mathbf{v}'_i) + \varphi(\mathbf{v}'_s) - \varphi(\mathbf{v}_i) - \varphi(\mathbf{v}_s) = 0$$

by virtue of the conservation of linear momentum given in equation (2.3.6) and the conservation of kinetic energy given in equation (2.3.7), respectively. Thus equation (2.3.57) is proven.

To prove equation (2.3.58), we add equations (2.3.49) and (2.3.52) to obtain:

$$\begin{aligned} & \int_{\mathbb{R}^3} J_{ij}^{b*E} \varphi(\mathbf{v}_i) d\mathbf{v}_i + \int_{\mathbb{R}^3} J_{ji}^{b*E} \varphi(\mathbf{v}_j) d\mathbf{v}_j \\ &= \beta_{ij} \sigma_{ij}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} f(\mathbf{v}_i) f(\mathbf{v}_j) [\varphi(\mathbf{v}'_i) + \varphi(\mathbf{v}'_j) - \varphi(\mathbf{v}_i) - \varphi(\mathbf{v}_j)] \\ & \quad \times \Theta(\langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_j \rangle - \Xi_{ij}) \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_j \rangle d\boldsymbol{\epsilon} d\mathbf{v}_j d\mathbf{v}_i. \end{aligned}$$

Setting $\varphi(\mathbf{v}_i) = m_i \mathbf{v}_i$, $\varphi(\mathbf{v}_j) = m_j \mathbf{v}_j$ and $\varphi(\mathbf{v}_i) = \frac{1}{2} m_i (\mathbf{v}_i)^2$, $\varphi(\mathbf{v}_j) = \frac{1}{2} m_j (\mathbf{v}_j)^2$, respectively, in

the previous equation one has that

$$\varphi(\mathbf{v}'_i) + \varphi(\mathbf{v}'_s) - \varphi(\mathbf{v}_i) - \varphi(\mathbf{v}_s) = 0$$

by virtue of the conservation of linear momentum given in equation (2.3.6) and the conservation of kinetic energy given in equation (2.3.7), respectively, with s replaced by j . Thus equation (2.3.58) is proven and the proof is complete. $\square$

Corollary 2.3.15. *For $i = 1, 2, 3, 4$, the reactive collision operator given in (2.3.27) satisfy the following property*

$$\int_{\mathbb{R}^3} J_1^R d\mathbf{v}_1 = \int_{\mathbb{R}^3} J_2^R d\mathbf{v}_2 = - \int_{\mathbb{R}^3} J_3^R d\mathbf{v}_3 = - \int_{\mathbb{R}^3} J_4^R d\mathbf{v}_4. \quad (2.3.59)$$

Proof. Let $\varphi = (\varphi(\mathbf{v}_1), \varphi(\mathbf{v}_2), \varphi(\mathbf{v}_3), \varphi(\mathbf{v}_4))$, then setting

$$\varphi = (1, 0, 0, 0), \quad \varphi = (0, 1, 0, 0), \quad \varphi = (0, 0, 1, 0), \quad \varphi = (0, 0, 0, 1),$$

respectively, in equation (2.3.53) gives the desired result. $\square$

Corollary 2.3.15 above assures the correct exchange rates for the species in the chemical reaction described in (2.3.1).

Corollary 2.3.16. *The elastic and reactive collision operators are such that*

$$\sum_{i=1}^4 \int_{\mathbb{R}^3} \varphi(\mathbf{v}_i) (J_i^E + J_i^R) d\mathbf{v}_i = 0, \quad (2.3.60)$$

Proof. This is an immediate consequence of corollaries 2.3.13, 2.3.14 and Lemma 2.3.12. $\square$

Corollary 2.3.16 indicates that, at least formally, the SRS model possesses seven independent macroscopic conservation laws, for the total number of particles of the reactant-product pairs of the form A_1 - A_3 , A_1 - A_4 and A_2 - A_3 , the three momentum components and the total energy of the mixture.

2.3.4 Equilibrium Solutions and $\mathcal{H}$ -Theorem

The equilibrium solutions of the SRS system are characterised as follows.

Definition 2.3.17. *The equilibrium solutions of the SRS kinetic equations given in equation (2.3.25) are distribution functions $f_i(t, \mathbf{x}, \mathbf{v}_i)$ such that the collision operators J_i^E and J_i^R given in equations (2.3.26) and (2.3.27) satisfy*

$$J_i^E + J_i^R = 0, \quad i = 1, \dots, 4. \quad (2.3.61)$$

Proposition 2.3.18. *If the coefficients β_{ij} and the reactive cross-sections are such that $\beta_{ij} = \beta_{ji}$ and $\beta_{12}\sigma_{12}^2 = \beta_{34}\sigma_{34}^2$, then the following statements are equivalent*

$$(a) f_i = c_i \left(\frac{m_i}{2\pi k_B T} \right)^{\frac{3}{2}} \exp \left(-\frac{m_i(\mathbf{v}_i - \mathbf{u})^2}{2k_B T} \right), \quad i = 1, \dots, 4,$$

with

$$c_1 c_2 = \left(\frac{\mu_{12}}{\mu_{34}} \right)^{1/2} c_3 c_4 \exp \left(\frac{Q_R}{k_B T} \right); \quad (2.3.62)$$

$$(b) J_i^E = 0 \text{ and } J_i^R = 0, \quad i = 1, \dots, 4;$$

$$(c) \sum_{i=1}^4 \int_{\mathbb{R}^3} [J_i^E + J_i^R] \log \left(\frac{f_i}{\mu_{ij}} \right) d\mathbf{v} = 0,$$

where

$$c_i := c_i(t, \mathbf{x}) = \int_{\mathbb{R}^3} f_i(t, \mathbf{x}, \mathbf{v}_i) d\mathbf{v}_i, \quad i = 1, \dots, 4, \quad (2.3.63a)$$

$$\mathbf{u} := \mathbf{u}(t, \mathbf{x}) = \frac{\sum_{i=1}^4 \int_{\mathbb{R}^3} m_i \mathbf{v}_i f_i(t, \mathbf{x}, \mathbf{v}_i) d\mathbf{v}_i}{\sum_{i=1}^4 \int_{\mathbb{R}^3} m_i f_i(t, \mathbf{x}, \mathbf{v}_i) d\mathbf{v}_i}, \quad (2.3.63b)$$

$$T := T(t, \mathbf{x}) = \frac{\frac{1}{3k} \sum_{i=1}^4 \int_{\mathbb{R}^3} m_i (\mathbf{v}_i - \mathbf{u})^2 f_i(t, \mathbf{x}, \mathbf{v}_i) d\mathbf{v}_i}{\sum_{i=1}^4 c_i(t, \mathbf{x})}. \quad (2.3.63c)$$

Proof. The proof of this proposition is given in Proposition 4.5.1 pages 108-112 of [33]. $\square$

Condition (2.3.62) represents the so called *mass action law* for the SRS kinetic model.

2.4 Reactive System of Polyatomic Gases

In this section, the kinetic model for a reactive multi-species mixture of polyatomic gases with a continuous structure of internal energy, proposed in [45] is presented. This kinetic model is the second model whose hydrodynamic limits will be studied. The presentation is restricted to: a brief description of the kinetic model, the central aspects of the collision dynamics, the kinetic equations, the properties of the collision operators that will be needed in our analysis, the conservation laws, the equilibrium states and the $\mathcal{H}$ -theorem.

2.4.1 Kinetic Model for a Reactive Polyatomic Gas Mixture

We consider a quaternary polyatomic gaseous mixture whose species are denoted by A_i with $i = 1, 2, 3, 4$. The species are endowed with a continuous structure of internal energy I_i . Furthermore, they participate in the bi-molecular reversible chemical reaction of type described in equation (2.3.1) and satisfy equation (2.3.3).

2.4.1.1 Collision Dynamics and Borgnakke-Larsen Procedure

The particles of the species in the mixture undergo binary collisions, either of elastic or reactive type. Elastic collisions can occur between particles of the same species (mono-species elastic collisions), and also between particles of different species (bi-species elastic collisions). The mono-species and bi-species elastic collisions result in changes in the velocities and internal energies of the colliding pair, but do not modify the species and consequently do not modify the molecular masses of the colliding particles. If we denote the velocities and internal energies of the colliding pair, say A_i, A_j before the collision by $\mathbf{v}_i, \mathbf{v}_j$ and I_i, I_j , respectively and denote their values after the collision by $\mathbf{v}'_i, \mathbf{v}'_j$ and I'_i, I'_j , then the conservation laws of linear momentum and total energy (kinetic and internal energy) for elastic collisions are given by:

$$m_i \mathbf{v}_i + m_j \mathbf{v}_j = m_i \mathbf{v}'_i + m_j \mathbf{v}'_j, \quad (2.4.1)$$

$$\frac{1}{2} m_i (\mathbf{v}_i)^2 + I_i + \frac{1}{2} m_j (\mathbf{v}_j)^2 + I_j = \frac{1}{2} m_i (\mathbf{v}'_i)^2 + I'_i + \frac{1}{2} m_j (\mathbf{v}'_j)^2 + I'_j. \quad (2.4.2)$$

In equations (2.4.1) and (2.4.2) above, $i \neq j$ represents bi-species collisions and $i = j$ represents mono-species collisions. In the latter case, the indices i and i_* is used to distinguish the velocities and internal energies of the two colliding pair.

On the other hand, reactive collisions occur between particles of species A_1, A_2 or A_3, A_4 following the reaction law (2.3.1). These reactive collisions result not just in changes in the velocities and internal energies of the colliding pair, but also they result in the transformation of the reactants into products of the reaction. Consequently, they imply a rearrangement of mass and a redistribution of chemical binding energy. If A_i, A_j and A_k, A_l represent the reactants and products of the chemical reaction, with $(i, j, k, l) \in ((1, 2, 3, 4), (2, 1, 4, 3))$ and $(i, j, k, l) \in (3, 4, 1, 2), (4, 3, 2, 1)$ for the forward and backward or reverse chemical reactions respectively, then the conservation laws of mass, linear momentum and total energy (kinetic, internal and chemical binding energies) for reactive collisions are given by:

$$m_i + m_j = m_k + m_l = M \quad (2.4.3)$$

$$m_i \mathbf{v}_i + m_j \mathbf{v}_j = m_k \mathbf{v}'_k + m_l \mathbf{v}'_l, \quad (2.4.4)$$

$$\frac{1}{2} m_i (\mathbf{v}_i)^2 + I_i + E_i + \frac{1}{2} m_j (\mathbf{v}_j)^2 + I_j + E_j = \frac{1}{2} m_k (\mathbf{v}'_k)^2 + I'_k + E_k + \frac{1}{2} m_l (\mathbf{v}'_l)^2 + I'_l + E_l. \quad (2.4.5)$$

Equation (2.4.5) can be written in an equivalent form as

$$\frac{1}{2} m_i (\mathbf{v}_i)^2 + I_i + \frac{1}{2} m_j (\mathbf{v}_j)^2 + I_j - \frac{Q_R}{2} = \frac{1}{2} m_k (\mathbf{v}'_k)^2 + I'_k + \frac{1}{2} m_l (\mathbf{v}'_l)^2 + I'_l + \frac{Q_R}{2}, \quad (2.4.5a)$$

where Q_R has been defined in (2.3.3).

As usual in kinetic theory, the post-collision velocities are expressed in terms of the pre-collision velocities. The corresponding expressions for both elastic and reactive post-collision velocities are derived from the conservation laws (2.4.1),(2.4.2) and (2.4.4),(2.4.5), respectively. In order to give the expressions for the post-collision velocities, we start by describing the Borgnakke-Larsen procedure [22]. Such procedure is based on the re-partition of the total energy of the colliding pair into kinetic and internal energies.

Let us consider first elastic collisions. To obtain the post-collision velocities, we first compute the total energy $\mathcal{E}$ of the colliding pair in the centre of mass reference frame. To do this, we define the centre of mass velocity $\mathbf{X}^*$ and the relative velocity $\mathbf{V}^*$, before the collision by

$$\mathbf{X}^* = \frac{m_i \mathbf{v}_i + m_j \mathbf{v}_j}{m_i + m_j}, \quad (2.4.6)$$

$$\mathbf{V}^* = \mathbf{v}_j - \mathbf{v}_i. \quad (2.4.7)$$

From equations (2.4.6) and (2.4.7) above, we have that

$$\mathbf{X}^*(m_i + m_j) = m_i \mathbf{v}_i + m_j \mathbf{v}_j, \quad (2.4.8)$$

$$\mathbf{v}_j = \mathbf{V}^* + \mathbf{v}_i, \quad (2.4.9)$$

respectively. Using equations (2.4.8) and (2.4.9), we can write $\mathbf{v}_i$ and $\mathbf{v}_j$ in terms of $\mathbf{X}^*$ and $\mathbf{V}^*$. To do this, observe that substituting equation (2.4.9) into equation (2.4.8) gives:

$$\mathbf{X}^*(m_i + m_j) = m_i \mathbf{v}_i + m_j (\mathbf{V}^* + \mathbf{v}_i) = (m_i + m_j) \mathbf{v}_i + m_j \mathbf{V}^*.$$

Dividing both side of the previous equation by $m_i + m_j$, we obtain:

$$\mathbf{X}^* = \mathbf{v}_i + \frac{m_j \mathbf{V}^*}{m_i + m_j}.$$

Therefore,

$$\mathbf{v}_i = \mathbf{X}^* - \frac{m_j \mathbf{V}^*}{m_i + m_j}. \quad (2.4.10)$$

Furthermore, substituting equation (2.4.10) into equation (2.4.9), we obtain:

$$\begin{aligned} \mathbf{v}_j &= \mathbf{V}^* + \mathbf{X}^* - \frac{m_j \mathbf{V}^*}{m_i + m_j} \\ &= \frac{(m_i + m_j) \mathbf{V}^* + (m_i + m_j) \mathbf{X}^* - m_j \mathbf{V}^*}{m_i + m_j} \\ &= \mathbf{X}^* + \frac{m_i \mathbf{V}^*}{m_i + m_j}. \end{aligned} \quad (2.4.11)$$

Using equations (2.4.10) and (2.4.11) above, we obtain:

$$m_i (\mathbf{v}_i)^2 = m_i \left(\mathbf{X}^* - \frac{m_j \mathbf{V}^*}{m_i + m_j} \right)^2 = m_i \left\{ X^{*2} - 2 \frac{m_j}{m_i + m_j} \mathbf{V}^* \cdot \mathbf{X}^* + \frac{m_j^2}{(m_i + m_j)^2} V^{*2} \right\}$$

$$m_j(\mathbf{v}_j)^2 = m_j \left(\mathbf{X}^* + \frac{m_i \mathbf{V}^*}{m_i + m_j} \right)^2 = m_j \left\{ X^{*2} + 2 \frac{m_i}{m_i + m_j} \mathbf{V}^* \cdot \mathbf{X}^* + \frac{m_i^2}{(m_i + m_j)^2} V^{*2} \right\},$$

respectively, where $X^* = \|\mathbf{X}^*\| = |\mathbf{X}^*|$ and $V^* = \|\mathbf{V}^*\| = |\mathbf{V}^*| = |\mathbf{v}_j - \mathbf{v}_i|$. Therefore,

$$\begin{aligned} m_i(\mathbf{v}_i)^2 + m_j(\mathbf{v}_j)^2 &= m_i X^{*2} + \frac{m_i m_j^2}{(m_i + m_j)^2} V^{*2} + m_j X^{*2} + \frac{m_j m_i^2}{(m_i + m_j)^2} V^{*2} \\ &= (m_i + m_j) X^{*2} + \frac{\mu_{ij}}{m_i + m_j} V^{*2} (m_i + m_j) \\ &= (m_i + m_j) X^{*2} + \mu_{ij} V^{*2}. \end{aligned} \quad (2.4.12)$$

Similarly, let $\mathbf{X}^{*'} and $\mathbf{V}^{*}'$ be the centre of mass velocity and relative velocity, respectively after the elastic collision, where$

$$\mathbf{X}^{*'} = \frac{m_i \mathbf{v}_i' + m_j \mathbf{v}_j'}{m_i + m_j}, \quad (2.4.13)$$

$$\mathbf{V}^{*'} = \mathbf{v}_j' - \mathbf{v}_i' \quad (2.4.14)$$

Following the steps used to obtain equations (2.4.10) and (2.4.11), we obtain:

$$\mathbf{v}_i' = \mathbf{X}^{*'} - \frac{m_j}{m_i + m_j} \mathbf{V}^{*'} \quad (2.4.15)$$

$$\mathbf{v}_j' = \mathbf{X}^{*'} + \frac{m_i}{m_i + m_j} \mathbf{V}^{*'} \quad (2.4.16)$$

Furthermore, Observe that using equation (2.4.1), we can rewrite equation (2.4.13) as follows:

$$\mathbf{X}^{*'} = \frac{m_i \mathbf{v}_i' + m_j \mathbf{v}_j'}{m_i + m_j} = \frac{m_i \mathbf{v}_i + m_j \mathbf{v}_j}{m_i + m_j} = \mathbf{X}^*. \quad (2.4.17)$$

Therefore, we can rewrite $\mathbf{v}_i'$ and $\mathbf{v}_j'$ given in equations (2.4.15) and (2.4.16), respectively as given below:

$$\begin{aligned} \mathbf{v}_i' &= \mathbf{X}^* - \frac{m_j}{m_i + m_j} \mathbf{V}^{*'}, \\ \mathbf{v}_j' &= \mathbf{X}^* + \frac{m_i}{m_i + m_j} \mathbf{V}^{*'} \end{aligned} \quad (2.4.18)$$

Using equation (2.4.18) above, we obtain:

$$m_i(\mathbf{v}_i')^2 = m_i \left(\mathbf{X}^* - \frac{m_j \mathbf{V}^{*'}}{m_i + m_j} \right)^2 = m_i \left\{ X^{*2} - 2 \frac{m_j}{m_i + m_j} \mathbf{V}^{*'} \cdot \mathbf{X}^* + \frac{m_j^2}{(m_i + m_j)^2} V^{*2} \right\},$$

$$m_j(\mathbf{v}_j')^2 = m_j \left(\mathbf{X}^* + \frac{m_i \mathbf{V}^{*'}}{m_i + m_j} \right)^2 = m_j \left\{ X^{*2} + 2 \frac{m_i}{m_i + m_j} \mathbf{V}^{*'} \cdot \mathbf{X}^* + \frac{m_i^2}{(m_i + m_j)^2} V^{*2} \right\},$$

where $V^{*'} = \|\mathbf{V}^{*'}\| = |\mathbf{V}^{*'}| = |\mathbf{v}_j' - \mathbf{v}_i'| = |\mathbf{v}_i' - \mathbf{v}_j'|$. Therefore, following the steps used to obtain equation (2.4.12), we obtain:

$$m_i(\mathbf{v}_i')^2 + m_j(\mathbf{v}_j')^2 = (m_i + m_j) X^{*2} + \mu_{ij} V^{*2}. \quad (2.4.19)$$

Multiplying both sides of equations (2.4.12) and (2.4.19) by $\frac{1}{2}$ and substituting the resulting equations into equation (2.4.2) gives:

$$\frac{1}{2}(m_i + m_j)X^{*2} + \frac{1}{2}\mu_{ij}V^{*2} + I_i + I_j = \frac{1}{2}(m_i + m_j)X^{*2} + \frac{1}{2}\mu_{ij}V^{*2} + I'_i + I'_j.$$

Subtracting $\frac{1}{2}(m_i + m_j)X^{*2}$ from both sides of the previous equation, we obtain that the total energy $\mathcal{E}$ for elastic collisions in the centre of mass reference frame is given by:

$$\mathcal{E} = \frac{1}{2}\mu_{ij}|\mathbf{v}_i - \mathbf{v}_j|^2 + I_i + I_j = \frac{1}{2}\mu_{ij}|\mathbf{v}'_i - \mathbf{v}'_j|^2 + I'_i + I'_j. \quad (2.4.20)$$

Next we introduce a parameter $R \in [0, 1]$ and attribute the portions $R\mathcal{E}$ and $(1 - R)\mathcal{E}$ of the total energy to the kinetic and internal energies, respectively, of the outgoing pair:

$$\frac{1}{2}\mu_{ij}|\mathbf{v}'_i - \mathbf{v}'_j|^2 = R\mathcal{E} \quad (2.4.21)$$

$$I'_i + I'_j = (1 - R)\mathcal{E}. \quad (2.4.22)$$

Equation (2.4.21) can be parameterized by a unit vector $\boldsymbol{\omega} \in \mathbb{S}^2$ to obtain:

$$\mathbf{v}'_i - \mathbf{v}'_j = \sqrt{\frac{2R\mathcal{E}}{\mu_{ij}}} T_{\boldsymbol{\omega}} \left[\frac{\mathbf{v}_i - \mathbf{v}_j}{|\mathbf{v}_i - \mathbf{v}_j|} \right], \quad (2.4.23)$$

where $T_{\boldsymbol{\omega}}[\mathbf{x}] = \mathbf{x} - 2(\boldsymbol{\omega} \cdot \mathbf{x})\boldsymbol{\omega}$ is the symmetry with respect to the plane $\{\boldsymbol{\omega}\}^\perp$.

Furthermore, we introduce another parameter, $r \in [0, 1]$ and allocate the portions $r(1 - R)\mathcal{E}$, $(1 - r)(1 - R)\mathcal{E}$ of the internal energy to the internal energies of each outgoing particle, that is:

$$I'_i = r(1 - R)\mathcal{E} \quad \text{and} \quad I'_j = (1 - r)(1 - R)\mathcal{E}.$$

From the conservation of momentum for elastic collision given in equation (2.4.1), we obtain:

$$\begin{aligned} m_j \mathbf{v}'_j &= m_i \mathbf{v}_i + m_j \mathbf{v}_j - m_i \mathbf{v}'_i, \\ m_i \mathbf{v}'_i &= m_i \mathbf{v}_i + m_j \mathbf{v}_j - m_j \mathbf{v}'_j. \end{aligned} \quad (2.4.24)$$

Dividing both sides of the first equation of (2.4.24) by m_j and the second by m_i gives:

$$\mathbf{v}'_j = \frac{m_i \mathbf{v}_i + m_j \mathbf{v}_j - m_i \mathbf{v}'_i}{m_j}. \quad (2.4.25)$$

$$\mathbf{v}'_i = \frac{m_i \mathbf{v}_i + m_j \mathbf{v}_j - m_j \mathbf{v}'_j}{m_i}. \quad (2.4.26)$$

Substituting equation (2.4.25) into equation (2.4.23), we obtain:

$$\mathbf{v}'_i - \frac{m_i \mathbf{v}_i + m_j \mathbf{v}_j - m_i \mathbf{v}'_i}{m_j} = \sqrt{\frac{2R\mathcal{E}}{\mu_{ij}}} T_{\boldsymbol{\omega}} \left[\frac{\mathbf{v}_i - \mathbf{v}_j}{|\mathbf{v}_i - \mathbf{v}_j|} \right].$$

Multiplying both sides by m_j , we obtain:

$$m_j \mathbf{v}'_i - (m_i \mathbf{v}_i + m_j \mathbf{v}_j - m_i \mathbf{v}'_i) = m_j \sqrt{\frac{2R\mathcal{E}}{\mu_{ij}}} T_\omega \left[\frac{\mathbf{v}_i - \mathbf{v}_j}{|\mathbf{v}_i - \mathbf{v}_j|} \right].$$

Rearranging, we obtain:

$$(m_j + m_i) \mathbf{v}'_i = m_i \mathbf{v}_i + m_j \mathbf{v}_j + m_j \sqrt{\frac{2R\mathcal{E}}{\mu_{ij}}} T_\omega \left[\frac{\mathbf{v}_i - \mathbf{v}_j}{|\mathbf{v}_i - \mathbf{v}_j|} \right]. \quad (2.4.27)$$

Similarly, substituting equation (2.4.26) into equation (2.4.23), then multiply both sides of the resulting equation by m_i and rearrange, we obtain:

$$(m_j + m_i) \mathbf{v}'_j = m_i \mathbf{v}_i + m_j \mathbf{v}_j - m_i \sqrt{\frac{2R\mathcal{E}}{\mu_{ij}}} T_\omega \left[\frac{\mathbf{v}_i - \mathbf{v}_j}{|\mathbf{v}_i - \mathbf{v}_j|} \right]. \quad (2.4.28)$$

Dividing both sides of equations (2.4.27) and (2.4.28) by $m_i + m_j$, we obtain that the elastic post-collision velocities for bi-species collisions can be written in terms of pre-collision velocities as given below:

$$\begin{aligned} \mathbf{v}'_i &= \frac{m_i \mathbf{v}_i + m_j \mathbf{v}_j}{m_i + m_j} + \frac{m_j}{m_i + m_j} \sqrt{\frac{2R\mathcal{E}}{\mu_{ij}}} T_\omega \left[\frac{\mathbf{v}_i - \mathbf{v}_j}{|\mathbf{v}_i - \mathbf{v}_j|} \right], \\ \mathbf{v}'_j &= \frac{m_i \mathbf{v}_i + m_j \mathbf{v}_j}{m_i + m_j} - \frac{m_i}{m_i + m_j} \sqrt{\frac{2R\mathcal{E}}{\mu_{ij}}} T_\omega \left[\frac{\mathbf{v}_i - \mathbf{v}_j}{|\mathbf{v}_i - \mathbf{v}_j|} \right]. \end{aligned} \quad (2.4.29)$$

Remark 2.4.1. *In the particular case of mono-species elastic collisions, the molecular masses are equal, that is, $m_i = m_j$. Furthermore, in order to distinguish the velocities of the colliding pair, we set $j = i^*$ in equation (2.4.29) above. Therefore, the post-collision velocities for mono-species collisions can be written in terms of the pre-collision velocities as given below:*

$$\begin{aligned} \mathbf{v}'_i &= \frac{\mathbf{v}_i + \mathbf{v}_{i^*}}{2} + \sqrt{\frac{R\mathcal{E}}{m_i}} T_\omega \left[\frac{\mathbf{v}_i - \mathbf{v}_{i^*}}{|\mathbf{v}_i - \mathbf{v}_{i^*}|} \right], \\ \mathbf{v}'_{i^*} &= \frac{\mathbf{v}_i + \mathbf{v}_{i^*}}{2} - \sqrt{\frac{R\mathcal{E}}{m_i}} T_\omega \left[\frac{\mathbf{v}_i - \mathbf{v}_{i^*}}{|\mathbf{v}_i - \mathbf{v}_{i^*}|} \right]. \end{aligned} \quad (2.4.30)$$

□

Now let us consider reactive collisions. To obtain the post-collision velocities, we first compute the total energy $\mathcal{E}^*$ of the colliding pair in the centre of mass reference frame. To do this, let

$$\mathbf{X} = \frac{m_k \mathbf{v}'_k + m_l \mathbf{v}'_l}{m_k + m_l}, \quad (2.4.31)$$

be the centre of mass velocity after reactive collision and

$$\mathbf{V} = \mathbf{v}'_l - \mathbf{v}'_k \quad (2.4.32)$$

the relative velocity after reactive collision. From equation (2.4.32) above, we have that

$$\mathbf{v}'_l = \mathbf{V} + \mathbf{v}'_k. \quad (2.4.33)$$

Following the steps used to obtain equations (2.4.10) and (2.4.11), we obtain:

$$\mathbf{v}'_k = \mathbf{X} - \frac{m_l \mathbf{V}}{m_k + m_l} \quad (2.4.34)$$

$$\mathbf{v}'_l = \mathbf{X} + \frac{m_k \mathbf{V}}{m_k + m_l}. \quad (2.4.35)$$

Using equations (2.4.34) and (2.4.35), we obtain:

$$\begin{aligned} m_k (\mathbf{v}'_k)^2 &= m_k \left(\mathbf{X} - \frac{m_l \mathbf{V}}{m_k + m_l} \right)^2 = m_k \left\{ X^2 - 2 \frac{m_l}{m_k + m_l} \mathbf{V} \cdot \mathbf{X} + \frac{m_l^2}{(m_k + m_l)^2} V^2 \right\}, \\ m_l (\mathbf{v}'_l)^2 &= m_l \left(\mathbf{X} + \frac{m_k \mathbf{V}}{m_k + m_l} \right)^2 = m_l \left\{ X^2 + 2 \frac{m_k}{m_k + m_l} \mathbf{V} \cdot \mathbf{X} + \frac{m_k^2}{(m_k + m_l)^2} V^2 \right\}, \end{aligned}$$

where $X = \|\mathbf{X}\| = |\mathbf{X}|$ and $V = \|\mathbf{V}\| = |\mathbf{V}| = |\mathbf{v}'_l - \mathbf{v}'_k| = |\mathbf{v}'_k - \mathbf{v}'_l|$. Therefore, following the steps used to obtain equation (2.4.12), we obtain:

$$m_k (\mathbf{v}'_k)^2 + m_l (\mathbf{v}'_l)^2 = (m_k + m_l) X^2 + \mu_{kl} V^2. \quad (2.4.36)$$

Observe that using equations (2.4.3) and (2.4.4), we can rewrite equation (2.4.31) as follows:

$$\mathbf{X} = \frac{m_k \mathbf{v}'_k + m_l \mathbf{v}'_l}{m_k + m_l} = \frac{m_i \mathbf{v}_i + m_j \mathbf{v}_j}{m_i + m_j} = \mathbf{X}^*. \quad (2.4.37)$$

From equation (2.4.37) above, we have that $X = |\mathbf{X}| = |\mathbf{X}^*| = X^*$. Therefore, equation (2.4.36) can be rewritten as

$$m_k (\mathbf{v}'_k)^2 + m_l (\mathbf{v}'_l)^2 = (m_k + m_l) X^{*2} + \mu_{kl} V^2.$$

Using the conservation of mass for reactive collisions given in equation (2.4.3), we have that the previous equation can be written as:

$$m_k (\mathbf{v}'_k)^2 + m_l (\mathbf{v}'_l)^2 = (m_i + m_j) X^{*2} + \mu_{kl} V^2. \quad (2.4.38)$$

Multiplying both sides of equation (2.4.12) and (2.4.38) by $\frac{1}{2}$ and substituting the resulting equations into equation (2.4.5a), we obtain:

$$\frac{1}{2} (m_i + m_j) X^{*2} + \frac{1}{2} \mu_{ij} V^{*2} + I_i + I_j - \frac{Q_R}{2} = \frac{1}{2} (m_i + m_j) X^{*2} + \frac{1}{2} \mu_{kl} V^2 + I'_k + I'_l + \frac{Q_R}{2}.$$

Subtracting $\frac{1}{2} (m_i + m_j) X^{*2}$ from both sides of the previous equation we obtain that the total energy (kinetic, internal and chemical binding energies) $\mathcal{E}^*$ for reactive collisions in the centre of mass reference frame is given by:

$$\mathcal{E}^* = \frac{1}{2} \mu_{ij} |\mathbf{v}_i - \mathbf{v}_j|^2 + I_i + I_j - \frac{Q_R}{2} = \frac{1}{2} \mu_{kl} |\mathbf{v}'_k - \mathbf{v}'_l|^2 + I'_k + I'_l + \frac{Q_R}{2}. \quad (2.4.39)$$

To obtain the post-collision velocities for the forward chemical reaction, that is, for

$$(i, j, k, l) \in ((1, 2, 3, 4)(2, 1, 3, 4)),$$

we write equation (2.4.39) as given below:

$$\mathcal{E}^* = \frac{1}{2}\mu_{12}|\mathbf{v}_1 - \mathbf{v}_2|^2 + I_1 + I_2 - \frac{Q_R}{2} = \frac{1}{2}\mu_{34}|\mathbf{v}'_3 - \mathbf{v}'_4|^2 + I'_3 + I'_4 + \frac{Q_R}{2}. \quad (2.4.40)$$

Next, we introduce the parameters $R, r \in [0, 1]$ and assume the following re-partition of the total energy for reactive collisions $\mathcal{E}^*$ into kinetic and internal energies of the outgoing particles:

$$\frac{1}{2}\mu_{34}|\mathbf{v}'_3 - \mathbf{v}'_4|^2 = R\mathcal{E}^* - \frac{Q_R}{6}, \quad (2.4.41)$$

$$I'_3 + I'_4 = (1 - R)\mathcal{E}^* - \frac{Q_R}{3}, \quad (2.4.42)$$

with

$$I'_3 = r(1 - R)\mathcal{E}^* - \frac{Q_R}{6}, \quad I'_4 = (1 - r)(1 - R)\mathcal{E}^* - \frac{Q_R}{6}, \quad (2.4.43)$$

Equation (2.4.41) can be parameterized by a unit vector $\boldsymbol{\omega} \in \mathbb{S}^2$ as given below:

$$\mathbf{v}'_3 - \mathbf{v}'_4 = \sqrt{\frac{2}{\mu_{34}}} \left(R\mathcal{E}^* - \frac{Q_R}{6} \right)^{1/2} T_{\boldsymbol{\omega}} \left[\frac{\mathbf{v}_1 - \mathbf{v}_2}{|\mathbf{v}_1 - \mathbf{v}_2|} \right]. \quad (2.4.44)$$

Using equation (2.4.44) together with the conservation law of linear momentum given in equation (2.4.4) with $(i, j, k, l) \in (1, 2, 3, 4)$, and then following similar procedures as those used to obtain equation (2.4.29), one obtains that the reactive post-collision velocities for the forward chemical reaction can be expressed in terms of pre-collision velocities as given in the following equation:

$$\begin{aligned} \mathbf{v}'_3 &= \frac{m_1\mathbf{v}_1 + m_2\mathbf{v}_2}{m_1 + m_2} + \frac{m_4}{m_3 + m_4} \sqrt{\frac{2}{\mu_{34}}} \left(R\mathcal{E}^* - \frac{Q_R}{6} \right)^{1/2} T_{\boldsymbol{\omega}} \left[\frac{\mathbf{v}_1 - \mathbf{v}_2}{|\mathbf{v}_1 - \mathbf{v}_2|} \right], \\ \mathbf{v}'_4 &= \frac{m_1\mathbf{v}_1 + m_2\mathbf{v}_2}{m_1 + m_2} - \frac{m_3}{m_3 + m_4} \sqrt{\frac{2}{\mu_{34}}} \left(R\mathcal{E}^* - \frac{Q_R}{6} \right)^{1/2} T_{\boldsymbol{\omega}} \left[\frac{\mathbf{v}_1 - \mathbf{v}_2}{|\mathbf{v}_1 - \mathbf{v}_2|} \right]. \end{aligned} \quad (2.4.45)$$

Analogously, to obtain the post-collision velocities for the backward chemical reaction, that is for $(i, j, k, l) \in (3, 4, 1, 2), (4, 3, 2, 1)$, we write equation (2.4.39) as follows:

$$\mathcal{E}^* = \frac{1}{2}\mu_{34}|\mathbf{v}_3 - \mathbf{v}_4|^2 + I_3 + I_4 + \frac{Q_R}{2} = \frac{1}{2}\mu_{12}|\mathbf{v}'_1 - \mathbf{v}'_2|^2 + I'_1 + I'_2 - \frac{Q_R}{2}. \quad (2.4.46)$$

Then, as before, we assume the following re-partition of the total energy for reactive collisions $\mathcal{E}^*$ into kinetic and internal energies of the outgoing particles, namely

$$\frac{1}{2}\mu_{12}|\mathbf{v}'_1 - \mathbf{v}'_2|^2 = R\mathcal{E}^* + \frac{Q_R}{6}, \quad (2.4.47)$$

$$I'_1 + I'_2 = (1 - R)\mathcal{E}^* + \frac{Q_R}{3}, \quad (2.4.48)$$

with

$$I'_1 = r(1 - R)\mathcal{E}^* + \frac{Q_R}{6}, \quad I'_2 = (1 - r)(1 - R)\mathcal{E}^* + \frac{Q_R}{6}. \quad (2.4.49)$$

Equation (2.4.47) can be parameterized by a unit vector $\boldsymbol{\omega} \in \mathbb{S}^2$ as given below:

$$\mathbf{v}'_1 - \mathbf{v}'_2 = \sqrt{\frac{2}{\mu_{12}}} \left(R\mathcal{E}^* + \frac{Q_R}{6} \right)^{1/2} T_{\boldsymbol{\omega}} \left[\frac{\mathbf{v}_3 - \mathbf{v}_4}{|\mathbf{v}_3 - \mathbf{v}_4|} \right]. \quad (2.4.50)$$

Using equation (2.4.50) together with the conservation law of linear momentum (2.4.4) with $(i, j, k, l) \in (3, 4, 1, 2)$ and following similar procedures as those used to obtain (2.4.29), we can express the reactive post-collision velocities for the backward chemical reaction in terms of pre-collision velocities as:

$$\begin{aligned} \mathbf{v}'_1 &= \frac{m_3 \mathbf{v}_3 + m_4 \mathbf{v}_4}{m_3 + m_4} + \frac{m_2}{m_1 + m_2} \sqrt{\frac{2}{\mu_{12}}} \left(R\mathcal{E}^* + \frac{Q_R}{6} \right)^{1/2} T_{\boldsymbol{\omega}} \left[\frac{\mathbf{v}_3 - \mathbf{v}_4}{|\mathbf{v}_3 - \mathbf{v}_4|} \right], \\ \mathbf{v}'_2 &= \frac{m_3 \mathbf{v}_3 + m_4 \mathbf{v}_4}{m_3 + m_4} - \frac{m_1}{m_1 + m_2} \sqrt{\frac{2}{\mu_{12}}} \left(R\mathcal{E}^* + \frac{Q_R}{6} \right)^{1/2} T_{\boldsymbol{\omega}} \left[\frac{\mathbf{v}_3 - \mathbf{v}_4}{|\mathbf{v}_3 - \mathbf{v}_4|} \right]. \end{aligned} \quad (2.4.51)$$

For other details on the collision dynamics, the reader is referred to [45].

2.4.1.2 Kinetic Equations for the Reactive Polyatomic Mixture

For each species A_i , with $i = 1, 2, 3, 4$, let

$$f_i = f_i(t, \mathbf{x}, \mathbf{v}, I) \quad \text{with} \quad (t, \mathbf{x}, \mathbf{v}, I) \in \mathbb{R}^3 \times \Omega \subset \mathbb{R}^3 \times \mathbb{R}^3 \times [0, +\infty[.$$

be the distribution function. For sake of simplicity, in many cases the dependence of each distribution function on t and $\mathbf{x}$ will be omitted. More precisely, $f_i(t, \mathbf{x}, \mathbf{v}, I)$ will be written as $f_i(\mathbf{v}, I)$.

An important aspect of the present description is that the moments of each distribution function f_i , are defined in $L^1(\varphi_i(I) dI d\mathbf{v})$. In particular, the number density n_i , mass density ϱ_i , mean velocity $\mathbf{u}_i$ and temperature T_i of each species are respectively given by:

$$n_i(t, \mathbf{x}) = \int_{\mathbb{R}^3} \int_0^{+\infty} f_i(t, \mathbf{x}, \mathbf{v}, I) \varphi_i(I) dI d\mathbf{v}, \quad (2.4.52)$$

$$\varrho_i(t, \mathbf{x}) = m_i n_i(t, \mathbf{x}), \quad (2.4.53)$$

$$\mathbf{u}_i(t, \mathbf{x}) = \frac{1}{n_i(t, \mathbf{x})} \int_{\mathbb{R}^3} \int_0^{+\infty} \mathbf{v} f_i(t, \mathbf{x}, \mathbf{v}, I) \varphi_i(I) dI d\mathbf{v}, \quad (2.4.54)$$

$$T_i(t, \mathbf{x}) = \frac{1}{3k_B n_i(t, \mathbf{x})} \int_{\mathbb{R}^3} \int_0^{+\infty} m_i (\mathbf{v} - \mathbf{u}_i(t, \mathbf{x}))^2 f_i(t, \mathbf{x}, \mathbf{v}, I) \varphi_i(I) dI d\mathbf{v}. \quad (2.4.55)$$

In the absence of external forces, the time-space evolution of the distribution functions $f_i(\mathbf{v}, I)$, with $i = 1, \dots, 4$, is given by the following Maxwell-Boltzmann type system of equations:

$$\frac{\partial f_i}{\partial t} + \mathbf{v} \cdot \nabla_{\mathbf{x}} f_i = \sum_{j=1}^4 Q_{ij}^e(f_i, f_j) + Q_i^{react}, \quad i = 1, \dots, 4. \quad (2.4.56)$$

In equation (2.4.56) above, when $i \neq j$, the notation Q_{ij}^e represents the bi-species elastic collision operator. It is associated to collisions between one particle of constituent i and another one of constituent j .

However, when $i = j$, it reduces to the mono-species elastic collision operator Q_{ii}^e . Moreover, Q_i^{react} represents the reactive collision operator. The operators Q_{ij}^e and Q_i^{react} are defined as follows.

$$Q_{ij}^e(f_i, f_j) = \int_{\mathbb{R}^3} \int_0^{+\infty} \int_0^1 \int_0^1 \int_{\mathbb{S}^2} [f_i(\mathbf{v}'_i, I'_i) f_j(\mathbf{v}'_j, I'_j) - f_i(\mathbf{v}, I) f_j(\mathbf{v}_j, I_j)] \times B_{ij}(\mathbf{v}, \mathbf{v}_j, I, I_j, R, r, \boldsymbol{\omega}) (1 - R) |\mathbf{v} - \mathbf{v}_j|^{-1} \varphi_i(I)^{-1} d\boldsymbol{\omega} dr dR dI_j d\mathbf{v}_j, \quad (2.4.57)$$

for $i \neq j$, where B_{ij} are suitable cross-sections. Furthermore, $\mathbf{v}'_i$, $\mathbf{v}'_j$, I'_i and I'_j are given by:

$$\begin{aligned} \mathbf{v}'_i &= \frac{m_i \mathbf{v} + m_j \mathbf{v}_j}{m_i + m_j} + \frac{m_j}{m_i + m_j} \sqrt{\frac{2R\mathcal{E}}{\mu_{ij}}} T_{\boldsymbol{\omega}} \left[\frac{\mathbf{v} - \mathbf{v}_j}{|\mathbf{v} - \mathbf{v}_j|} \right], \\ \mathbf{v}'_j &= \frac{m_i \mathbf{v} + m_j \mathbf{v}_j}{m_i + m_j} - \frac{m_i}{m_i + m_j} \sqrt{\frac{2R\mathcal{E}}{\mu_{ij}}} T_{\boldsymbol{\omega}} \left[\frac{\mathbf{v} - \mathbf{v}_j}{|\mathbf{v} - \mathbf{v}_j|} \right], \\ I'_i &= \left(\frac{1}{2} \mu_{ij} |\mathbf{v} - \mathbf{v}_j|^2 + I + I_j \right) r (1 - R), \\ I'_j &= \left(\frac{1}{2} \mu_{ij} |\mathbf{v} - \mathbf{v}_j|^2 + I + I_j \right) (1 - r) (1 - R). \end{aligned}$$

In the case of mono-species elastic collisions, that is replacing the subscript j of the velocity variable with i_* , the operators have the following structure:

$$Q_{ii}^e(f_i, f_i) = \int_{\mathbb{R}^3} \int_0^{+\infty} \int_0^1 \int_0^1 \int_{\mathbb{S}^2} [f_i(\mathbf{v}'_i, I'_i) f_i(\mathbf{v}'_{i_*}, I'_{i_*}) - f_i(\mathbf{v}, I) f_i(\mathbf{v}_{i_*}, I_{i_*})] \times B_{ii}(\mathbf{v}, \mathbf{v}_{i_*}, I, I_{i_*}, R, r, \boldsymbol{\omega}) (1 - R) |\mathbf{v} - \mathbf{v}_{i_*}|^{-1} \varphi_i(I)^{-1} d\boldsymbol{\omega} dr dR dI_{i_*} d\mathbf{v}_{i_*}, \quad (2.4.58)$$

where B_{ii} are suitable cross-sections and $\mathbf{v}'_i$, $\mathbf{v}'_{i_*}$, I'_i and I'_{i_*} are given as defined below:

$$\begin{aligned} \mathbf{v}'_i &= \frac{\mathbf{v} + \mathbf{v}_{i_*}}{2} + \sqrt{\frac{R\mathcal{E}}{m_i}} T_{\boldsymbol{\omega}} \left[\frac{\mathbf{v} - \mathbf{v}_{i_*}}{|\mathbf{v} - \mathbf{v}_{i_*}|} \right], \\ \mathbf{v}'_{i_*} &= \frac{\mathbf{v} + \mathbf{v}_{i_*}}{2} - \sqrt{\frac{R\mathcal{E}}{m_i}} T_{\boldsymbol{\omega}} \left[\frac{\mathbf{v} - \mathbf{v}_{i_*}}{|\mathbf{v} - \mathbf{v}_{i_*}|} \right], \\ I'_i &= \left(\frac{m_i}{4} |\mathbf{v} - \mathbf{v}_{i_*}|^2 + I + I_{i_*} \right) r (1 - R), \\ I'_{i_*} &= \left(\frac{m_i}{4} |\mathbf{v} - \mathbf{v}_{i_*}|^2 + I + I_{i_*} \right) (1 - r) (1 - R). \end{aligned}$$

The reactive collision operators are defined in a more involved way. To give their forms, we consider for some suitable sets F_i the Heaviside-like function

$$H_i(\xi) = \begin{cases} 1, & \xi \in F_i \\ 0, & \xi \notin F_i, \end{cases} \quad i = 1, \dots, 4,$$

and let $B^{react} : \mathbb{R}^3 \times \mathbb{R}^3 \times \mathbb{R}^+ \times \mathbb{R}^+ \times [0, 1]^2 \times \mathbb{S}^2 \rightarrow \mathbb{R}^+$ be a suitable cross-section.

Let us first treat the case of the forward reaction. To do this, we define the total energy

$$\mathcal{E}_1^* = \frac{1}{2} \mu_{12} |\mathbf{v} - \mathbf{v}_2|^2 + I + I_2 - \frac{Q_R}{2},$$

the reactive post-collision velocities and internal energies

$$\begin{aligned} \mathbf{v}'_3 &= \frac{m_1 \mathbf{v} + m_2 \mathbf{v}_2}{m_1 + m_2} + \frac{m_4}{m_3 + m_4} \sqrt{\frac{2}{\mu_{34}}} \left(R \mathcal{E}_1^* - \frac{Q_R}{6} \right)^{1/2} T_\omega \left[\frac{\mathbf{v} - \mathbf{v}_2}{|\mathbf{v} - \mathbf{v}_2|} \right], \\ \mathbf{v}'_4 &= \frac{m_1 \mathbf{v} + m_2 \mathbf{v}_2}{m_1 + m_2} - \frac{m_3}{m_3 + m_4} \sqrt{\frac{2}{\mu_{34}}} \left(R \mathcal{E}_1^* - \frac{Q_R}{6} \right)^{1/2} T_\omega \left[\frac{\mathbf{v} - \mathbf{v}_2}{|\mathbf{v} - \mathbf{v}_2|} \right], \\ I'_3 &= r(1 - R) \mathcal{E}_1^* - \frac{Q_R}{6}, \\ I'_4 &= (1 - r)(1 - R) \mathcal{E}_1^* - \frac{Q_R}{6}, \end{aligned}$$

as well as the admissible set

$$F_1 = \left\{ (I, I_2, r, R, \mathbf{v}, \mathbf{v}_2) : I \geq \frac{Q_R}{6}, I_2 \geq \frac{Q_R}{6}, R \mathcal{E}_1^* \geq \frac{Q_R}{6}, \right. \\ \left. \frac{\mu_{12}}{2} |\mathbf{v} - \mathbf{v}_2|^2 \geq \frac{Q_R}{6}, (1 - R)r \mathcal{E}_1^* \geq \frac{Q_R}{6}, (1 - R)(1 - r) \mathcal{E}_1^* \geq \frac{Q_R}{6} \right\}.$$

The first collision operator describing the forward chemical reaction is hence:

$$\begin{aligned} Q_1^{react}(\mathbf{v}, I) &= \int_{\mathbb{R}^3} \int_0^{+\infty} \int_0^1 \int_0^1 \int_{\mathbb{S}^2} \left[\left(\frac{m_1 m_2}{m_3 m_4} \right)^3 f_3(\mathbf{v}'_3, I'_3) f_4(\mathbf{v}'_4, I'_4) - f_1(\mathbf{v}, I) f_2(\mathbf{v}_2, I_2) \right] \\ &\quad \times H_1(I, I_2, r, R, \mathbf{v}, \mathbf{v}_2) B^{react}(\mathbf{v}, \mathbf{v}_2, I, I_2, R, r, \omega) (m_1 m_2)^{-2} \\ &\quad \times |\mathbf{v} - \mathbf{v}_2|^{-1} (1 - R) \varphi_1(I)^{-1} d\omega dr dR dI_2 d\mathbf{v}_2. \end{aligned} \quad (2.4.59)$$

The structure of Q_2^{react} is similar and to obtain it, we define the total energy

$$\mathcal{E}_2^* = \frac{1}{2} \mu_{12} |\mathbf{v} - \mathbf{v}_1|^2 + I + I_1 - \frac{Q_R}{2},$$

the reactive post-collision velocities and internal energies

$$\begin{aligned} \mathbf{v}'_3 &= \frac{m_1 \mathbf{v}_1 + m_2 \mathbf{v}}{m_1 + m_2} + \frac{m_4}{m_3 + m_4} \sqrt{\frac{2}{\mu_{34}}} \left(R \mathcal{E}_2^* - \frac{Q_R}{6} \right)^{1/2} T_\omega \left[\frac{\mathbf{v}_1 - \mathbf{v}}{|\mathbf{v}_1 - \mathbf{v}|} \right], \\ \mathbf{v}'_4 &= \frac{m_1 \mathbf{v}_1 + m_2 \mathbf{v}}{m_1 + m_2} - \frac{m_3}{m_3 + m_4} \sqrt{\frac{2}{\mu_{34}}} \left(R \mathcal{E}_2^* - \frac{Q_R}{6} \right)^{1/2} T_\omega \left[\frac{\mathbf{v}_1 - \mathbf{v}}{|\mathbf{v}_1 - \mathbf{v}|} \right], \\ I'_3 &= r(1 - R) \mathcal{E}_2^* - \frac{Q_R}{6}, \\ I'_4 &= (1 - r)(1 - R) \mathcal{E}_2^* - \frac{Q_R}{6}, \end{aligned}$$

as well as the admissible set

$$F_2 = \left\{ (I, I_1, r, R, \mathbf{v}, \mathbf{v}_1) : I \geq \frac{Q_R}{6}, I_1 \geq \frac{Q_R}{6}, R \mathcal{E}_2^* \geq \frac{Q_R}{6}, \right. \\ \left. \frac{\mu_{12}}{2} |\mathbf{v} - \mathbf{v}_1|^2 \geq \frac{Q_R}{6}, (1 - R)r \mathcal{E}_2^* \geq \frac{Q_R}{6}, (1 - R)(1 - r) \mathcal{E}_2^* \geq \frac{Q_R}{6} \right\}.$$

The collision operator Q_2^{react} describing the forward chemical reaction is hence:

$$\begin{aligned}
Q_2^{react}(\mathbf{v}, I) = & \int_{\mathbb{R}^3} \int_0^{+\infty} \int_0^1 \int_{\mathbb{S}^2} \left[\left(\frac{m_1 m_2}{m_3 m_4} \right)^3 f_3(\mathbf{v}'_3, I'_3) f_4(\mathbf{v}'_4, I'_4) - f_2(\mathbf{v}, I) f_1(\mathbf{v}_1, I_1) \right] \\
& \times H_2(I, I_1, r, R, \mathbf{v}, \mathbf{v}_1) B^{react}(\mathbf{v}, \mathbf{v}_1, I, I_1, R, r, \boldsymbol{\omega}) (m_1 m_2)^{-2} \\
& \times |\mathbf{v} - \mathbf{v}_1|^{-1} (1 - R) \varphi_2(I)^{-1} d\boldsymbol{\omega} dr dR dI_1 d\mathbf{v}_1.
\end{aligned} \tag{2.4.60}$$

In the case of the backward chemical reaction, we have to treat two cases. To do this, let

$$\mathcal{E}_3^* = \frac{1}{2} \mu_{34} |\mathbf{v} - \mathbf{v}_4|^2 + I + I_4 + \frac{Q_R}{2}$$

be the total energy. Then, as before, we write the reactive post collision velocities and internal energies, respectively as given below:

$$\begin{aligned}
\mathbf{v}'_1 &= \frac{m_3 \mathbf{v} + m_4 \mathbf{v}_4}{m_3 + m_4} + \frac{m_2}{m_1 + m_2} \sqrt{\frac{2}{\mu_{12}}} \left(R \mathcal{E}_3^* + \frac{Q_R}{6} \right)^{1/2} T_{\boldsymbol{\omega}} \left[\frac{\mathbf{v} - \mathbf{v}_4}{|\mathbf{v} - \mathbf{v}_4|} \right], \\
\mathbf{v}'_2 &= \frac{m_3 \mathbf{v} + m_4 \mathbf{v}_4}{m_3 + m_4} - \frac{m_1}{m_1 + m_2} \sqrt{\frac{2}{\mu_{12}}} \left(R \mathcal{E}_3^* + \frac{Q_R}{6} \right)^{1/2} T_{\boldsymbol{\omega}} \left[\frac{\mathbf{v} - \mathbf{v}_4}{|\mathbf{v} - \mathbf{v}_4|} \right], \\
I'_1 &= r(1 - R) \mathcal{E}_3^* + \frac{Q_R}{6}, \\
I'_2 &= (1 - r)(1 - R) \mathcal{E}_3^* + \frac{Q_R}{6}.
\end{aligned}$$

The admissible set F_3 is

$$F_3 = \left\{ (I_4, r, R, \mathbf{v}_4) : I_4 \geq 0, \mathbf{v}_4 \in \mathbb{R}^3, r, R \in [0, 1] \right\}.$$

Hence the reactive collision operator Q_3^{react} describing the backward reaction is given by:

$$\begin{aligned}
Q_3^{react}(\mathbf{v}, I) = & \int_{\mathbb{R}^3} \int_0^{+\infty} \int_0^1 \int_{\mathbb{S}^2} \left[\left(\frac{m_3 m_4}{m_1 m_2} \right)^3 f_1(\mathbf{v}'_1, I'_1) f_2(\mathbf{v}'_2, I'_2) - f_3(\mathbf{v}, I) f_4(\mathbf{v}_4, I_4) \right] \\
& \times H_3(I_4, r, R, \mathbf{v}_4) B^{react}(\mathbf{v}, \mathbf{v}_4, I, I_4, R, r, \boldsymbol{\omega}) (m_3 m_4)^{-2} \\
& \times |\mathbf{v} - \mathbf{v}_4|^{-1} (1 - R) \varphi_3(I)^{-1} d\boldsymbol{\omega} dr dR dI_4 d\mathbf{v}_4.
\end{aligned} \tag{2.4.61}$$

We conclude the description of the reactive collision operators by defining Q_4^{react} . Let

$$\mathcal{E}_4^* = \frac{1}{2} \mu_{34} |\mathbf{v} - \mathbf{v}_3|^2 + I + I_3 + \frac{Q_R}{2}$$

be the total energy. Then, as before, we write the reactive post collision velocities and internal energies, respectively as given below:

$$\mathbf{v}'_1 = \frac{m_3 \mathbf{v}_3 + m_4 \mathbf{v}}{m_3 + m_4} + \frac{m_2}{m_1 + m_2} \sqrt{\frac{2}{\mu_{12}}} \left(R \mathcal{E}_4^* + \frac{Q_R}{6} \right)^{1/2} T_{\boldsymbol{\omega}} \left[\frac{\mathbf{v}_3 - \mathbf{v}}{|\mathbf{v}_3 - \mathbf{v}|} \right], \tag{2.4.62}$$

$$\mathbf{v}'_2 = \frac{m_3 \mathbf{v}_3 + m_4 \mathbf{v}}{m_3 + m_4} - \frac{m_1}{m_1 + m_2} \sqrt{\frac{2}{\mu_{12}}} \left(R \mathcal{E}_4^* + \frac{Q_R}{6} \right)^{1/2} T_{\boldsymbol{\omega}} \left[\frac{\mathbf{v}_3 - \mathbf{v}}{|\mathbf{v}_3 - \mathbf{v}|} \right]. \tag{2.4.63}$$

$$I'_1 = r(1 - R) \mathcal{E}_4^* + \frac{Q_R}{6}, \tag{2.4.64}$$

$$I'_2 = (1-r)(1-R)\mathcal{E}_4^* + \frac{Q_R}{6}. \quad (2.4.65)$$

The admissible set F_4 is

$$F_4 = \left\{ (I_3, r, R, \mathbf{v}_3) : I_3 \geq 0, \mathbf{v}_3 \in \mathbb{R}^3, r, R \in [0, 1] \right\}.$$

Hence the reactive collision operator Q_4^{react} describing the backward reaction is given by:

$$\begin{aligned} Q_4^{react}(\mathbf{v}, I) = & \int_{\mathbb{R}^3} \int_0^{+\infty} \int_0^1 \int_0^1 \int_{\mathbb{S}^2} \left[\left(\frac{m_3 m_4}{m_1 m_2} \right)^3 f_1(\mathbf{v}'_1, I'_1) f_2(\mathbf{v}'_2, I'_2) - f_4(\mathbf{v}, I) f_3(\mathbf{v}_3, I_3) \right] \\ & \times H_4(I_3, r, R, \mathbf{v}_3) B^{react}(\mathbf{v}, \mathbf{v}_3, I, I_3, R, r, \omega) (m_3 m_4)^{-2} \\ & \times |\mathbf{v} - \mathbf{v}_3|^{-1} (1-R) \varphi_4(I)^{-1} d\omega dr dR dI_3 d\mathbf{v}_3. \end{aligned} \quad (2.4.66)$$

2.4.2 Properties of the Collision Operators

In this subsection, a review of some of the properties of the collision operators given in [45] will be given. These properties will be used later in the analysis of the kinetic model. In particular, in the study of the hydrodynamic limits.

Lemma 2.4.2. *Let $\psi: \mathbb{R}^3 \times [0, +\infty) \rightarrow \mathbb{R}$ be a function such that the weak formulation*

$$\int_{\mathbb{R}^3} \int_0^{+\infty} Q_{ii}^e \psi(\mathbf{v}, I) \varphi_i(I) dI d\mathbf{v}$$

makes sense. Then

$$\begin{aligned} & \int_{\mathbb{R}^3} \int_0^{+\infty} Q_{ii}^e \psi(\mathbf{v}, I) \varphi_i(I) dI d\mathbf{v} \\ &= -\frac{1}{4} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_0^{+\infty} \int_0^{+\infty} \int_0^1 \int_0^1 \int_{\mathbb{S}^2} \left[f_i(\mathbf{v}'_i, I'_i) f_i(\mathbf{v}'_{i_*}, I'_{i_*}) - f_i(\mathbf{v}, I) f_i(\mathbf{v}_{i_*}, I_{i_*}) \right] \\ & \quad \left[\psi(\mathbf{v}'_i, I'_i) + \psi(\mathbf{v}'_{i_*}, I'_{i_*}) - \psi(\mathbf{v}, I) - \psi(\mathbf{v}_{i_*}, I_{i_*}) \right] B_{ii}(\mathbf{v}, \mathbf{v}_{i_*}, I, I_{i_*}, R, r, \omega) \\ & \quad \times (1-R) |\mathbf{v} - \mathbf{v}_{i_*}|^{-1} d\omega dr dR dI_{i_*} dI d\mathbf{v}_{i_*} d\mathbf{v}. \end{aligned} \quad (2.4.67)$$

Proof. See Lemma 2, page 223 of [45]. □

Lemma 2.4.3. *Let $j \neq i$ and $\psi: \mathbb{R}^3 \times [0, +\infty) \rightarrow \mathbb{R}$ be a function such that the formulas*

$$\begin{aligned} & \int_{\mathbb{R}^3} \int_0^{+\infty} Q_{ij}^e \psi(\mathbf{v}, I) \varphi_i(I) dI d\mathbf{v} \\ & \int_{\mathbb{R}^3} \int_0^{+\infty} Q_{ji}^e \psi(\mathbf{v}_j, I_j) \varphi_j(I_j) dI_j d\mathbf{v}_j \end{aligned}$$

make sense. Then

$$\begin{aligned}
& \int_{\mathbb{R}^3} \int_0^{+\infty} Q_{ij}^e \psi(\mathbf{v}, I) \varphi_i(I) dI d\mathbf{v} \\
&= -\frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_0^{+\infty} \int_0^{+\infty} \int_0^1 \int_0^1 \int_{\mathbb{S}^2} \left[f_i(\mathbf{v}'_i, I'_i) f_j(\mathbf{v}'_j, I'_j) - f_i(\mathbf{v}, I) f_j(\mathbf{v}_j, I_j) \right] \\
&\times \left[\psi(\mathbf{v}'_i, I'_i) - \psi(\mathbf{v}, I) \right] B_{ij}(\mathbf{v}, \mathbf{v}_j, I, I_j, R, r, \omega) (1-R) |\mathbf{v} - \mathbf{v}_j|^{-1} d\boldsymbol{\omega} dr dR dI_j dI d\mathbf{v}_j d\mathbf{v}
\end{aligned} \tag{2.4.68}$$

and

$$\begin{aligned}
& \int_{\mathbb{R}^3} \int_0^{+\infty} Q_{ij}^e \psi(\mathbf{v}, I) \varphi_i(I) dI d\mathbf{v} + \int_{\mathbb{R}^3} \int_0^{+\infty} Q_{ji}^e \psi(\mathbf{v}_j, I_j) \varphi_j(I_j) dI_j d\mathbf{v}_j \\
&= -\frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_0^{+\infty} \int_0^{+\infty} \int_0^1 \int_0^1 \int_{\mathbb{S}^2} \left[f_i(\mathbf{v}'_i, I'_i) f_j(\mathbf{v}'_j, I'_j) - f_i(\mathbf{v}, I) f_j(\mathbf{v}_j, I_j) \right] \\
&\times \left[\psi(\mathbf{v}'_i, I'_i) + \psi(\mathbf{v}'_j, I'_j) - \psi(\mathbf{v}, I) - \psi(\mathbf{v}_j, I_j) \right] B_{ij}(\mathbf{v}, \mathbf{v}_j, I, I_j, R, r, \omega) \\
&\times (1-R) |\mathbf{v} - \mathbf{v}_j|^{-1} d\boldsymbol{\omega} dr dR dI_j dI d\mathbf{v}_j d\mathbf{v}.
\end{aligned} \tag{2.4.69}$$

Proof. See Lemma 3, page 224 of [45]. □

Lemma 2.4.4. Let $\psi : \mathbb{R}^3 \times [0, +\infty) \rightarrow \mathbb{R}$ be a function such that for all $i = 1, 2, 3, 4$, the formula

$$\int_{\mathbb{R}^3} \int_0^{+\infty} Q_i^{react} \psi(\mathbf{v}, I) \varphi_i(I) dI d\mathbf{v}$$

makes sense. Additionally, if $B^{react}(\mathbf{v}_i, \mathbf{v}_j, I_i, I_j, R, r, \omega)$ for $(i, j, k, l) \in \{(1, 2, 3, 4), (2, 1, 4, 3)\}$ is equal to $B^{react}(\mathbf{v}_i, \mathbf{v}_j, I_i, I_j, R, r, \omega)$ for $(i, j, k, l) \in \{(3, 4, 1, 2), (4, 3, 2, 1)\}$, then

$$\begin{aligned}
& \sum_{i=1}^4 \int_{\mathbb{R}^3} \int_0^{+\infty} Q_i^{react} \psi(\mathbf{v}, I) \varphi_i(I) dI d\mathbf{v} \\
&= -\int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_0^{+\infty} \int_0^{+\infty} \int_0^1 \int_0^1 \int_{\mathbb{S}^2} \left[\frac{f_k(\mathbf{v}'_k, I'_k) f_l(\mathbf{v}'_l, I'_l)}{(m_k m_l)^3} - \frac{f_i(\mathbf{v}_i, I_i) f_j(\mathbf{v}_j, I_j)}{(m_i m_j)^3} \right] \\
&\times \left[\psi(\mathbf{v}'_k, I'_k) + \psi(\mathbf{v}'_l, I'_l) - \psi(\mathbf{v}_i, I_i) - \psi(\mathbf{v}_j, I_j) \right] H_i B^{react}(\mathbf{v}_i, \mathbf{v}_j, I_i, I_j, R, r, \omega) \\
&\times m_i m_j (1-R) |\mathbf{v}_i - \mathbf{v}_j|^{-1} d\boldsymbol{\omega} dr dR dI_j dI_i d\mathbf{v}_j d\mathbf{v}_i.
\end{aligned} \tag{2.4.70}$$

Proof. See Lemma 5, page 229 of [45]. □

2.4.3 Conservation Laws and Chemical Rates

The conservation laws of the model are obtained from the properties stated in lemmas 2.4.2, 2.4.3 and 2.4.4 of subsection 2.4.2.

Lemma 2.4.5. Consider the functions $\Psi(\mathbf{v}, I)$ defined by $\Psi = (1, 0, 1, 0)$, $\Psi = (1, 0, 0, 1)$, $\Psi = (0, 1, 1, 0)$ and also $\Psi(\mathbf{v}, I)$ such that $\Psi = (\psi_1, \psi_2, \psi_3, \psi_4)$, with $\psi_i = m_i \mathbf{v}_{x_1}$ or $m_i \mathbf{v}_{x_2}$ or $m_i \mathbf{v}_{x_3}$, as well as $\Psi = (\psi_1, \psi_2, \psi_3, \psi_4)$, with $\psi_i = \frac{1}{2} m_i (\mathbf{v})^2 + I + E_i$. Then,

$$\sum_{i=1}^4 \int_{\mathbb{R}^3} \int_0^{+\infty} \left(\sum_{j=1}^4 Q_{ij}^e + Q_i^{react} \right) \psi_i(\mathbf{v}, I) \varphi_i(I) dI d\mathbf{v} = 0. \quad (2.4.71)$$

Proof. This is an immediate consequences of lemmas 2.4.2, 2.4.3 and 2.4.4. See equations (22), (27), (28), (45), pages 224, 225, 226, 231 of [45]. $\square$

Property (2.4.71) indicates that elastic and reactive collision operators are consistent with the conservation of physical quantities, namely partial number densities $n_1 + n_3$, $n_1 + n_4$, $n_2 + n_3$, momentum and total energy of the whole mixture (kinetic, internal and chemical binding).

Lemma 2.4.6. *The reactive collision operators are such that*

$$\begin{aligned} \int_{\mathbb{R}^3} \int_0^{+\infty} Q_1^{react} \varphi_1(I_1) dI_1 d\mathbf{v}_1 &= \int_{\mathbb{R}^3} \int_0^{+\infty} Q_2^{react} \varphi_2(I_2) dI_2 d\mathbf{v}_2 \\ &= - \int_{\mathbb{R}^3} \int_0^{+\infty} Q_3^{react} \varphi_3(I_3) dI_3 d\mathbf{v}_3 \\ &= - \int_{\mathbb{R}^3} \int_0^{+\infty} Q_4^{react} \varphi_4(I_4) dI_4 d\mathbf{v}_4. \end{aligned} \quad (2.4.72)$$

Proof. Let $\varphi = (\varphi(\mathbf{v}_1), \varphi(\mathbf{v}_2), \varphi(\mathbf{v}_3), \varphi(\mathbf{v}_4))$ then setting

$$\varphi = (1, 0, 0, 0), \quad \varphi = (0, 1, 0, 0), \quad \varphi = (0, 0, 1, 0), \quad \varphi = (0, 0, 0, 1),$$

respectively, in equation (2.4.70) with

$$(i, j, k, l) \in \left((1, 2, 3, 4), (2, 1, 4, 3), (3, 4, 1, 2), (4, 3, 2, 1) \right)$$

gives the desired result. $\square$

The property of the reactive collision operator given in equation (2.4.72) indicate that reactive collision terms assure the correct chemical exchange rates for the considered chemical reaction (2.3.1).

2.4.4 Equilibrium state and $\mathcal{H}$ -Theorem

In paper [45], the equilibrium solutions of the kinetic equations given in equation (2.4.56) were studied in two steps. In the first step, the mechanical equilibrium associated to the mono-species and bi-species elastic collision operators were considered. In the second step, the chemical equilibrium associated to the reactive collision operator was considered.

The mechanical equilibrium is defined by distribution functions $f_i(\mathbf{v}, I)$, with $i = 1, \dots, 4$, such that

$$Q_{ij}^e(f_i, f_j) = 0, \quad i, j = 1, \dots, 4. \quad (2.4.73)$$

Assuming that the mechanical equilibrium is reached, the chemical equilibrium is then defined in paper [45] by distribution functions satisfying, besides conditions (2.4.73), the further condition

$$Q_i^{react} = 0, \quad i = 1, \dots, 4. \quad (2.4.74)$$

The following proposition summarises the $\mathcal{H}$ -theorems stated in paper [45] and characterises the equilibrium states of the model.

Proposition 2.4.7. *Let $B_{ij}(\mathbf{v}, \mathbf{v}_j, I, I_j, R, r, \omega)$ and $B^{react}(\mathbf{v}, \mathbf{v}_j, I, I_j, R, r, \omega)$ be strictly positive almost everywhere and let the distribution functions f_i be non-negative for all $i = 1, \dots, 4$ such that the collision operators Q_{ij}^e and Q_i^{react} are well defined.*

1. *Concerning the mechanical equilibrium, the following properties are equivalent.*

$$(a) \quad Q_{ij}^e(f_i, f_j) = 0 \text{ for all } i, j = 1, \dots, 4, \quad \mathbf{v} \in \mathbb{R}^3, \quad I \in \mathbb{R}^+;$$

$$(b) \quad \sum_{i,j=1}^4 \int_{\mathbb{R}^3} \int_0^{+\infty} Q_{ij}^e(f_i, f_j) \log\left(\frac{f_i(\mathbf{v}, I)}{m_i^3}\right) \varphi_i(I) dI d\mathbf{v} = 0;$$

$$(c) \quad \text{There exist } n_i \geq 0, \quad i = 1, \dots, 4, \quad \mathbf{u} \in \mathbb{R}^3 \text{ and } T > 0 \text{ such that } f_i(\mathbf{v}, I) = M(n_i, \mathbf{u}, T), \text{ where}$$

$$M(n_i, \mathbf{u}, T) = \frac{n_i(t, \mathbf{x})}{q_i(T(t, \mathbf{x}))} \left(\frac{m_i}{2\pi k_B T(t, \mathbf{x})} \right)^{3/2} \times \exp\left(-\frac{m_i(\mathbf{v} - \mathbf{u}(t, \mathbf{x}))^2}{2k_B T(t, \mathbf{x})} - \frac{I}{k_B T(t, \mathbf{x})} \right) \quad (2.4.75)$$

and

$$q_i(T(t, \mathbf{x})) = \int_0^{+\infty} \varphi_i(I) \exp\left(-\frac{I}{k_B T(t, \mathbf{x})} \right) dI, \quad (2.4.76)$$

i.e. f_i are Maxwellian distributions.

2. *Assuming that the mechanical equilibrium is reached, that is, the distribution functions f_i are given by equation (2.4.75), then the following three properties related to chemical equilibrium are equivalent*

$$(a) \quad Q_i^{react} = 0 \text{ for all } i = 1, \dots, 4, \quad \mathbf{v} \in \mathbb{R}^3, \quad I \in \mathbb{R}^+;$$

$$(b) \quad \sum_{i=1}^4 \int_{\mathbb{R}^3} \int_0^{+\infty} Q_i^{react} \log\left(\frac{f_i(\mathbf{v}, I)}{m_i^3}\right) \varphi_i(I) dI d\mathbf{v} = 0;$$

(c) *The following mass action law holds*

$$\frac{n_1 n_2}{n_3 n_4} = \left(\frac{m_1 m_2}{m_3 m_4} \right)^{3/2} \frac{q_1(T) q_2(T)}{q_3(T) q_4(T)} \exp\left(\frac{Q_R}{k_B T} \right). \quad (2.4.77)$$

Proof. See Propositions 1 and 2, pages 231–233 of [45]

□

Chapter 3

Diffusion in Multicomponent Mixtures

This chapter, deals with the continuum physics approach to multicomponent diffusion. Specifically, the continuum physics derivation of two different diffusion and reaction-diffusion models will be presented. Furthermore, an introduce of how to derive hydrodynamic models from the Maxwell-Boltzmann equations for reactive mixtures will be given. Finally, the types of diffusion problems to be studied in this thesis will be described.

3.1 The Continuum Physics Approach to Diffusion Modelling in Multicomponent Fluids

Consider a multi-species reactive gaseous mixture of four species A_i with $i = 1, 2, 3, 4$, participating in a chemical reaction of type described by the chemical equation (2.3.1). The starting point for the derivation of diffusion models in continuum physics is the mass balance equations for the species.

3.1.1 Mass Balance Equation

For each species A_i , let $\varrho_i(t, \mathbf{x}) \geq 0$ be the mass density, $\mathbf{u}_i(t, \mathbf{x})$ the mean or average velocity and $r_i(t, \mathbf{x})$ the production rate of mass density due to the chemical reaction, where $\mathbf{x} \in \Omega$ and $t > 0$. The mass balance equation for each constituent in the reactive mixture reads:

$$\frac{\partial \varrho_i}{\partial t} + \frac{\partial}{\partial \mathbf{x}}(\varrho_i \mathbf{u}_i) = r_i, \quad i = 1, 2, 3, 4 \quad \mathbf{x} \in \Omega, \quad t > 0. \quad (3.1.1)$$

Due to the type of chemical reaction (2.3.1), the rate of production of the species satisfy the condition

$$\sum_{i=1}^4 r_i = 0, \quad (3.1.2)$$

which results in the conservation of total mass.

For a molar based description of the reactive mixture (see, for example [46]), one has to introduce for each species A_i the molar mass M_i and define the following quantities:

$$c_i(t, \mathbf{x}) = \frac{\varrho_i}{M_i}, \quad (\text{molar concentration}) \quad (3.1.3)$$

$$\mathcal{J}_i(t, \mathbf{x}) = \frac{r_i}{M_i}, \quad (\text{rate of production of the molar concentration}) \quad (3.1.4)$$

$$v_i(t, \mathbf{x}) = \frac{c_i}{c}, \quad (\text{mole fraction}) \quad (3.1.5)$$

$$\mathbf{J}_i(t, \mathbf{x}) = c_i(\mathbf{u}_i - \mathbf{u}), \quad (\text{molar diffusion flux}) \quad (3.1.6)$$

$$\mathbf{N}_i(t, \mathbf{x}) = c_i \mathbf{u}_i. \quad (\text{molar flux}) \quad (3.1.7)$$

In equation (3.1.5), $c := c(t, \mathbf{x})$ is the molar concentration of the mixture, while in equation (3.1.6) $\mathbf{u} := \mathbf{u}(t, \mathbf{x})$ is the molar average velocity of the mixture. The quantities c and $\mathbf{u}$ are defined as given below:

$$c(t, \mathbf{x}) = \sum_{i=1}^4 c_i, \quad \mathbf{x} \in \Omega, \quad t > 0 \quad (3.1.8)$$

$$\mathbf{u}(t, \mathbf{x}) = \sum_{i=1}^4 v_i \mathbf{u}_i = \sum_{i=1}^4 \frac{c_i}{c} \mathbf{u}_i = \frac{1}{c} \sum_{i=1}^4 c_i \mathbf{u}_i \quad \mathbf{x} \in \Omega, \quad t > 0. \quad (3.1.9)$$

Observe that multiplying both sides of the molar average velocity of the mixture $\mathbf{u}$, that is, equation (3.1.9) by the molar concentration of the mixture c we obtain:

$$c\mathbf{u} = \sum_{i=1}^4 c_i \mathbf{u}_i. \quad (3.1.10)$$

Summing the molar diffusion flux over all species and using equations (3.1.8), (3.1.10), we obtain the following constraint:

$$\sum_{i=1}^4 \mathbf{J}_i = \sum_{i=1}^4 (c_i \mathbf{u}_i - c_i \mathbf{u}) = \sum_{i=1}^4 c_i \mathbf{u}_i - \mathbf{u} \sum_{i=1}^4 c_i = c\mathbf{u} - c\mathbf{u} = 0. \quad (3.1.11)$$

Multiplying both sides of equations (3.1.3) and (3.1.4) by M_i , we obtain:

$$M_i c_i = \rho_i, \quad M_i \mathcal{J}_i = r_i, \quad (3.1.12)$$

respectively. Substituting both equations of (3.1.12) into equation (3.1.1), we obtain:

$$\frac{\partial}{\partial t}(M_i c_i) + \frac{\partial}{\partial \mathbf{x}}(M_i c_i \mathbf{u}_i) = M_i \mathcal{J}_i, \quad i = 1, 2, 3, 4 \quad \mathbf{x} \in \Omega, \quad t > 0.$$

Since M_i is independent of $\mathbf{x}$ and t , we can rewrite the previous equation as given below:

$$M_i \frac{\partial c_i}{\partial t} + M_i \frac{\partial}{\partial \mathbf{x}}(c_i \mathbf{u}_i) = M_i \mathcal{J}_i, \quad i = 1, 2, 3, 4 \quad \mathbf{x} \in \Omega, \quad t > 0.$$

Dividing both sides of the previous equation by M_i gives:

$$\frac{\partial c_i}{\partial t} + \frac{\partial}{\partial \mathbf{x}}(c_i \mathbf{u}_i) = \mathcal{J}_i, \quad i = 1, 2, 3, 4 \quad \mathbf{x} \in \Omega, \quad t > 0. \quad (3.1.13)$$

Using equation (3.1.7), we can rewrite equation (3.1.13) above as follows:

$$\frac{\partial c_i}{\partial t} + \frac{\partial \mathbf{N}_i}{\partial \mathbf{x}} = \mathcal{J}_i, \quad i = 1, 2, 3, 4 \quad \mathbf{x} \in \Omega, \quad t > 0. \quad (3.1.14)$$

Furthermore, using equation (3.1.6) together with the fact that

$$\mathbf{J}_i = c_i(\mathbf{u}_i - \mathbf{u}) = c_i\mathbf{u}_i - c_i\mathbf{u} \iff c_i\mathbf{u}_i = \mathbf{J}_i + c_i\mathbf{u}, \quad (3.1.15)$$

we can rewrite equation (3.1.13) as given below:

$$\frac{\partial c_i}{\partial t} + \frac{\partial}{\partial \mathbf{x}}(\mathbf{J}_i + c_i\mathbf{u}) = \mathcal{J}_i, \quad i = 1, 2, 3, 4 \quad \mathbf{x} \in \Omega, \quad t > 0. \quad (3.1.16)$$

To obtain diffusion and reaction-diffusion models from equation (3.1.14), one needs to derive a relationship between the species concentrations and the molar fluxes of the species. Similarly, to obtain diffusion and reaction-diffusion models from equation (3.1.16), one needs to derive a relationship between the species concentrations and molar diffusion fluxes of the species. The type of diffusion and reaction-diffusion models obtained in both cases will depend on the derived relationship between the concentration and flux. Here, the constitutive relations derived by Fick and the one derived independently by Maxwell and Stefan called the Maxwell-Stefan (MS) equations will be presented.

3.1.2 Description of Diffusion by Fick

The most classical theory of diffusion goes back to Fick [52, 53]. He postulated a linear dependence of flux and concentration gradient. Therefore, if one considers a multicomponent mixture of four species A_i with $i = 1, 2, 3, 4$, then Fick's law of diffusion in terms of the molar diffusion flux $\mathbf{J}_i$ and the molar flux $\mathbf{N}_i$ are given mathematically as follows:

$$\mathbf{J}_i = -D_i \frac{\partial c_i}{\partial \mathbf{x}}, \quad i = 1, 2, 3, 4, \quad (3.1.17)$$

$$\mathbf{N}_i = -\bar{D}_i \frac{\partial c_i}{\partial \mathbf{x}}, \quad i = 1, 2, 3, 4, \quad (3.1.18)$$

where $D_i > 0$ and $\bar{D}_i > 0$ are the respective Fick's diffusivities of the species.

3.1.3 The Maxwell-Stefan Equations

The MS equations is based of the principle that the driving force of each species in the multicomponent mixture is in local equilibrium with the total friction force. Following the description of [107], and using the notations of this thesis, the MS equations in terms of the molar diffusion flux $\mathbf{J}_i$ read:

$$d_i = - \sum_{\substack{s=1 \\ s \neq i}}^4 \frac{c_s \mathbf{J}_i - c_i \mathbf{J}_s}{c D_{is}}, \quad \mathbf{x} \in \Omega, \quad t > 0, \quad i = 1, 2, 3, 4. \quad (3.1.19)$$

In equation (3.1.19) above, the terms D_{is} are the binary diffusion coefficients known as the MS diffusivities. They are such that $D_{is} = D_{si} > 0$. The terms d_i represent the diffusion driving forces and are

given by the chemical potential of the species. The chemical potential generally depend on the species concentration c_i , temperature T and pressure p of the mixture.

To obtain the MS equations in terms of the molar flux $\mathbf{N}_i$, we use the fact that the molar flux $\mathbf{N}_i$ and the molar diffusion flux $\mathbf{J}_i$ given in equations (3.1.7) and (3.1.6), respectively, are related by the following formula:

$$\mathbf{N}_i = \mathbf{J}_i + c_i \mathbf{u} \iff \mathbf{J}_i = \mathbf{N}_i - c_i \mathbf{u}. \quad (3.1.20)$$

More precisely, using equation (3.1.20), observe that

$$c_s \mathbf{J}_i - c_i \mathbf{J}_s = c_s (\mathbf{N}_i - c_i \mathbf{u}) - c_i (\mathbf{N}_s - c_s \mathbf{u}) = c_s \mathbf{N}_i - c_s c_i \mathbf{u} - c_i \mathbf{N}_s + c_s c_i \mathbf{u} = c_s \mathbf{N}_i - c_i \mathbf{N}_s.$$

Therefore,

$$d_i = - \sum_{\substack{s=1 \\ s \neq i}}^4 \frac{c_s \mathbf{N}_i - c_i \mathbf{N}_s}{c D_{is}}, \quad \mathbf{x} \in \Omega, \quad t > 0, \quad i = 1, 2, 3, 4. \quad (3.1.21)$$

Furthermore, the MS equations are linearly dependent. More precisely, there are exactly 3 independent quantities of type (3.1.19) and (3.1.21). This linear dependence can be seen if one sum the respective equations over all species.

3.2 Multicomponent Diffusion and Reaction-Diffusion Models

In this section, multicomponent diffusion and reaction-diffusion models, where the diffusion processes is modelled by the Fick's constitutive relation and the MS equations, respectively, are given.

3.2.1 Multicomponent Diffusion Models

Multicomponent diffusion models are obtained in the absence of chemical reaction. To achieve this, we put together the balance equations (3.1.14), (3.1.16) with their right-hand sides equal to zero and the constitutive relations (3.1.17), (3.1.18), (3.1.19), (3.1.21).

A multicomponent diffusion model where the diffusion process is modelled by Fick's law, defined in terms of the molar flux $\mathbf{N}_i$, is obtained by putting together equation (3.1.14) with the right-hand side equal to zero and equation (3.1.18):

$$\begin{aligned} \frac{\partial c_i}{\partial t} + \frac{\partial \mathbf{N}_i}{\partial \mathbf{x}} &= 0, \quad i = 1, 2, 3, 4 \quad \mathbf{x} \in \Omega, \quad t > 0, \\ \mathbf{N}_i &= -\bar{D}_i \frac{\partial c_i}{\partial \mathbf{x}}. \end{aligned} \quad (3.2.1)$$

Therefore,

$$\frac{\partial c_i}{\partial t} - \frac{\partial}{\partial \mathbf{x}} \left(\bar{D}_i \frac{\partial c_i}{\partial \mathbf{x}} \right) = 0, \quad i = 1, 2, 3, 4 \quad \mathbf{x} \in \Omega, \quad t > 0.$$

A multicomponent diffusion models where the diffusion processes is described by Fick's law, defined in terms of the molar diffusive flux $\mathbf{J}_i$, is obtained by putting together equation (3.1.16) with the right-hand

side equal to zero and equation (3.1.17), then neglect convective effects. More precisely, putting together equations (3.1.16) with the right-hand side equal to zero and (3.1.17), we obtain:

$$\begin{aligned}\frac{\partial c_i}{\partial t} + \frac{\partial}{\partial \mathbf{x}}(\mathbf{J}_i + c_i \mathbf{u}) &= 0, \quad i = 1, 2, 3, 4 \quad \mathbf{x} \in \Omega, \quad t > 0, \\ \mathbf{J}_i &= -D_i \frac{\partial c_i}{\partial \mathbf{x}}.\end{aligned}\tag{3.2.2}$$

Neglecting convective effects implies that

$$\frac{\partial}{\partial \mathbf{x}}(c_i \mathbf{u}) = 0.\tag{3.2.3}$$

Therefore,

$$\begin{aligned}\frac{\partial c_i}{\partial t} + \frac{\partial \mathbf{J}_i}{\partial \mathbf{x}} &= 0, \quad i = 1, 2, 3, 4 \quad \mathbf{x} \in \Omega, \quad t > 0, \\ \mathbf{J}_i &= -D_i \frac{\partial c_i}{\partial \mathbf{x}}.\end{aligned}\tag{3.2.4}$$

Equation (3.2.4) above can equivalently be written as:

$$\frac{\partial c_i}{\partial t} - \frac{\partial}{\partial \mathbf{x}} \left(D_i \frac{\partial c_i}{\partial \mathbf{x}} \right) = 0, \quad i = 1, 2, 3, 4 \quad \mathbf{x} \in \Omega, \quad t > 0.$$

A multicomponent diffusion model where the diffusion process is modelled by the MS equations, defined in terms of the molar flux $\mathbf{N}_i$, is obtained by putting together equation (3.1.14) with the right-hand side equal to zero and equation (3.1.21):

$$\begin{aligned}\frac{\partial c_i}{\partial t} + \frac{\partial \mathbf{N}_i}{\partial \mathbf{x}} &= 0, \quad \mathbf{x} \in \Omega, \quad t > 0, \quad i = 1, 2, 3, 4, \\ d_i &= - \sum_{\substack{s=1 \\ s \neq i}}^4 \frac{c_s \mathbf{N}_i - c_i \mathbf{N}_s}{c D_{is}}.\end{aligned}\tag{3.2.5}$$

A multicomponent diffusion model where the diffusion process is modelled by the MS equations, defined in terms of the molar diffusion flux $\mathbf{J}_i$, is obtained by putting together equation (3.1.16) with the right-hand side equal to zero and equation (3.1.19):

$$\begin{aligned}\frac{\partial c_i}{\partial t} + \frac{\partial}{\partial \mathbf{x}}(\mathbf{J}_i + c_i \mathbf{u}_i) &= 0, \quad \mathbf{x} \in \Omega, \quad t > 0, \quad i = 1, 2, 3, 4, \\ d_i &= - \sum_{\substack{s=1 \\ s \neq i}}^4 \frac{c_s \mathbf{J}_i - c_i \mathbf{J}_s}{c D_{is}},\end{aligned}\tag{3.2.6}$$

Using equation (3.2.3), we obtain:

$$\begin{aligned}\frac{\partial c_i}{\partial t} + \frac{\partial \mathbf{J}_i}{\partial \mathbf{x}} &= 0, \quad \mathbf{x} \in \Omega, \quad t > 0, \quad i = 1, 2, 3, 4, \\ d_i &= - \sum_{\substack{s=1 \\ s \neq i}}^4 \frac{c_s \mathbf{J}_i - c_i \mathbf{J}_s}{c D_{is}}.\end{aligned}\tag{3.2.7}$$

3.2.2 Multicomponent Reaction-Diffusion Models

To obtain multicomponent reaction-diffusion models, we put together the balance equations (3.1.14), (3.1.16) and the constitutive relations (3.1.17), (3.1.18), (3.1.19), (3.1.21).

A multicomponent reaction-diffusion model where the diffusion process is modelled by Fick's law, defined in terms of the molar flux $\mathbf{N}_i$, is obtained by putting together equations (3.1.14) and (3.1.18):

$$\begin{aligned}\frac{\partial c_i}{\partial t} + \frac{\partial \mathbf{N}_i}{\partial \mathbf{x}} &= \mathcal{J}_i, \quad i = 1, 2, 3, 4 \quad \mathbf{x} \in \Omega, \quad t > 0, \\ \mathbf{N}_i &= -\bar{D}_i \frac{\partial c_i}{\partial \mathbf{x}}.\end{aligned}\tag{3.2.8}$$

Equation (3.2.8) above can be rewritten as:

$$\frac{\partial c_i}{\partial t} - \frac{\partial}{\partial \mathbf{x}} \left(\bar{D}_i \frac{\partial c_i}{\partial \mathbf{x}} \right) = \mathcal{J}_i, \quad i = 1, 2, 3, 4 \quad \mathbf{x} \in \Omega, \quad t > 0.$$

A multicomponent reaction-diffusion models where the diffusion processes is modelled by Fick's law, defined in terms of the molar diffusive flux $\mathbf{J}_i$, is obtained by putting together equations (3.1.16) and (3.1.17), then neglect convective effects. More precisely, putting together equations (3.1.16) and (3.1.17) gives:

$$\begin{aligned}\frac{\partial c_i}{\partial t} + \frac{\partial}{\partial \mathbf{x}} (\mathbf{J}_i + c_i \mathbf{u}) &= \mathcal{J}_i, \quad i = 1, 2, 3, 4 \quad \mathbf{x} \in \Omega, \quad t > 0, \\ \mathbf{J}_i &= -D_i \frac{\partial c_i}{\partial \mathbf{x}}.\end{aligned}\tag{3.2.9}$$

Using equation (3.2.3), we obtain:

$$\begin{aligned}\frac{\partial c_i}{\partial t} + \frac{\partial \mathbf{J}_i}{\partial \mathbf{x}} &= \mathcal{J}_i, \quad i = 1, 2, 3, 4 \quad \mathbf{x} \in \Omega, \quad t > 0, \\ \mathbf{J}_i &= -D_i \frac{\partial c_i}{\partial \mathbf{x}}.\end{aligned}\tag{3.2.10}$$

Therefore,

$$\frac{\partial c_i}{\partial t} - \frac{\partial}{\partial \mathbf{x}} \left(D_i \frac{\partial c_i}{\partial \mathbf{x}} \right) = \mathcal{J}_i, \quad i = 1, 2, 3, 4 \quad \mathbf{x} \in \Omega, \quad t > 0.$$

A multicomponent reaction-diffusion model where the diffusion process is modelled by the MS equations, defined in terms of the molar flux $\mathbf{N}_i$, is obtained by putting together equations (3.1.14) and (3.1.21):

$$\begin{aligned}\frac{\partial c_i}{\partial t} + \frac{\partial \mathbf{N}_i}{\partial \mathbf{x}} &= \mathcal{J}_i, \quad \mathbf{x} \in \Omega, \quad t > 0, \quad i = 1, 2, 3, 4, \\ d_i &= - \sum_{\substack{s=1 \\ s \neq i}}^4 \frac{c_s \mathbf{N}_i - c_i \mathbf{N}_s}{c D_{is}}.\end{aligned}\tag{3.2.11}$$

A multicomponent diffusion model where the diffusion process is modelled by the MS equations, defined in terms of the molar diffusion flux $\mathbf{J}_i$, is obtained by putting together equations (3.1.16) and (3.1.19):

$$\begin{aligned} \frac{\partial c_i}{\partial t} + \frac{\partial}{\partial \mathbf{x}}(\mathbf{J}_i + c_i \mathbf{u}_i) &= \mathcal{J}_i, \quad \mathbf{x} \in \Omega, \quad t > 0, \quad i = 1, 2, 3, 4, \\ d_i &= - \sum_{\substack{s=1 \\ s \neq i}}^4 \frac{c_s \mathbf{J}_i - c_i \mathbf{J}_s}{c D_{is}}, \end{aligned} \quad (3.2.12)$$

Using equation (3.2.3), we obtain:

$$\begin{aligned} \frac{\partial c_i}{\partial t} + \frac{\partial \mathbf{J}_i}{\partial \mathbf{x}} &= \mathcal{J}_i, \quad \mathbf{x} \in \Omega, \quad t > 0, \quad i = 1, 2, 3, 4, \\ d_i &= - \sum_{\substack{s=1 \\ s \neq i}}^4 \frac{c_s \mathbf{J}_i - c_i \mathbf{J}_s}{c D_{is}}. \end{aligned} \quad (3.2.13)$$

Equations (3.2.2) and (3.2.9) can be rewritten as:

$$\begin{aligned} \frac{\partial c_i}{\partial t} - \frac{\partial}{\partial \mathbf{x}} \left(\bar{D}_i \frac{\partial c_i}{\partial \mathbf{x}} \right) + \frac{\partial}{\partial \mathbf{x}}(c_i \mathbf{u}) &= 0, \quad i = 1, 2, 3, 4 \quad \mathbf{x} \in \Omega, \quad t > 0, \\ \frac{\partial c_i}{\partial t} - \frac{\partial}{\partial \mathbf{x}} \left(D_i \frac{\partial c_i}{\partial \mathbf{x}} \right) + \frac{\partial}{\partial \mathbf{x}}(c_i \mathbf{u}) &= \mathcal{J}_i, \quad i = 1, 2, 3, 4 \quad \mathbf{x} \in \Omega, \quad t > 0. \end{aligned}$$

These equations are reaction-convection-diffusion models. They are not well posed unless a choice of $\mathbf{u}$ is made. This can be achieved by solving for $\mathbf{u}$ via the Cauchy momentum equation.

Equations (3.2.5), (3.2.7), (3.2.11) and (3.2.13) are not closed. This is because of the linear dependence of the MS equations and the fact that d_i depends on c_i , T and p . More precisely, there are seven equations in ten unknowns $(c_i, \mathbf{J}_i, p, T)$ or $(c_i, \mathbf{N}_i, p, T)$. To obtain closed system of equations for the variables $(c_i, \mathbf{J}_i, p, T)$ one has to add to equations (3.2.7) and (3.2.13) the constraint (3.1.11), an equation for the temperature of the mixture and the equation of state for the pressure. To obtain closed system of equations for the variables $(c_i, \mathbf{N}_i, p, T)$ one has to add to equations (3.2.5) and (3.2.11) an equation for the temperature of the mixture, the equation of state for the pressure and the following constraint which signifies equimolar diffusion:

$$\sum_{i=1}^4 \mathbf{N}_i = 0. \quad (3.2.14)$$

Equations (3.2.6) and (3.2.12) are not closed. This is because in addition to the linear dependence of the MS equations and the fact that d_i depends on c_i , T and p , a choice has to be made for $\mathbf{u}$. More precisely, there are seven equations in thirteen unknowns $(c_i, \mathbf{J}_i, p, T, \mathbf{u})$. To obtain a closed system of equations for the variables $(c_i, \mathbf{J}_i, p, T, \mathbf{u})$, one has to add to equations (3.2.6) and (3.2.12) the constraint (3.1.11), an equation for the temperature of the mixture an equation for the convective velocity and the equation of state for the pressure.

The equation for the temperature of the mixture mentioned above can be the energy balance equation for the mixture. The equation for the convective velocity mentioned above can be the momentum balance equation for the mixture. In the case of an ideal gas, the equation of state for the pressure mentioned above is given by:

$$p = cRT, \quad \text{where } R \text{ is the universal gas constant.}$$

Remark 3.2.1. In the special case of isobaric¹ and isothermal² conditions, d_i in the MS equations depends only on c_i . Therefore, in this case, the closed system of diffusion equations for the unknowns $(c_i, \mathbf{N}_i)$ and $(c_i, \mathbf{J}_i)$ are:

$$\begin{aligned} \frac{\partial c_i}{\partial t} + \frac{\partial \mathbf{N}_i}{\partial \mathbf{x}} &= 0, \quad \mathbf{x} \in \Omega, \quad t > 0, \quad i = 1, 2, 3, 4, \\ \bar{d}_i &= - \sum_{\substack{s=1 \\ s \neq i}}^4 \frac{c_s \mathbf{N}_i - c_i \mathbf{N}_s}{c D_{is}}, \\ \sum_{i=1}^4 \mathbf{N}_i &= 0, \end{aligned} \tag{3.2.15}$$

and

$$\begin{aligned} \frac{\partial c_i}{\partial t} + \frac{\partial \mathbf{J}_i}{\partial \mathbf{x}} &= 0, \quad \mathbf{x} \in \Omega, \quad t > 0, \quad i = 1, 2, 3, 4, \\ \bar{d}_i &= - \sum_{\substack{s=1 \\ s \neq i}}^4 \frac{c_s \mathbf{J}_i - c_i \mathbf{J}_s}{c D_{is}}, \\ \sum_{i=1}^4 \mathbf{J}_i &= 0, \end{aligned} \tag{3.2.16}$$

respectively, where $\bar{d}_i$ is a function c_i only.

The closed system of reaction-diffusion equations for the unknowns $(c_i, \mathbf{N}_i)$ and $(c_i, \mathbf{J}_i)$ are:

$$\begin{aligned} \frac{\partial c_i}{\partial t} + \frac{\partial \mathbf{N}_i}{\partial \mathbf{x}} &= \mathcal{J}_i, \quad \mathbf{x} \in \Omega, \quad t > 0, \quad i = 1, 2, 3, 4, \\ \bar{d}_i &= - \sum_{\substack{s=1 \\ s \neq i}}^4 \frac{c_s \mathbf{N}_i - c_i \mathbf{N}_s}{c D_{is}}, \\ \sum_{i=1}^4 \mathbf{N}_i &= 0, \end{aligned} \tag{3.2.17}$$

and

$$\begin{aligned} \frac{\partial c_i}{\partial t} + \frac{\partial \mathbf{J}_i}{\partial \mathbf{x}} &= \mathcal{J}_i, \quad \mathbf{x} \in \Omega, \quad t > 0, \quad i = 1, 2, 3, 4, \\ \bar{d}_i &= - \sum_{\substack{s=1 \\ s \neq i}}^4 \frac{c_s \mathbf{J}_i - c_i \mathbf{J}_s}{c D_{is}}, \\ \sum_{i=1}^4 \mathbf{J}_i &= 0, \end{aligned} \tag{3.2.18}$$

respectively, where $\bar{d}_i$ is a function c_i only.

¹Constant total or mixture pressure.

²Constant temperature. More precisely, uniform in space and constant in time mixture temperature.

In the case of isobaric condition only. More precisely, constant mixture pressure and non-isothermal condition, the closed system of diffusion equations for the unknowns $(c_i, \mathbf{N}_i, T)$ and $(c_i, \mathbf{J}_i, T)$ are obtained by adding the conservation of energy equation to the following equations:

$$\begin{aligned}\frac{\partial c_i}{\partial t} + \frac{\partial \mathbf{N}_i}{\partial \mathbf{x}} &= 0, \quad \mathbf{x} \in \Omega, \quad t > 0, \quad i = 1, 2, 3, 4, \\ \hat{d}_i &= - \sum_{\substack{s=1 \\ s \neq i}}^4 \frac{c_s \mathbf{N}_i - c_i \mathbf{N}_s}{c D_{is}}, \\ \sum_{i=1}^4 \mathbf{N}_i &= 0,\end{aligned}\tag{3.2.19}$$

and

$$\begin{aligned}\frac{\partial c_i}{\partial t} + \frac{\partial \mathbf{J}_i}{\partial \mathbf{x}} &= 0, \quad \mathbf{x} \in \Omega, \quad t > 0, \quad i = 1, 2, 3, 4, \\ \hat{d}_i &= - \sum_{\substack{s=1 \\ s \neq i}}^4 \frac{c_s \mathbf{J}_i - c_i \mathbf{J}_s}{c D_{is}}, \\ \sum_{i=1}^4 \mathbf{J}_i &= 0,\end{aligned}\tag{3.2.20}$$

respectively, where $\hat{d}_i$ is a function of c_i and T .

The closed system of non-isothermal reaction-diffusion models for the unknowns $(c_i, \mathbf{N}_i, T)$ and $(c_i, \mathbf{J}_i, T)$ are obtained by adding the energy balance equation for the mixture to the following equations:

$$\begin{aligned}\frac{\partial c_i}{\partial t} + \frac{\partial \mathbf{N}_i}{\partial \mathbf{x}} &= \mathcal{J}_i, \quad \mathbf{x} \in \Omega, \quad t > 0, \quad i = 1, 2, 3, 4, \\ \hat{d}_i &= - \sum_{\substack{s=1 \\ s \neq i}}^4 \frac{c_s \mathbf{N}_i - c_i \mathbf{N}_s}{c D_{is}}, \\ \sum_{i=1}^4 \mathbf{N}_i &= 0,\end{aligned}\tag{3.2.21}$$

and

$$\begin{aligned}\frac{\partial c_i}{\partial t} + \frac{\partial \mathbf{J}_i}{\partial \mathbf{x}} &= \mathcal{J}_i, \quad \mathbf{x} \in \Omega, \quad t > 0, \quad i = 1, 2, 3, 4, \\ \hat{d}_i &= - \sum_{\substack{s=1 \\ s \neq i}}^4 \frac{c_s \mathbf{J}_i - c_i \mathbf{J}_s}{c D_{is}}, \\ \sum_{i=1}^4 \mathbf{J}_i &= 0,\end{aligned}\tag{3.2.22}$$

respectively, where $\hat{d}_i$ is a function of c_i and T .

3.3 Derivation of Hydrodynamic Models from Kinetic Theory

Consider a system of Maxwell-Boltzmann type equations that describe a reactive multicomponent gaseous mixture. In order to pass from the Maxwell-Boltzmann description of the reactive gaseous mixture, which holds on a microscopic time and space scales to a hydrodynamic description, holding on a macroscopic time and space scales, it is usually convenient to measure all quantities in terms of characteristic values. This is followed by scaling time and space in terms of macroscopic units. Consequently, one obtains a dimensionless parameter which is of considerable importance in the derivation of hydrodynamic models from the kinetic theory. This dimensionless parameter is called the Knudsen number and is denoted by Kn . The Knudsen number appears naturally when the MBEs are written in dimensionless form.

Definition 3.3.1. *The Knudsen number is the ration of mean free path to the macroscopic length scale, that is,*

$$Kn = \frac{\text{mean free path}}{\text{macroscopic length scale}}.$$

3.3.1 The Dimensionless Maxwell-Boltzmann Type Equations for Reactive Multi-Species Mixtures

The starting point for the derivation of macroscopic (hydrodynamic) models from the Maxwell-Boltzmann type equations is the scaled or dimensionless Maxwell-Boltzmann type kinetic equations. To write the Maxwell-Boltzmann type kinetic equations for the reactive multi-species mixture of monatomic gases given in equation (2.3.25) in dimensionless form, we need to first choose macroscopic scales for the independent variables t , $\mathbf{x}$, and $\mathbf{v}_i$. In particular, let us choose τ for time, L for length and T_0 for reference temperature. These macroscopic scales define two macroscopic velocity scales. The first is the speed at which some macroscopic portion of the gas is transported through a distance L in a time τ . This speed is denoted by $\mathbf{u}_0$ and is given by:

$$\mathbf{u}_0 = \frac{L}{\tau}. \quad (3.3.1)$$

The second is the thermal speed of the molecules. This speed will be denoted by c_0 and it is defined as given below:

$$c_0 = \sqrt{\frac{5}{3} \frac{k_B T_0}{m}},$$

where k_B is the Boltzmann constant, m_i is the molecular mass of the species. The quantity c_0 is the speed of sound in a monatomic gas at temperature T_0 .

Now, with the macroscopic scales τ , L and c_0 , one can define the dimensionless time, space, velocity, number density and cross-section, respectively, as given below:

$$\begin{aligned} \hat{t} &= \frac{t}{\tau}, \quad \hat{\mathbf{x}} = \frac{\mathbf{x}}{L}, \quad \hat{\mathbf{v}}_i = \frac{\mathbf{v}_i}{c_0}, \quad \hat{f}_i(\hat{t}, \hat{\mathbf{x}}, \hat{\mathbf{v}}_i) = \frac{L^3 c_0^3}{N} f(t, \mathbf{x}, \mathbf{v}_i) \iff \frac{N}{L^3 c_0^3} \hat{f}_i(\hat{t}, \hat{\mathbf{x}}, \hat{\mathbf{v}}_i) = f_i(t, \mathbf{x}, \mathbf{v}_i) \\ \hat{\sigma}_{ij}^2 \langle \epsilon, c_0 \hat{\mathbf{v}}_i - c_0 \hat{\mathbf{v}}_s \rangle &= \frac{\sigma_{ij}^2}{\pi r^2} \langle \epsilon, c_0 \mathbf{v}_i - c_0 \mathbf{v}_s \rangle \iff \sigma_{ij}^2 \langle \epsilon, c_0 \mathbf{v}_i - c_0 \mathbf{v}_s \rangle = \hat{\sigma}_{ij}^2 \langle \epsilon, c_0 \hat{\mathbf{v}}_i - c_0 \hat{\mathbf{v}}_s \rangle \pi r^2, \end{aligned}$$

where r is the molecular radius and N the total number of particles in a volume L^3 . Observe that

$$\frac{\partial f_i}{\partial t} = \frac{\partial}{\partial t} \left(\frac{N}{L^3 c_0^3} \widehat{f}_i \right) \cdot \frac{\partial \widehat{t}}{\partial t} = \frac{N}{L^3 c_0^3} \frac{\partial \widehat{f}_i}{\partial \widehat{t}} \cdot \frac{\partial \widehat{t}}{\partial t} = \frac{N}{L^3 c_0^3} \frac{\partial \widehat{f}_i}{\partial \widehat{t}} \cdot \frac{1}{\tau} = \frac{N}{\tau L^3 c_0^3} \frac{\partial \widehat{f}_i}{\partial \widehat{t}}, \quad (3.3.2)$$

$$\mathbf{v}_i \cdot \frac{\partial f_i}{\partial \mathbf{x}} = c_0 \widehat{\mathbf{v}}_i \cdot \frac{\partial}{\partial \widehat{\mathbf{x}}} \left(\frac{N}{L^3 c_0^3} \widehat{f}_i \right) \cdot \frac{\partial \widehat{\mathbf{x}}}{\partial \mathbf{x}} = \frac{c_0 N}{L^3 c_0^3} \widehat{\mathbf{v}}_i \cdot \frac{\partial \widehat{f}_i}{\partial \widehat{\mathbf{x}}} \cdot \frac{1}{L} = \frac{N}{L^4 c_0^2} \widehat{\mathbf{v}}_i \cdot \frac{\partial \widehat{f}_i}{\partial \widehat{\mathbf{x}}}, \quad (3.3.3)$$

$$\begin{aligned} J_i^{mE} &= \frac{N^2}{L^6 c_0^6} \widehat{\sigma}_{ii}^2 \pi r^2 \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} \left[\widehat{f}_i' \widehat{f}_{i*}' - \widehat{f}_i \widehat{f}_{i*} \right] \langle \boldsymbol{\epsilon}, c_0 \widehat{\mathbf{v}}_i - c_0 \widehat{\mathbf{v}}_{i*} \rangle c_0^3 d\boldsymbol{\epsilon} d\widehat{\mathbf{v}}_{i*} \\ &= \frac{N^2}{L^6 c_0^6} \widehat{\sigma}_{ii}^2 \pi r^2 \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} \left[\widehat{f}_i' \widehat{f}_{i*}' - \widehat{f}_i \widehat{f}_{i*} \right] \langle \boldsymbol{\epsilon}, \widehat{\mathbf{v}}_i - \widehat{\mathbf{v}}_{i*} \rangle c_0^4 d\boldsymbol{\epsilon} d\widehat{\mathbf{v}}_{i*} \\ &= \frac{N^2}{L^6 c_0^2} \widehat{\sigma}_{ii}^2 \pi r^2 \widehat{J}_i^{mE}, \end{aligned} \quad (3.3.4)$$

where

$$d\mathbf{v}_{i*} = dv_{i*}^x dv_{i*}^y dv_{i*}^z = c_0 d\widehat{v}_{i*}^x c_0 d\widehat{v}_{i*}^y c_0 d\widehat{v}_{i*}^z = c_0^3 d\widehat{\mathbf{v}}_{i*}$$

have been used to obtain the first equality of equation (3.3.4) and

$$\langle \boldsymbol{\epsilon}, c_0 \widehat{\mathbf{v}}_i - c_0 \widehat{\mathbf{v}}_{i*} \rangle = c_0 \langle \boldsymbol{\epsilon}, \widehat{\mathbf{v}}_i - \widehat{\mathbf{v}}_{i*} \rangle, \quad \Longleftrightarrow \quad \langle \boldsymbol{\epsilon}, c_0 \widehat{\mathbf{v}}_i - c_0 \widehat{\mathbf{v}}_{i*} \rangle c_0^3 = \langle \boldsymbol{\epsilon}, \widehat{\mathbf{v}}_i - \widehat{\mathbf{v}}_{i*} \rangle c_0^4.$$

to obtain the second equality of equation (3.3.4). Similarly,

$$J_i^{bE} = \frac{N^2}{L^6 c_0^2} \pi r^2 \widehat{J}_i^{bE}, \quad (3.3.5)$$

$$J_i^{b*E} = \frac{N^2}{L^6 c_0^2} \pi r^2 \widehat{J}_i^{b*E'}, \quad (3.3.6)$$

$$J_i^R = \frac{N^2}{L^6 c_0^2} \pi r^2 \widehat{J}_i^R. \quad (3.3.7)$$

Substituting equations (3.3.2), (3.3.3), (3.3.4), (3.3.5), (3.3.6) and (3.3.7) into equation (2.3.25), we obtain for $i = 1, 2, 3, 4$:

$$\frac{N}{\tau L^3 c_0^3} \frac{\partial \widehat{f}_i}{\partial \widehat{t}} + \frac{N}{L^4 c_0^2} \widehat{\mathbf{v}}_i \cdot \frac{\partial \widehat{f}_i}{\partial \widehat{\mathbf{x}}} = \frac{N^2}{L^6 c_0^2} \pi r^2 \widehat{J}_i^{mE} + \frac{N^2}{L^6 c_0^2} \pi r^2 \widehat{J}_i^{bE} - \frac{N^2}{L^6 c_0^2} \pi r^2 \widehat{J}_i^{b*E} + \frac{N^2}{L^6 c_0^2} \pi r^2 \widehat{J}_i^R,$$

Multiplying both sides of the previous equation by $\frac{L^4 c_0^2}{N}$, we obtain:

$$\frac{L}{\tau c_0} \frac{\partial \widehat{f}_i}{\partial \widehat{t}} + \widehat{\mathbf{v}}_i \cdot \frac{\partial \widehat{f}_i}{\partial \widehat{\mathbf{x}}} = \frac{N}{L^2} \pi r^2 \widehat{J}_i^{mE} + \frac{N}{L^2} \pi r^2 \widehat{J}_i^{bE} - \frac{N}{L^2} \pi r^2 \widehat{J}_i^{b*E} + \frac{N}{L^2} \pi r^2 \widehat{J}_i^R. \quad (3.3.8)$$

The mean free path which is the average distance travelled by the particles between two successive collisions is given by:

$$\text{mean free path} = \frac{L^3}{N \pi r^2},$$

see [103] for a mathematical justification of the above formula.

Observe that the factor multiplying the collision operators can be written as:

$$L \times \frac{N\pi r^2}{L^3} = \frac{L}{\text{mean free path}} = \frac{1}{Kn}.$$

Since the reactive and non-reactive collisions may be characterised by different mean free paths, this implies two different Knudsen numbers. It is not restrictive to write them as

$$Kn_e = \alpha^p \quad \text{and} \quad Kn_r = \alpha^q$$

where Kn_e denotes the Knudsen number for non-reactive collisions, Kn_r denotes the Knudsen number for collisions with sufficient energy to result in a chemical reaction and p, q are real numbers. Therefore, we can rewrite equation (3.3.8) as follows:

$$\frac{L}{\tau c_0} \frac{\partial \widehat{f}_i}{\partial \widehat{t}} + \widehat{\mathbf{v}}_i \cdot \frac{\partial \widehat{f}_i}{\partial \widehat{\mathbf{x}}} = \frac{1}{\alpha^p} \widehat{J}_i^{mE} + \frac{1}{\alpha^p} \widehat{J}_i^{bE} - \frac{1}{\alpha^q} \widehat{J}_i^{b*E} + \frac{1}{\alpha^q} \widehat{J}_i^R, \quad i = 1, 2, 3, 4. \quad (3.3.9)$$

The factor multiplying the time derivative is another dimensionless parameter called the kinetic Strouhal number, it is denoted by St . Thus equation (3.3.9) can be rewritten as:

$$St \frac{\partial \widehat{f}_i}{\partial \widehat{t}} + \widehat{\mathbf{v}}_i \cdot \frac{\partial \widehat{f}_i}{\partial \widehat{\mathbf{x}}} = \frac{1}{\alpha^p} \widehat{J}_i^{mE} + \frac{1}{\alpha^p} \widehat{J}_i^{bE} - \frac{1}{\alpha^q} \widehat{J}_i^{b*E} + \frac{1}{\alpha^q} \widehat{J}_i^R, \quad i = 1, 2, 3, 4. \quad (3.3.10)$$

Furthermore, there is some arbitrariness in the way the time, length and temperatures scales were chosen. However, it is known, see for example, [101] that if these scales are chosen in manner that is consistent with: the geometry of the domain containing the gaseous mixture, the time necessary to observe significant motion of the gas and the distribution function at time equal to zero, then the ratio L/τ corresponds to the bulk velocity $\mathbf{u}_0$ of the flow. As a result, the Strouhal number becomes the Mach number, which is often denoted by Ma and is defined as follows:

$$Ma = \frac{\mathbf{u}_0}{c_0}.$$

If one assumes that the March number is such that

$$St = Ma = \alpha \ll 1,$$

then equation (3.3.10) becomes:

$$\alpha \frac{\partial \widehat{f}_i}{\partial \widehat{t}} + \widehat{\mathbf{v}}_i \cdot \frac{\partial \widehat{f}_i}{\partial \widehat{\mathbf{x}}} = \frac{1}{\alpha^p} \widehat{J}_i^{mE} + \frac{1}{\alpha^p} \widehat{J}_i^{bE} - \frac{1}{\alpha^q} \widehat{J}_i^{b*E} + \frac{1}{\alpha^q} \widehat{J}_i^R, \quad i = 1, 2, 3, 4. \quad (3.3.11)$$

Removing the hats for simplicity and adding a superscript α to the distribution functions, as well as to the collision operators, we can rewrite equation (3.3.11) as given below:

$$\alpha \frac{\partial f_i^\alpha}{\partial t} + \mathbf{v}_i \cdot \frac{\partial f_i^\alpha}{\partial \mathbf{x}} = \frac{1}{\alpha^p} J_i^{\alpha mE} + \frac{1}{\alpha^p} J_i^{\alpha bE} - \frac{1}{\alpha^q} J_i^{\alpha b*E} + \frac{1}{\alpha^q} J_i^{\alpha R}, \quad i = 1, 2, 3, 4, \quad (3.3.12)$$

where

$$J_i^{\alpha m E} = \sigma_{ii}^2 \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} \left[f_i^{\alpha'} f_{i*}^{\alpha'} - f_i^\alpha f_{i*}^\alpha \right] \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_{i*} \rangle d\boldsymbol{\epsilon} d\mathbf{v}_{i*}, \quad (3.3.13)$$

$$J_i^{\alpha b E} = \sum_{\substack{s=1 \\ s \neq i}}^4 \sigma_{is}^2 \underbrace{\int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} \left[f_i^{\alpha'} f_s^{\alpha'} - f_i^\alpha f_s^\alpha \right] \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_s \rangle d\boldsymbol{\epsilon} d\mathbf{v}_s}_{Q_{is}}, \quad (3.3.14)$$

$$J_{ij}^{\alpha b * E} = \beta_{ij} \sigma_{ij}^2 \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} \left[f_i^{\alpha'} f_j^{\alpha'} - f_i^\alpha f_j^\alpha \right] \Theta(\langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_j \rangle - \Xi_{ij}) \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_j \rangle d\boldsymbol{\epsilon} d\mathbf{v}_j, \quad (3.3.15)$$

$$J_i^{\alpha R} = \beta_{ij} \sigma_{ij}^2 \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} \left[\left(\frac{\mu_{ij}}{\mu_{kl}} \right)^2 f_k^{\alpha \circ} f_l^{\alpha \circ} - f_i^\alpha f_j^\alpha \right] \Theta(\langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_j \rangle - \Xi_{ij}) \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_j \rangle d\boldsymbol{\epsilon} d\mathbf{v}_j, \quad (3.3.16)$$

are the scaled collision operators and $f_i^\alpha, f_{i*}^\alpha, f_j^\alpha, f_s^\alpha, f_i^{\alpha'}, f_{i*}^{\alpha'}, f_j^{\alpha'}, f_s^{\alpha'}, f_k^{\alpha \circ}, f_l^{\alpha \circ}$ are the scaled distribution functions.

The equations given in (3.3.12) together with equations (3.3.13) (3.3.14), (3.3.15) and (3.3.16) are the dimensionless or scaled SRS kinetic equations.

Remark 3.3.2. If the reactive mean free path for the SRS kinetic model is defined as

$$\text{reactive mean free path} = \frac{L^3}{\pi r^2 \beta_{ij} N},$$

one has that the elastic and reactive Knudsen numbers are related by

$$\frac{Kn_r}{Kn_e} = \frac{\alpha^q}{\alpha^p} = \frac{1}{\beta_{ij}} \iff Kn_r = \frac{Kn_e}{\beta_{ij}}.$$

Therefore, in the case, the scaled $J_{ij}^{b * E}$ and J_i^R becomes:

$$\tilde{J}_{ij}^{\alpha b * E} = \sigma_{ij}^2 \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} \left[f_i^{\alpha'} f_j^{\alpha'} - f_i^\alpha f_j^\alpha \right] \Theta(\langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_j \rangle - \Xi_{ij}) \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_j \rangle d\boldsymbol{\epsilon} d\mathbf{v}_j, \quad (3.3.17)$$

$$\tilde{J}_i^{\alpha R} = \sigma_{ij}^2 \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} \left[\left(\frac{\mu_{ij}}{\mu_{kl}} \right)^2 f_k^{\alpha \circ} f_l^{\alpha \circ} - f_i^\alpha f_j^\alpha \right] \Theta(\langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_j \rangle - \Xi_{ij}) \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_j \rangle d\boldsymbol{\epsilon} d\mathbf{v}_j. \quad (3.3.18)$$

□

Similarly, the kinetic equations for polyatomic gaseous mixture with a continuous structure of internal energy given in equation (2.4.56) can be written in dimensionless form as:

$$\varepsilon \frac{\partial f_i^\varepsilon}{\partial t} + \mathbf{v} \cdot \nabla_x f_i^\varepsilon = \frac{1}{\varepsilon^p} \sum_{j=1}^4 Q_{ij}^\varepsilon(f_i^\varepsilon, f_j^\varepsilon) + \frac{1}{\varepsilon^q} Q_i^{\text{react}}, \quad i = 1, \dots, 4. \quad (3.3.19)$$

where

$$\begin{aligned} Q_{ij}^\varepsilon(f_i^\varepsilon, f_j^\varepsilon) &= \int_{\mathbb{R}^3} \int_0^{+\infty} \int_0^1 \int_0^1 \int_{\mathbb{S}^2} \left[f_i^\varepsilon(\mathbf{v}'_i, I'_i) f_j^\varepsilon(\mathbf{v}'_j, I'_j) - f_i^\varepsilon(\mathbf{v}_i, I_i) f_j^\varepsilon(\mathbf{v}_j, I_j) \right] \\ &\quad \times B_{ij}(\mathbf{v}_i, \mathbf{v}_j, I, I_j, R, r, \boldsymbol{\omega}) (1-R) |\mathbf{v}_i - \mathbf{v}_j|^{-1} \varphi_i(I)^{-1} d\boldsymbol{\omega} dr dR dI_j d\mathbf{v}_j, \end{aligned} \quad (3.3.20)$$

$$\begin{aligned}
Q_i^{react}(\mathbf{v}_i, I_i) = & \int_{\mathbb{R}^3} \int_0^{+\infty} \int_0^1 \int_0^1 \int_{\mathbb{S}^2} \left[\left(\frac{m_i m_j}{m_k m_l} \right)^3 f_k^\varepsilon(\mathbf{v}'_k, I'_k) f_l^\varepsilon(\mathbf{v}'_l, I'_l) - f_i^\varepsilon(\mathbf{v}_i, I_i) f_j^\varepsilon(\mathbf{v}_j, I_j) \right] \\
& \times H_i B^{react}(\mathbf{v}_i, \mathbf{v}_j, I_i, I_j, R, r, \boldsymbol{\omega}) (m_i m_j)^{-2} |\mathbf{v}_i - \mathbf{v}_j|^{-1} \\
& \times (1 - R) \varphi_1(I)^{-1} d\boldsymbol{\omega} dr dR dI_j d\mathbf{v}_j.
\end{aligned} \tag{3.3.21}$$

are the scaled collision operators and

$$f_k^\varepsilon(\mathbf{v}'_k, I'_k), \quad f_l^\varepsilon(\mathbf{v}'_l, I'_l), \quad f_i^\varepsilon(\mathbf{v}'_i, I'_i), \quad f_j^\varepsilon(\mathbf{v}'_j, I'_j)$$

are the scaled distribution functions with

$$(i, j, k, l) \in \{(1, 2, 3, 4), (2, 1, 4, 3), (3, 4, 1, 2), (4, 3, 2, 1)\}.$$

Here, the notations ε^p and ε^q have been used in order to distinguish the elastic and reactive Knudsen numbers for the polyatomic mixture from that of the monatomic mixture.

Remark 3.3.3. *All hydrodynamic limits of the Maxwell-Boltzmann equation are analogous to situations where the Knudsen number Kn is such that*

$$Kn \ll 1.$$

This means that the Knudsen number governs the transition from the kinetic theory of gases, more precisely from the Maxwell-Boltzmann equation to hydrodynamic models. Also, in the context of hydrodynamics limits, there is no universal prescription for the Strouhal number. This is because different hydrodynamic regimes can be obtained from the scaled Maxwell-Boltzmann equation with an appropriate choice of the Strouhal number.

In addition, the scaled kinetic equations (3.3.12) and (3.3.19) can be used to study different hydrodynamic regimes. This can be done by choosing appropriate values for the parameters p and q to describe the physical situation under consideration.

3.3.2 Methods for Deriving Hydrodynamic Models from Kinetic Theory

There are three methods to derive macroscopic models from the scaled MBEs. The first is the Hilbert expansion method which was developed by David Hilbert [64]. The second method is the Chapman-Enskog method which was developed independently by Chapman [38, 39] and Enskog [48, 49]. The third is referred to as the moment method. The moment method was developed by Grad [60] and was extended to a more general framework by Levermore [80]. In this thesis, the interest is on the derivation of hydrodynamic models from the scaled kinetic equations (3.3.12) and (3.3.19) using the moment method.

The moment method consists of passing to the limit as the Knudsen number vanishes in the macroscopic equations (i.e., equations obtained by multiplying the dimensionless MBEs by a text function of

velocity space and integrating the resulting equation over all possible velocities) that are satisfied by well-behaved solutions of the MBEs.

3.4 The Derivation of Multicomponent Diffusion Models from Kinetic Theory

The derivation of reaction-diffusion models from the kinetic theory of chemically reactive gaseous mixtures is the objective of this thesis. More precisely, this thesis is focused on the derivation of reaction-diffusion models where the diffusion process is modelled by the MS equations as hydrodynamics limits of the MBEs for reactive multi-species mixtures. This is because the direct proportionality between flux and concentration gradient postulated by Fick is sometimes too simplistic and cannot be used to describe non-typical diffusion phenomena like osmotic diffusion, uphill or reverse diffusion and diffusion barrier observed experimentally in multi-species mixtures, see, for example [47, 77]. Specifically, this thesis is focused on:

1. The derivation a of reaction-diffusion model of type given in equation (3.2.18) as a hydrodynamic limit of the SRS kinetic equations.
2. The derivation of a reaction-diffusion model of type given in equation (3.2.22) as a hydrodynamic limit of the kinetic equations for a reactive mixture of polyatomic gases with a continuous structure of internal energy.
3. The derivation of extensions to the MS equations in the forms:

$$\bar{d}_i = - \sum_{\substack{s=1 \\ s \neq i}}^4 \frac{c_s \mathbf{J}_i - c_i \mathbf{J}_s}{c D_{is}} + \bar{\mathcal{A}}_i, \quad \mathbf{x} \in \Omega, \quad t > 0, \quad i = 1, 2, 3, 4, \quad (3.4.1)$$

and

$$\hat{d}_i = - \sum_{\substack{s=1 \\ s \neq i}}^4 \frac{c_s \mathbf{J}_i - c_i \mathbf{J}_s}{c D_{is}} + \hat{\mathcal{A}}_i, \quad \mathbf{x} \in \Omega, \quad t > 0, \quad i = 1, 2, 3, 4, \quad (3.4.2)$$

as a hydrodynamic limit of the SRS kinetic equations. In equations (3.4.1) and (3.4.2) the terms $\bar{\mathcal{A}}_i$ and $\hat{\mathcal{A}}_i$ with $i = 1, 2, 3, 4$ are additional diffusion term resulting from chemical interactions whose explicit forms will be obtained.

Chapter 4

From the simple reacting sphere kinetic model to the reaction-diffusion system of Maxwell-Stefan type

This chapter contains the results published in COMMUN. MATH SCI. 2019, in collaboration with Patrícia Gonçalves and Ana Jacinta Soares.

4.1 Introduction

The description and modelling of chemically reactive mixtures is a topic of great importance due to many engineering applications related, for example, to chemical industry and biotechnology [55, 107, 110]. In particular, a proper description of diffusion phenomena in multicomponent mixtures, with or without chemical reactions, is crucial in many simulations and design processes used by chemical engineers [77]. In this context, the MS equations are used by many applied and experimental researchers to model and predict diffusion as well as mass transfer processes in multicomponent mixtures [107, 43, 110]. In fact, it is well known that the MS equations are adequate to describe non-typical diffusion that appears as a consequence of some thermodynamic non-idealities, by introducing the chemical potential gradients as driving forces [77, 110]. When a multicomponent mixture with chemical reaction is considered, a hydrodynamic system which consists of the continuity equations for the constituents in the mixture and the MS equations, can be used to describe diffusion of the constituents and how their concentrations change as a consequence of the chemical reaction.

Despite the practical interest and applications of the MS equations in the modelling of multicomponent mixtures with or without chemical reaction, not much is known about the mathematical analysis of these equations. Rigorous results have been published over the past few years, see, for example, [23, 26, 28, 29, 63, 68, 71]. In particular, [28, 29, 68] dealt with the formal derivation of hydrodynamic systems of MS type from a kinetic (mesoscopic) system of MBEs for non-reactive multicomponent mixture and obtained explicit expressions for the diffusion coefficients in terms of the kinetic model parameters. These hydrodynamic systems consist of the MS equations coupled with the continuity equations for the

species. They were obtained using the well established line of research initiated by Golse and co-workers [9, 10, 11] on the transition from kinetic Maxwell-Boltzmann models to hydrodynamic equations of fluid mechanics. In close connection with these works, but considering chemically reactive mixtures, the papers [13, 14, 15] dealt with the derivation of macroscopic reaction-diffusion equations from a system of reactive MBEs. In these papers, using an appropriate scaling of the reactive MBEs and assuming different types of molecular interactions, the evolution equations for the species number densities were explicitly derived in the asymptotic limit of small Knudsen number. Moreover, the convergence from the reactive MBEs to the reaction-diffusion system was proven and discussed in [13, 14]. Reaction-diffusion equations for chemically reactive mixtures were also derived in [97, 98, 113], starting from kinetic equations of Fokker-Planck type. Various scalings were considered in view of analysing the interactions between transport processes and chemical reactions.

In this chapter, the interest is on the limiting process that leads from the SRS kinetic model described in section 2.3 to a reaction-diffusion system of MS type. This is achieved by, considering a scaling of the SRS kinetic equations for which elastic collisions are dominant and reactive collisions are less frequent. By assuming isothermal condition, the reaction-diffusion system of MS type is formally derived from the evolution of the number density and momentum balance of the species, in the limit as the scaling parameter vanishes. The formal derivation of these equations from a Maxwell-Boltzmann type kinetic model is the main contribution of this chapter. To the best of my knowledge, this is the first attempt in this direction. The isothermal condition assumption is met by assuming that the chemical reaction is slow enough to allow the surroundings to continuously compensate for the balance of reaction heat between the reactants and products [23, 24, 25, 63, 114, 115]. The reaction-diffusion system obtained in this chapter is similar to the one given in equation (3.2.18) and those studied in [23, 24, 25]. If the isothermal assumption is disregarded, the evolution equation for the temperature of the mixture should be considered. In this case, the reaction-diffusion system will be similar to that given in equation (3.2.22) and the one obtained in [69] for a non-reactive mixture.

After this introduction, the remaining part of this chapter is organised as follows. In section 4.2, the scaling of the SRS kinetic equations which corresponds to the chemical regime to be studied is presented. This is followed by the assumptions needed to derive a reaction-diffusion system with the diffusion process modelled by the MS equations, as a hydrodynamic limit of the scaled SRS kinetic equations. In section 4.3, the concentration balance equations for the species in the reactive mixture is obtained. In section 4.4, the momentum balance equations for the species in the reactive mixture is obtained. The macroscopic isothermal equations and their formal diffusive asymptotics towards the reaction-diffusion system of MS type are studied in section 4.5. Finally, the conclusions are given in section 4.6.

4.2 Scaled Kinetic Equations and Assumptions

In this section, the scaling of the kinetic equations to be studied will be introduced. This scaling corresponds to a physical situation where the dominant role in the evolution of the species is played by mechanical interactions, while chemical reactions are assumed to be very slow. Furthermore, the relevant assumptions

needed to obtain the result presented in this chapter will be given.

4.2.1 Scaled Kinetic Equation

The starting point for the derivation of the reaction-diffusion system of MS type from the SRS kinetic equations given in equation (2.3.25), is an appropriately scaled SRS kinetic equations that describe the chemical regime under consideration. In this chapter, the interest is on the chemical regime of dominant elastic collisions and slow chemical reactions. More precisely, the chemical reactions are assumed to be slow enough to allow the surroundings to continually compensate for the balance of reaction heat between the reactants and products. This regime corresponds to a physical situation in which the elastic mean free path is shorter than the reactive mean free path. To this aim, in order to adapt the scaled SRS kinetic equations given in equation (3.3.12) to the chemical regime considered in this chapter, we set $p = 1$ and $q = -1$ in equation (3.3.12) to obtain:

$$\alpha \frac{\partial f_i^\alpha}{\partial t} + \mathbf{v}_i \cdot \frac{\partial f_i^\alpha}{\partial \mathbf{x}} = \frac{1}{\alpha} J_i^{\alpha m E} + \frac{1}{\alpha} J_i^{\alpha b E} - \alpha \tilde{J}_{ij}^{\alpha b * E} + \alpha \tilde{J}_i^{\alpha R}, \quad i = 1, 2, 3, 4, \quad (4.2.1)$$

where $J_i^{\alpha m E}$, $J_i^{\alpha b E}$, $\tilde{J}_{ij}^{\alpha b * E}$ and $\tilde{J}_i^{\alpha R}$ are, as defined in (3.3.13), (3.3.14), (3.3.17) and (3.3.18), respectively.

Equations (4.2.1) emphasise that $J_i^{\alpha m E}$ and $J_i^{\alpha b E}$ (i.e., the mono-species and bi-species elastic operators) are associated to predominant effects, whereas the reactive operator $\tilde{J}_i^{\alpha R}$ and the elastic correction term $\tilde{J}_{ij}^{\alpha b * E}$ are associated to rare effects.

Remark 4.2.1. *The properties of the collision operators for the SRS kinetic model given in subsection 2.3.2 and the conservation laws given in subsection 2.3.3 are still valid for the scaled collision operators given in equations (3.3.13), (3.3.14), (3.3.15), (3.3.16), (3.3.17) and (3.3.18).* □

4.2.2 Assumptions

Besides the chemical regime of slow chemical reaction, the central assumptions required to derive the reaction-diffusion system of MS type from the scaled equations (4.2.1) are:

- (a) The initial conditions are local Maxwellian functions centred at the mean (average) velocity of the species.
- (b) The evolution of the system leaves the distribution functions in the local Maxwellian state.
- (c) The bulk velocity of the mixture is small and goes to zero as $\alpha \rightarrow 0$.
- (d) The evolution of the mixture is considered under isothermal condition.

Assumption (d) implies that the temperature T of the mixture is uniform in space and constant in time. It is compatible with the physical situation of slow chemical reaction and signifies that the chemical process

takes place at a rate slow enough to allow the surroundings to continuously compensate for the balance of reaction heat between the reactants and products (see [114]). Assumption (c) allows one to neglect convective effects and describe a physical system governed by diffusion and chemical reaction. Assumptions (a) and (b) correspond to the physical situation in which the system evolves not far away from the local Maxwellian equilibrium.

From assumption (a) above, following the advice given in [58, 57] for $Ma = O(\alpha)$, the initial conditions for equation (4.2.1) are distribution functions of the following form

$$f_i^{\alpha(in)}(\mathbf{x}, \mathbf{v}_i) = c_i^{\alpha(in)}(\mathbf{x}) \left(\frac{m_i}{2\pi k_B T} \right)^{\frac{3}{2}} \exp \left(- \frac{m_i (\mathbf{v}_i - \alpha \mathbf{u}_i^{\alpha(in)}(\mathbf{x}))^2}{2k_B T} \right), \quad \mathbf{x} \in \Omega, \quad \mathbf{v}_i \in \mathbb{R}^3, \quad (4.2.2)$$

for $i = 1, 2, 3, 4$, where $T > 0$ is constant (isothermal condition), $c_i^{\alpha(in)} : \Omega \rightarrow \mathbb{R}_+$, and $\mathbf{u}_i^{\alpha(in)} : \Omega \rightarrow \mathbb{R}^3$. From assumption (b), the distribution functions at time $t > 0$ are local Maxwellians centred at the mean velocity of the species:

$$f_i^\alpha(t, \mathbf{x}, \mathbf{v}_i) = c_i^\alpha(t, \mathbf{x}) \left(\frac{m_i}{2\pi k_B T} \right)^{\frac{3}{2}} \exp \left(- \frac{m_i (\mathbf{v}_i - \alpha \mathbf{u}_i^\alpha(t, \mathbf{x}))^2}{2k_B T} \right), \quad \mathbf{x} \in \Omega, \quad \mathbf{v}_i \in \mathbb{R}^3, \quad (4.2.3)$$

for $i = 1, \dots, 4$, where $c_i^\alpha : \mathbb{R}_+ \times \Omega \rightarrow \mathbb{R}_+$ and $\mathbf{u}_i^\alpha : \mathbb{R}_+ \times \Omega \rightarrow \mathbb{R}^3$.

An important step in the passage from a kinetic model to hydrodynamic equations is the explicit computation of the integral contributions appearing in the kinetic equations. When a reactive mixture is involved, the computations can be very intricate, essentially because of the redistribution of masses and energies among the constituents. Having this in mind, the distribution functions given in equation (4.2.3) will be approximated by expanding to obtain a first order corrections to the Maxwellian distributions. In particular,

$$f_i^\alpha(t, \mathbf{x}, \mathbf{v}_i) \approx M_i^\alpha(t, \mathbf{x}, \mathbf{v}_i) \left(1 + \frac{\alpha m_i \mathbf{v}_i \cdot \mathbf{u}_i^\alpha(t, \mathbf{x})}{k_B T} \right), \quad (4.2.4)$$

with

$$M_i^\alpha(t, \mathbf{x}, \mathbf{v}_i) = c_i^\alpha(t, \mathbf{x}) \left(\frac{m_i}{2\pi k_B T} \right)^{\frac{3}{2}} \exp \left(- \frac{m_i (\mathbf{v}_i)^2}{2k_B T} \right). \quad (4.2.5)$$

Expressions (4.2.4) will be used in sections 4.3 and 4.4 for the explicit computation of the integral contributions. As stated in [95], pg.147, first-order corrections to the Maxwellian distributions as those given by (4.2.4) were first used by J. Stefan to capture the diffusion effects in a mixture of gases.

4.3 Concentration Balance Equations

The balance equations for the species concentration can formally be derived from the scaled SRS equations given in equation (4.2.1), by integrating over the velocity space.

Lemma 4.3.1. *The concentration balance equations for the species in the reactive mixture can be written as*

$$\frac{\partial c_i^\alpha}{\partial t} + \frac{\partial}{\partial \mathbf{x}}(c_i^\alpha \mathbf{u}_i^\alpha) = \mathcal{J}_i, \quad i = 1, \dots, 4, \quad (4.3.1)$$

with $\mathcal{J}_i$ being the reaction rate of the i -th species whose form is given below:

$$\begin{aligned} \mathcal{J}_i = \sigma_{ij}^2 \left(\frac{2\pi\mu_{ij}}{k_B T} \right)^{\frac{1}{2}} \left[\left(\frac{\mu_{ij}}{\mu_{kl}} \right)^{\frac{1}{2}} c_k^\alpha c_l^\alpha \exp \left(\frac{Q_R}{k_B T} \right) - c_i^\alpha c_j^\alpha \right] \\ \times \left[\frac{2k_B T}{\mu_{ij}} \Gamma(2, z_i^*) - \left(\frac{\Xi_{ij}}{c_0} \right)^2 \Gamma(1, z_i^*) \right], \end{aligned} \quad (4.3.2)$$

where the terms $\Gamma(1, z_i^*)$, $\Gamma(2, z_i^*)$ are the incomplete Euler gamma functions:

$$\Gamma(\eta, x) = \int_x^\infty t^{\eta-1} e^{-t} dt \quad (4.3.3)$$

with

$$x = z_i^* = \frac{\mu_{ij}}{2k_B T} \left(\frac{\Xi_{ij}}{c_0} \right)^2, \quad (4.3.4)$$

$\eta = 1$ and $\eta = 2$, respectively. Moreover, for $i = 1, \dots, 4$, $\mathcal{J}_i = \lambda_i \mathcal{J}_1$, where $\lambda_1 = \lambda_2 = 1$ and $\lambda_3 = \lambda_4 = -1$.

Proof. Integrating both sides of the scaled SRS kinetic equations given in equation (4.2.1) with respect to $\mathbf{v}_i \in \mathbb{R}^3$, gives:

$$\begin{aligned} \alpha \int_{\mathbb{R}^3} \frac{\partial f_i^\alpha}{\partial t} d\mathbf{v}_i + \int_{\mathbb{R}^3} \mathbf{v}_i \cdot \frac{\partial f_i^\alpha}{\partial \mathbf{x}} d\mathbf{v}_i \\ = \frac{1}{\alpha} \int_{\mathbb{R}^3} J_i^{\alpha m E} d\mathbf{v}_i + \frac{1}{\alpha} \int_{\mathbb{R}^3} J_i^{\alpha b E} d\mathbf{v}_i - \alpha \int_{\mathbb{R}^3} \tilde{J}_{ij}^{\alpha b * E} d\mathbf{v}_i + \alpha \int_{\mathbb{R}^3} \tilde{J}_i^{\alpha R} d\mathbf{v}_i, \end{aligned}$$

Applying the Leibniz integral rule to the two terms on the left-hand side of the previous equation, we obtain:

$$\begin{aligned} \alpha \frac{\partial}{\partial t} \left(\int_{\mathbb{R}^3} f_i^\alpha d\mathbf{v}_i \right) + \frac{\partial}{\partial \mathbf{x}} \left(\int_{\mathbb{R}^3} \mathbf{v}_i f_i^\alpha d\mathbf{v}_i \right) \\ = \frac{1}{\alpha} \int_{\mathbb{R}^3} J_i^{\alpha m E} d\mathbf{v}_i + \frac{1}{\alpha} \int_{\mathbb{R}^3} J_i^{\alpha b E} d\mathbf{v}_i - \alpha \int_{\mathbb{R}^3} \tilde{J}_{ij}^{\alpha b * E} d\mathbf{v}_i + \alpha \int_{\mathbb{R}^3} \tilde{J}_i^{\alpha R} d\mathbf{v}_i. \end{aligned} \quad (4.3.5)$$

Using the definition of the distribution functions given in equation (4.2.3), the first integral on the left-hand side of the previous equation can be written as follows:

$$\int_{\mathbb{R}^3} f_i^\alpha d\mathbf{v}_i = c_i^\alpha \left(\frac{m_i}{2\pi k_B T} \right)^{\frac{3}{2}} \int_{\mathbb{R}^3} \exp \left(- \frac{m_i (\mathbf{v}_i - \alpha \mathbf{u}_i^\alpha)^2}{2k_B T} \right) d\mathbf{v}_i. \quad (4.3.6)$$

Introducing the peculiar velocity

$$\boldsymbol{\xi}_i = \mathbf{v}_i - \alpha \mathbf{u}_i^\alpha \quad \Longleftrightarrow \quad \mathbf{v}_i = \boldsymbol{\xi}_i + \alpha \mathbf{u}_i^\alpha \quad \text{and} \quad d\mathbf{v}_i = d\boldsymbol{\xi}_i, \quad (4.3.7)$$

we can rewrite equation (4.3.6) as follows:

$$\int_{\mathbb{R}^3} f_i^\alpha d\mathbf{v}_i = c_i^\alpha \left(\frac{m_i}{2\pi k_B T} \right)^{\frac{3}{2}} \int_{\mathbb{R}^3} \exp \left(- \frac{m_i(\boldsymbol{\xi}_i)^2}{2k_B T} \right) d\boldsymbol{\xi}_i.$$

Writing the previous equation in spherical coordinates and integrating gives:

$$\begin{aligned} \int_{\mathbb{R}^3} f_i^\alpha d\mathbf{v}_i &= c_i^\alpha \left(\frac{m_i}{2\pi k_B T} \right)^{\frac{3}{2}} \int_0^\infty \int_0^\pi \int_0^{2\pi} \exp \left(- \frac{m_i(\boldsymbol{\xi}_i)^2}{2k_B T} \right) \xi_i^2 \sin \theta d\phi d\theta d\xi_i \\ &= c_i^\alpha \left(\frac{m_i}{2\pi k_B T} \right)^{\frac{3}{2}} \int_0^\infty \xi_i^2 \exp \left(- \frac{m_i(\boldsymbol{\xi}_i)^2}{2k_B T} \right) d\xi_i \underbrace{\int_0^\pi \sin \theta d\theta}_2 \underbrace{\int_0^{2\pi} d\phi}_{2\pi} \\ &= c_i^\alpha \left(\frac{m_i}{2\pi k_B T} \right)^{\frac{3}{2}} 4\pi \int_0^\infty \xi_i^2 \exp \left(- \frac{m_i(\boldsymbol{\xi}_i)^2}{2k_B T} \right) d\xi_i, \end{aligned}$$

where $\xi_i^2 = \boldsymbol{\xi}_i \cdot \boldsymbol{\xi}_i = |\boldsymbol{\xi}_i|^2$. Using the integral representation of gamma function defined as given below:

$$\int_0^\infty x^n e^{-\eta x^2} dx = \frac{1}{2} \Gamma \left(\frac{n+1}{2} \right) \left(\frac{1}{\eta} \right)^{\frac{n+1}{2}}, \quad (4.3.8)$$

we obtain that

$$\int_0^\infty \xi_i^2 \exp \left(- \frac{m_i(\boldsymbol{\xi}_i)^2}{2k_B T} \right) d\xi_i = \frac{1}{2} \Gamma \left(\frac{2+1}{2} \right) \left(\frac{2k_B T}{m_i} \right)^{\frac{2+1}{2}} = \frac{1}{2} \frac{\sqrt{\pi}}{2} \left(\frac{2k_B T}{m_i} \right)^{\frac{3}{2}}.$$

Therefore,

$$\begin{aligned} \int_{\mathbb{R}^3} f_i^\alpha d\mathbf{v}_i &= c_i^\alpha \left(\frac{m_i}{2\pi k_B T} \right)^{\frac{3}{2}} 4\pi \frac{1}{2} \frac{\sqrt{\pi}}{2} \left(\frac{2k_B T}{m_i} \right)^{\frac{3}{2}} \\ &= c_i^\alpha \left(\frac{m_i}{2\pi k_B T} \right)^{\frac{3}{2}} \left(\frac{2\pi k_B T}{m_i} \right)^{\frac{3}{2}} \\ &= c_i^\alpha. \end{aligned} \quad (4.3.9)$$

Using Eq. (4.2.3), the second integral on the left-hand side of Eq. (4.3.5) can be written as:

$$\int_{\mathbb{R}^3} \mathbf{v}_i f_i^\alpha d\mathbf{v}_i = c_i^\alpha \left(\frac{m_i}{2\pi k_B T} \right)^{\frac{3}{2}} \int_{\mathbb{R}^3} \mathbf{v}_i \exp \left(- \frac{m_i(\mathbf{v}_i - \alpha \mathbf{u}_i^\alpha)^2}{2k_B T} \right) d\mathbf{v}_i.$$

Using equation (4.3.7), the previous equation can be written as follows:

$$\begin{aligned} \int_{\mathbb{R}^3} \mathbf{v}_i f_i^\alpha d\mathbf{v}_i &= c_i^\alpha \left(\frac{m_i}{2\pi k_B T} \right)^{\frac{3}{2}} \int_{\mathbb{R}^3} (\boldsymbol{\xi}_i + \alpha \mathbf{u}_i^\alpha) \exp \left(- \frac{m_i(\boldsymbol{\xi}_i)^2}{2k_B T} \right) d\boldsymbol{\xi}_i \\ &= c_i^\alpha \left(\frac{m_i}{2\pi k_B T} \right)^{\frac{3}{2}} \left[\int_{\mathbb{R}^3} \boldsymbol{\xi}_i \exp \left(- \frac{m_i(\boldsymbol{\xi}_i)^2}{2k_B T} \right) d\boldsymbol{\xi}_i + \alpha \mathbf{u}_i^\alpha \int_{\mathbb{R}^3} \exp \left(- \frac{m_i(\boldsymbol{\xi}_i)^2}{2k_B T} \right) d\boldsymbol{\xi}_i \right]. \end{aligned}$$

Using the fact that any vector can be written in terms of a unit vector, we have that $\boldsymbol{\xi}_i$ can be written as $\boldsymbol{\xi}_i = \xi_i \vec{v}$, where $\xi_i = \|\boldsymbol{\xi}_i\| = |\boldsymbol{\xi}_i|$ and $\vec{v}$ is a unit vector. Thus the first integral in the last equality of the

previous equation can be written in spherical coordinates and evaluated as given below:

$$\begin{aligned}
& \int_{\mathbb{R}^3} \xi_i \vec{v} \exp \left(-\frac{m_i(\xi_i)^2}{2k_B T} \right) d\xi_i \\
&= \int_0^\infty \int_0^\pi \int_0^{2\pi} \xi_i (\hat{x} \sin \theta \cos \phi + \hat{y} \sin \theta \sin \phi + \hat{z} \cos \theta) \exp \left(-\frac{m_i(\xi_i)^2}{2k_B T} \right) \xi_i^2 \sin \theta d\phi d\theta d\xi_i \\
&= \int_0^\infty \xi_i^3 \exp \left(-\frac{m_i(\xi_i)^2}{2k_B T} \right) d\xi_i \left(\underbrace{\hat{x} \int_0^\pi \sin^2 \theta d\theta}_{\frac{\pi}{2}} \underbrace{\int_0^{2\pi} \cos \phi d\phi}_0 + \underbrace{\hat{y} \int_0^\pi \sin^2 \theta d\theta}_{\frac{\pi}{2}} \underbrace{\int_0^{2\pi} \sin \phi d\phi}_0 \right. \\
&\quad \left. + \underbrace{\hat{z} \int_0^\pi \cos \theta \sin \theta d\theta}_0 \underbrace{\int_0^{2\pi} d\phi}_{2\pi} \right),
\end{aligned}$$

where $\hat{x}, \hat{y}, \hat{z}$ are the Cartesian unit vectors in $\mathbb{R}^3$. The integral in ξ_i can be evaluated using the integral representation of gamma function given in Eq. (4.3.8) as given below:

$$\int_0^\infty \xi_i^3 \exp \left(-\frac{m_i(\xi_i)^2}{2k_B T} \right) d\xi_i = \frac{1}{2} \Gamma \left(\frac{3+1}{2} \right) \left(\frac{2k_B T}{m_i} \right)^{\frac{3+1}{2}} = \frac{1}{2} \Gamma(2) \left(\frac{2k_B T}{m_i} \right)^2 = \frac{1}{2} \left(\frac{2k_B T}{m_i} \right)^2.$$

Therefore,

$$\begin{aligned}
\int_{\mathbb{R}^3} \xi \exp \left(-\frac{m_i(\xi_i)^2}{2k_B T} \right) d\xi_i &= \frac{1}{2} \left(\frac{2k_B T}{m_i} \right)^2 \left[\hat{x} \left(\frac{\pi}{2} \times 0 \right) + \hat{y} \left(\frac{\pi}{2} \times 0 \right) + \hat{z} (0 \times 2\pi) \right] \\
&= \mathbf{0}.
\end{aligned} \tag{4.3.10}$$

Hence

$$\begin{aligned}
\int_{\mathbb{R}^3} \mathbf{v}_i f_i^\alpha d\mathbf{v}_i &= c_i^\alpha \left(\frac{m_i}{2\pi k_B T} \right)^{\frac{3}{2}} \left[\mathbf{0} + \alpha \mathbf{u}_i^\alpha \int_{\mathbb{R}^3} \exp \left(-\frac{m_i(\xi_i)^2}{2k_B T} \right) d\xi_i \right] \\
&= \alpha \mathbf{u}_i^\alpha c_i^\alpha \left(\frac{m_i}{2\pi k_B T} \right)^{\frac{3}{2}} \int_{\mathbb{R}^3} \exp \left(-\frac{m_i(\xi_i)^2}{2k_B T} \right) d\xi_i \\
&= \alpha \mathbf{u}_i^\alpha c_i^\alpha \left(\frac{m_i}{2\pi k_B T} \right)^{\frac{3}{2}} \int_{\mathbb{R}^3} \exp \left(-\frac{m_i(\mathbf{v}_i - \alpha \mathbf{u}_i^\alpha)^2}{2k_B T} \right) d\mathbf{v}_i \\
&= \alpha \mathbf{u}_i^\alpha \int_{\mathbb{R}^3} f_i^\alpha d\mathbf{v}_i,
\end{aligned}$$

where use have been made of equations (4.3.7) and (4.3.6) to obtain the third and fourth equalities, respectively, of the previous equation. Using equation (4.3.9), we obtain:

$$\int_{\mathbb{R}^3} \mathbf{v}_i f_i^\alpha d\mathbf{v}_i = \alpha c_i^\alpha \mathbf{u}_i^\alpha. \tag{4.3.11}$$

Substituting equations (4.3.9) and (4.3.11) into equation (4.3.5), we obtain:

$$\alpha \frac{\partial c_i^\alpha}{\partial t} + \alpha \frac{\partial}{\partial \mathbf{x}} (c_i^\alpha \mathbf{u}_i^\alpha) = \frac{1}{\alpha} \int_{\mathbb{R}^3} J_i^{\alpha m E} d\mathbf{v}_i + \frac{1}{\alpha} \int_{\mathbb{R}^3} J_i^{\alpha b E} d\mathbf{v}_i - \alpha \int_{\mathbb{R}^3} \tilde{J}_{ij}^{\alpha b * E} d\mathbf{v}_i + \alpha \int_{\mathbb{R}^3} \tilde{J}_i^{\alpha R} d\mathbf{v}_i. \quad (4.3.12)$$

Since the properties of the scaled collision operators are similar to their un-scaled version, using the first equation of (2.3.54) given in Corollary 2.3.13 with $m_i = 1$ for the first term on the right-hand side of equation (4.3.12), equations (2.3.55) and (2.3.56) of Corollary 2.3.14 with $m_i = 1$ for the second and third terms on the right-hand side, we obtain:

$$\alpha \frac{\partial c_i^\alpha}{\partial t} + \alpha \frac{\partial}{\partial \mathbf{x}} (c_i^\alpha \mathbf{u}_i^\alpha) = \alpha \int_{\mathbb{R}^3} \tilde{J}_i^{\alpha R} d\mathbf{v}_i.$$

Dividing both sides by α , we obtain

$$\frac{\partial c_i^\alpha}{\partial t} + \frac{\partial}{\partial \mathbf{x}} (c_i^\alpha \mathbf{u}_i^\alpha) = \int_{\mathbb{R}^3} \tilde{J}_i^{\alpha R} d\mathbf{v}_i. \quad (4.3.13)$$

Now let us derive an explicit expression for the integral on the right-hand side of equation (4.3.13). To do this, we replace the distribution functions by their approximations given in equation (4.2.4). For sake of simplicity, the approximations are written in the form:

$$f_i^\alpha \approx M_i^\alpha (1 + \mathbf{a}_i \cdot \mathbf{v}_i), \quad i = 1, 2, 3, 4, \quad \text{with} \quad \mathbf{a}_i = \frac{\alpha m_i \mathbf{u}_i^\alpha}{k_B T}. \quad (4.3.14)$$

Using equation (4.3.14), one obtains the following equations:

$$f_i^\alpha f_j^\alpha = M_i^\alpha M_j^\alpha (1 + \mathbf{a}_i \cdot \mathbf{v}_i + \mathbf{a}_j \cdot \mathbf{v}_j + (\mathbf{a}_i \cdot \mathbf{v}_i)(\mathbf{a}_j \cdot \mathbf{v}_j)), \quad (4.3.15)$$

$$\left(\frac{\mu_{ij}}{\mu_{kl}} \right)^2 f_k^{\alpha\circ} f_l^{\alpha\circ} = \left(\frac{\mu_{ij}}{\mu_{kl}} \right)^2 M_k^{\alpha\circ} M_l^{\alpha\circ} (1 + \mathbf{a}_k \cdot \mathbf{v}_k^\circ + \mathbf{a}_l \cdot \mathbf{v}_l^\circ + (\mathbf{a}_k \cdot \mathbf{v}_k^\circ)(\mathbf{a}_l \cdot \mathbf{v}_l^\circ)). \quad (4.3.16)$$

Therefore,

$$\begin{aligned} \left(\frac{\mu_{ij}}{\mu_{kl}} \right)^2 f_k^{\alpha\circ} f_l^{\alpha\circ} - f_i^\alpha f_j^\alpha &= \left(\frac{\mu_{ij}}{\mu_{kl}} \right)^2 M_k^{\alpha\circ} M_l^{\alpha\circ} (1 + \mathbf{a}_k \cdot \mathbf{v}_k^\circ + \mathbf{a}_l \cdot \mathbf{v}_l^\circ + (\mathbf{a}_k \cdot \mathbf{v}_k^\circ)(\mathbf{a}_l \cdot \mathbf{v}_l^\circ)) \\ &\quad - M_i^\alpha M_j^\alpha (1 + \mathbf{a}_i \cdot \mathbf{v}_i + \mathbf{a}_j \cdot \mathbf{v}_j + (\mathbf{a}_i \cdot \mathbf{v}_i)(\mathbf{a}_j \cdot \mathbf{v}_j)). \end{aligned}$$

Expanding, rearranging and neglecting the terms of order α^2 , that is, the terms with coefficients $(\mathbf{a}_k \cdot \mathbf{v}_k^\circ)(\mathbf{a}_l \cdot \mathbf{v}_l^\circ)$ and $(\mathbf{a}_i \cdot \mathbf{v}_i)(\mathbf{a}_j \cdot \mathbf{v}_j)$, we obtain:

$$\begin{aligned} \left(\frac{\mu_{ij}}{\mu_{kl}} \right)^2 f_k^{\alpha\circ} f_l^{\alpha\circ} - f_i^\alpha f_j^\alpha &= \left[\left(\frac{\mu_{ij}}{\mu_{kl}} \right)^2 M_k^{\alpha\circ} M_l^{\alpha\circ} - M_i^\alpha M_j^\alpha \right] + \left[\left(\frac{\mu_{ij}}{\mu_{kl}} \right)^2 M_k^{\alpha\circ} M_l^{\alpha\circ} \right. \\ &\quad \left. \times (\mathbf{a}_k \cdot \mathbf{v}_k^\circ + \mathbf{a}_l \cdot \mathbf{v}_l^\circ) - M_i^\alpha M_j^\alpha (\mathbf{a}_i \cdot \mathbf{v}_i + \mathbf{a}_j \cdot \mathbf{v}_j) \right]. \end{aligned} \quad (4.3.17)$$

Substituting the previous equation into the scaled reactive collision operator $\tilde{J}_i^{\alpha R}$ given in equation (3.3.18), we can write the integral appearing on the right-hand side of equation (4.3.13) as the sum of the following three terms:

$$\begin{aligned}
\mathcal{D} &= \sigma_{ij}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} \left[\left(\frac{\mu_{ij}}{\mu_{kl}} \right)^2 M_k^{\alpha\circ} M_l^{\alpha\circ} - M_i^\alpha M_j^\alpha \right] \\
&\quad \times \Theta \left(\langle \boldsymbol{\epsilon}, c_0 \mathbf{v}_i - c_0 \mathbf{v}_j \rangle - \Xi_{ij} \right) \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_j \rangle d\boldsymbol{\epsilon} d\mathbf{v}_j d\mathbf{v}_i, \\
\bar{\mathcal{E}} &= \sigma_{ij}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} \left(\frac{\mu_{ij}}{\mu_{kl}} \right)^2 M_k^{\alpha\circ} M_l^{\alpha\circ} (\mathbf{a}_k \cdot \mathbf{v}_k^\circ + \mathbf{a}_l \cdot \mathbf{v}_l^\circ) \\
&\quad \times \Theta \left(\langle \boldsymbol{\epsilon}, c_0 \mathbf{v}_i - c_0 \mathbf{v}_j \rangle - \Xi_{ij} \right) \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_j \rangle d\boldsymbol{\epsilon} d\mathbf{v}_j d\mathbf{v}_i, \\
\mathcal{F} &= -\sigma_{ij}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} M_i^\alpha M_j^\alpha (\mathbf{a}_i \cdot \mathbf{v}_i + \mathbf{a}_j \cdot \mathbf{v}_j) \\
&\quad \times \Theta \left(\langle \boldsymbol{\epsilon}, c_0 \mathbf{v}_i - c_0 \mathbf{v}_j \rangle - \Xi_{ij} \right) \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_j \rangle d\boldsymbol{\epsilon} d\mathbf{v}_j d\mathbf{v}_i.
\end{aligned} \tag{4.3.18}$$

Now let us evaluate the integrals $\mathcal{D}$, $\bar{\mathcal{E}}$ and $\mathcal{F}$ starting with $\mathcal{D}$. Using equation (4.2.5), observe that

$$\begin{aligned}
&\left(\frac{\mu_{ij}}{\mu_{kl}} \right)^2 M_k^{\alpha\circ} M_l^{\alpha\circ} - M_i^\alpha M_j^\alpha \\
&= \left(\frac{\mu_{ij}}{\mu_{kl}} \right)^2 c_k^\alpha c_l^\alpha \frac{(m_k m_l)^{\frac{3}{2}}}{(2\pi k_B T)^3} \exp \left(-\frac{m_k (\mathbf{v}_k^\circ)^2 + m_l (\mathbf{v}_l^\circ)^2}{2k_B T} \right) \\
&\quad - c_i^\alpha c_j^\alpha \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} \exp \left(-\frac{m_i (\mathbf{v}_i)^2 + m_j (\mathbf{v}_j)^2}{2k_B T} \right) \\
&= \left[\left(\frac{\mu_{ij}}{\mu_{kl}} \right)^2 c_k^\alpha c_l^\alpha \frac{(m_k m_l)^{\frac{3}{2}}}{(2\pi k_B T)^3} \exp \left(-\frac{m_k (\mathbf{v}_k^\circ)^2 + m_l (\mathbf{v}_l^\circ)^2 - m_i (\mathbf{v}_i)^2 - m_j (\mathbf{v}_j)^2}{2k_B T} \right) \right. \\
&\quad \left. - c_i^\alpha c_j^\alpha \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} \right] \exp \left(-\frac{m_i (\mathbf{v}_i)^2 + m_j (\mathbf{v}_j)^2}{2k_B T} \right).
\end{aligned}$$

Using the conservation of total energy given in equation (2.3.12), we have that

$$\exp \left(-\frac{m_k (\mathbf{v}_k^\circ)^2 + m_l (\mathbf{v}_l^\circ)^2 - m_i (\mathbf{v}_i)^2 - m_j (\mathbf{v}_j)^2}{2k_B T} \right) = \exp \left(\frac{Q_R}{k_B T} \right),$$

where Q_R is as defined in equation (2.3.3). Therefore,

$$\begin{aligned}
&\left(\frac{\mu_{ij}}{\mu_{kl}} \right)^2 M_k^{\alpha\circ} M_l^{\alpha\circ} - M_i^\alpha M_j^\alpha \\
&= \left[\left(\frac{\mu_{ij}}{\mu_{kl}} \right)^2 c_k^\alpha c_l^\alpha \frac{(m_k m_l)^{\frac{3}{2}}}{(2\pi k_B T)^3} \exp \left(\frac{Q_R}{k_B T} \right) - c_i^\alpha c_j^\alpha \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} \right] \\
&\quad \times \exp \left(-\frac{m_i (\mathbf{v}_i)^2 + m_j (\mathbf{v}_j)^2}{2k_B T} \right) \\
&= \left[\left(\frac{m_i m_j}{m_k m_l} \right)^2 c_k^\alpha c_l^\alpha \frac{(m_k m_l)^{\frac{3}{2}}}{(2\pi k_B T)^3} \exp \left(\frac{Q_R}{k_B T} \right) - c_i^\alpha c_j^\alpha \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} \right] \\
&\quad \times \exp \left(-\frac{m_i (\mathbf{v}_i)^2 + m_j (\mathbf{v}_j)^2}{2k_B T} \right)
\end{aligned}$$

$$\begin{aligned}
&= \frac{1}{(2\pi k_B T)^3} \left[\frac{(m_i m_j)^2}{(m_k m_l)^{\frac{1}{2}}} c_k^\alpha c_l^\alpha \exp\left(\frac{Q_R}{k_B T}\right) - c_i^\alpha c_j^\alpha (m_i m_j)^{\frac{3}{2}} \right] \\
&\quad \times \exp\left(-\frac{m_i(\mathbf{v}_i)^2 + m_j(\mathbf{v}_j)^2}{2k_B T}\right) \\
&= \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} \left[\frac{(m_i m_j)^{\frac{1}{2}}}{(m_k m_l)^{\frac{1}{2}}} c_k^\alpha c_l^\alpha \exp\left(\frac{Q_R}{k_B T}\right) - c_i^\alpha c_j^\alpha \right] \exp\left(-\frac{m_i(\mathbf{v}_i)^2 + m_j(\mathbf{v}_j)^2}{2k_B T}\right) \\
&= \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} \left[\left(\frac{\mu_{ij}}{\mu_{kl}}\right)^{\frac{1}{2}} c_k^\alpha c_l^\alpha \exp\left(\frac{Q_R}{k_B T}\right) - c_i^\alpha c_j^\alpha \right] \exp\left(-\frac{m_i(\mathbf{v}_i)^2 + m_j(\mathbf{v}_j)^2}{2k_B T}\right), \quad (4.3.19)
\end{aligned}$$

where

$$\mu_{ij} = \frac{m_i m_j}{m_i + m_j}, \quad \mu_{kl} = \frac{m_k m_l}{m_k + m_l} \quad \text{and} \quad m_i + m_j = m_k + m_l = M$$

have been used to obtain equation (4.3.19). Substituting equation (4.3.19) into the integral $\mathcal{D}$ given in equation (4.3.18), we obtain:

$$\begin{aligned}
\mathcal{D} &= \sigma_{ij}^2 \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} \left[\left(\frac{\mu_{ij}}{\mu_{kl}}\right)^{\frac{1}{2}} c_k^\alpha c_l^\alpha \exp\left(\frac{Q_R}{k_B T}\right) - c_i^\alpha c_j^\alpha \right] \\
&\quad \times \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} \exp\left(-\frac{m_i(\mathbf{v}_i)^2 + m_j(\mathbf{v}_j)^2}{2k_B T}\right) \Theta(\langle \boldsymbol{\epsilon}, c_0 \mathbf{v}_i - c_0 \mathbf{v}_j \rangle - \Xi_{ij}) \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_j \rangle d\boldsymbol{\epsilon} d\mathbf{v}_j d\mathbf{v}_i.
\end{aligned}$$

Observe that

$$\begin{aligned}
&\int_{\mathbb{S}_+^2} \Theta(\langle \boldsymbol{\epsilon}, c_0 \mathbf{v}_i - c_0 \mathbf{v}_j \rangle - \Xi_{ij}) \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_j \rangle d\boldsymbol{\epsilon} \\
&= \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) \int_0^{\arccos\left(\frac{\Xi_{ij}}{c_0 V^*}\right)} \int_0^{2\pi} V^* \cos\theta \sin\theta d\phi d\theta \\
&= 2\pi V^* \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) \int_0^{\arccos\left(\frac{\Xi_{ij}}{c_0 V^*}\right)} \cos\theta \sin\theta d\theta \\
&= 2\pi V^* \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) \left[-\frac{\cos^2\theta}{2}\right]_0^{\arccos\left(\frac{\Xi_{ij}}{c_0 V^*}\right)} \\
&= \pi V^* \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) \left[-\left(\frac{\Xi_{ij}}{c_0 V^*}\right)^2 + 1\right] \\
&= \pi V^* \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) \left[1 - \left(\frac{\Xi_{ij}}{c_0 V^*}\right)^2\right], \quad (4.3.20)
\end{aligned}$$

where equation (2.4.7) have been used together with the fact that $V^* = |\mathbf{v}_j - \mathbf{v}_i| = |\mathbf{v}_i - \mathbf{v}_j|$. Therefore,

$$\begin{aligned}
\mathcal{D} &= \sigma_{ij}^2 \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} \left[\left(\frac{\mu_{ij}}{\mu_{kl}}\right)^{\frac{1}{2}} c_k^\alpha c_l^\alpha \exp\left(\frac{Q_R}{k_B T}\right) - c_i^\alpha c_j^\alpha \right] \\
&\quad \times \pi \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \exp\left(-\frac{m_i(\mathbf{v}_i)^2 + m_j(\mathbf{v}_j)^2}{2k_B T}\right) V^* \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) \left[1 - \left(\frac{\Xi_{ij}}{c_0 V^*}\right)^2\right] d\mathbf{v}_j d\mathbf{v}_i.
\end{aligned}$$

It is convenient to transform the above six fold integral from $\mathbf{v}_i$ and $\mathbf{v}_j$ to the centre of mass velocity $\mathbf{X}^*$ and relative velocity $\mathbf{V}^*$ defined as given in equations (2.4.6) and (2.4.7), respectively. Now using equation (2.4.12) with $m_i + m_j = M$ together with the fact that the Jacobian of the transformation $(\mathbf{v}_i, \mathbf{v}_j) \rightarrow (\mathbf{X}^*, \mathbf{V}^*)$ has absolute value 1, which implies that

$$d\mathbf{v}_i d\mathbf{v}_j = d\mathbf{X}^* d\mathbf{V}^*, \quad (4.3.21)$$

we can rewrite the integral $\mathcal{D}$ as follows:

$$\begin{aligned} \mathcal{D} &= \sigma_{ij}^2 \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} \left[\left(\frac{\mu_{ij}}{\mu_{kl}} \right)^{\frac{1}{2}} c_k^\alpha c_l^\alpha \exp\left(\frac{Q_R}{k_B T}\right) - c_i^\alpha c_j^\alpha \right] \\ &\times \pi \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \exp\left(-\frac{MX^{*2} + \mu_{ij}V^{*2}}{2k_B T}\right) V^* \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) \left[1 - \left(\frac{\Xi_{ij}}{c_0 V^*}\right)^2\right] d\mathbf{X}^* d\mathbf{V}^* \\ &= \sigma_{ij}^2 \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} \left[\left(\frac{\mu_{ij}}{\mu_{kl}} \right)^{\frac{1}{2}} c_k^\alpha c_l^\alpha \exp\left(\frac{Q_R}{k_B T}\right) - c_i^\alpha c_j^\alpha \right] \pi \\ &\times \int_{\mathbb{R}^3} \exp\left(-\frac{MX^{*2}}{2k_B T}\right) d\mathbf{X}^* \int_{\mathbb{R}^3} \exp\left(-\frac{\mu_{ij}V^{*2}}{2k_B T}\right) V^* \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) \left[1 - \left(\frac{\Xi_{ij}}{c_0 V^*}\right)^2\right] d\mathbf{V}^*. \end{aligned}$$

Integrating the first integral in the last equality in the previous equation in spherical coordinates gives:

$$\begin{aligned} \int_{\mathbb{R}^3} \exp\left(-\frac{MX^{*2}}{2k_B T}\right) d\mathbf{X}^* &= \int_0^\infty \int_0^\pi \int_0^{2\pi} \exp\left(-\frac{MX^{*2}}{2k_B T}\right) X^{*2} \sin\theta \, d\phi \, d\theta \, dX^* \\ &= 2\pi \int_0^\infty \int_0^\pi \exp\left(-\frac{MX^{*2}}{2k_B T}\right) X^{*2} \sin\theta \, d\theta \, dX^* \\ &= 4\pi \int_0^\infty \exp\left(-\frac{MX^{*2}}{2k_B T}\right) X^{*2} \, dX^*. \end{aligned}$$

Using the integral representation of gamma function given in equation (4.3.8) with $n = 2$ and $\eta = \left(\frac{M}{2k_B T}\right)$ gives:

$$\begin{aligned} \int_{\mathbb{R}^3} \exp\left(-\frac{MX^{*2}}{2k_B T}\right) d\mathbf{X}^* &= 4\pi \frac{1}{2} \Gamma\left(\frac{3}{2}\right) \left(\frac{2k_B T}{M}\right)^{\frac{3}{2}} \\ &= 2\pi \times \frac{\sqrt{\pi}}{2} \left(\frac{2k_B T}{M}\right)^{\frac{3}{2}} \\ &= \left(\frac{2\pi k_B T}{M}\right)^{\frac{3}{2}}. \end{aligned} \quad (4.3.22)$$

Therefore, the integral $\mathcal{D}$ reduces to:

$$\begin{aligned} \mathcal{D} &= \sigma_{ij}^2 \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} \left[\left(\frac{\mu_{ij}}{\mu_{kl}} \right)^{\frac{1}{2}} c_k^\alpha c_l^\alpha \exp\left(\frac{Q_R}{k_B T}\right) - c_i^\alpha c_j^\alpha \right] \pi \left(\frac{2\pi k_B T}{M}\right)^{\frac{3}{2}} \\ &\times \int_{\mathbb{R}^3} \exp\left(-\frac{\mu_{ij}V^{*2}}{2k_B T}\right) V^* \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) \left[1 - \left(\frac{\Xi_{ij}}{c_0 V^*}\right)^2\right] d\mathbf{V}^* \end{aligned}$$

$$\begin{aligned}
&= \sigma_{ij}^2 \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} \left[\left(\frac{\mu_{ij}}{\mu_{kl}} \right)^{\frac{1}{2}} c_k^\alpha c_l^\alpha \exp\left(\frac{Q_R}{k_B T}\right) - c_i^\alpha c_j^\alpha \right] \pi \left(\frac{2\pi k_B T}{M} \right)^{\frac{3}{2}} \\
&\quad \left[\int_{\mathbb{R}^3} \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) V^* \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) d\mathbf{V}^* \right. \\
&\quad \left. - \int_{\mathbb{R}^3} \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) V^* \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) \left(\frac{\Xi_{ij}}{c_0 V^*}\right)^2 d\mathbf{V}^* \right].
\end{aligned}$$

Integrating the first integral in the last equality of the previous equation in spherical coordinates gives:

$$\begin{aligned}
&\int_{\mathbb{R}^3} \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) V^* \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) d\mathbf{V}^* \\
&= \int_0^\infty \int_0^\pi \int_0^{2\pi} \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) V^* \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) V^{*2} \sin\theta \, d\phi \, d\theta \, dV^* \\
&= \int_0^\infty \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) V^* \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) V^{*2} dV^* \underbrace{\int_0^\pi \sin\theta \, d\theta}_2 \underbrace{\int_0^{2\pi} d\phi}_{2\pi} \\
&= 4\pi \int_{V^* \geq \frac{\Xi_{ij}}{c_0}}^\infty V^{*3} \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) dV^*.
\end{aligned}$$

Let

$$z^{\frac{1}{2}} = V^* \left(\frac{\mu_{ij}}{2k_B T} \right)^{\frac{1}{2}} \iff z = \left(\frac{\mu_{ij} V^{*2}}{2k_B T} \right). \quad (4.3.23)$$

Therefore,

$$\begin{aligned}
V^* &= z^{\frac{1}{2}} \left(\frac{2k_B T}{\mu_{ij}} \right)^{\frac{1}{2}} \iff V^{*3} = z^{\frac{3}{2}} \left(\frac{2k_B T}{\mu_{ij}} \right)^{\frac{3}{2}}, \\
\frac{dV^*}{dz} &= \frac{1}{2} z^{-\frac{1}{2}} \left(\frac{2k_B T}{\mu_{ij}} \right)^{\frac{1}{2}} \iff dV^* = \frac{1}{2z^{\frac{1}{2}}} \left(\frac{2k_B T}{\mu_{ij}} \right)^{\frac{1}{2}} dz.
\end{aligned} \quad (4.3.24)$$

With the change of variable given in equation (4.3.23), the condition $V^* \geq \frac{\Xi_{ij}}{c_0}$ becomes

$$z^{\frac{1}{2}} \left(\frac{2k_B T}{\mu_{ij}} \right)^{\frac{1}{2}} \geq \frac{\Xi_{ij}}{c_0} \iff z^{\frac{1}{2}} \geq \frac{\Xi_{ij}}{c_0} \left(\frac{\mu_{ij}}{2k_B T} \right)^{\frac{1}{2}} \iff z \geq \left(\frac{\Xi_{ij}}{c_0} \right)^2 \frac{\mu_{ij}}{2k_B T} = z_i^*. \quad (4.3.25)$$

Thus

$$\begin{aligned}
\int_{\mathbb{R}^3} \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) V^* \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) d\mathbf{V}^* &= 4\pi \int_{z_i^*}^\infty z^{\frac{3}{2}} \left(\frac{2k_B T}{\mu_{ij}} \right)^{\frac{3}{2}} \exp(-z) \frac{1}{2z^{\frac{1}{2}}} \left(\frac{2k_B T}{\mu_{ij}} \right)^{\frac{1}{2}} dz \\
&= 2\pi \left(\frac{2k_B T}{\mu_{ij}} \right)^2 \int_{z_i^*}^\infty z \exp(-z) dz.
\end{aligned}$$

Using the incomplete Euler gamma function given in equation (4.3.3) with $\eta - 1 = 1$, i.e., $\eta = 2$ gives:

$$\int_{\mathbb{R}^3} \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) V^* \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) d\mathbf{V}^* = 2\pi \left(\frac{2k_B T}{\mu_{ij}} \right)^2 \Gamma(2, z_i^*).$$

Therefore, the integral $\mathcal{D}$ reduces to:

$$\mathcal{D} = \sigma_{ij}^2 \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} \left[\left(\frac{\mu_{ij}}{\mu_{kl}} \right)^{\frac{1}{2}} c_k^\alpha c_l^\alpha \exp\left(\frac{Q_R}{k_B T}\right) - c_i^\alpha c_j^\alpha \right] \pi \left(\frac{2\pi k_B T}{M} \right)^{\frac{3}{2}} \left[2\pi \left(\frac{2k_B T}{\mu_{ij}} \right)^2 \Gamma(2, z_i^*) - \int_{\mathbb{R}^3} \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) V^* \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) \left(\frac{\Xi_{ij}}{c_0 V^*}\right)^2 d\mathbf{V}^* \right].$$

Integrating the integral on the right-hand side of the previous equation in spherical coordinates gives:

$$\begin{aligned} & \int_{\mathbb{R}^3} \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) V^* \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) \left(\frac{\Xi_{ij}}{c_0 V^*}\right)^2 d\mathbf{V}^* \\ &= \int_0^\infty \int_0^\pi \int_0^{2\pi} \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) V^* \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) \left(\frac{\Xi_{ij}}{c_0 V^*}\right)^2 V^{*2} \sin\theta d\phi d\theta dV^* \\ &= \int_0^\infty \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) V^* \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) \left(\frac{\Xi_{ij}}{c_0 V^*}\right)^2 V^{*2} dV^* \underbrace{\int_0^\pi \sin\theta d\theta}_2 \underbrace{\int_0^{2\pi} d\phi}_{2\pi} \\ &= 4\pi \left(\frac{\Xi_{ij}}{c_0}\right)^2 \int_{V^* \geq \frac{\Xi_{ij}}{c_0}}^\infty V^* \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) dV^*. \end{aligned}$$

Using the change of variable given in equation (4.3.23) together with equations (4.3.24) and (4.3.25), we have that the previous equation can be rewritten as:

$$\begin{aligned} & \int_{\mathbb{R}^3} \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) V^* \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) \left(\frac{\Xi_{ij}}{c_0 V^*}\right)^2 d\mathbf{V}^* \\ &= 4\pi \left(\frac{\Xi_{ij}}{c_0}\right)^2 \int_{z_i^*}^\infty z^{\frac{1}{2}} \left(\frac{2k_B T}{\mu_{ij}}\right)^{\frac{1}{2}} \exp(-z) \frac{1}{2z^{\frac{1}{2}}} \left(\frac{2k_B T}{\mu_{ij}}\right)^{\frac{1}{2}} dz \\ &= 2\pi \left(\frac{\Xi_{ij}}{c_0}\right)^2 \left(\frac{2k_B T}{\mu_{ij}}\right) \int_{z_i^*}^\infty \exp(-z) dz. \end{aligned}$$

Using the incomplete Euler gamma function given in equation (4.3.3) with $\eta - 1 = 0$, i.e., $\eta = 1$, gives:

$$\int_{\mathbb{R}^3} \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) V^* \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) \left(\frac{\Xi_{ij}}{c_0 V^*}\right)^2 d\mathbf{V}^* = 2\pi \left(\frac{\Xi_{ij}}{c_0}\right)^2 \left(\frac{2k_B T}{\mu_{ij}}\right) \Gamma(1, z_i^*).$$

Therefore, the integral $\mathcal{D}$ reduces to:

$$\begin{aligned} \mathcal{D} &= \sigma_{ij}^2 \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} \left[\left(\frac{\mu_{ij}}{\mu_{kl}} \right)^{\frac{1}{2}} c_k^\alpha c_l^\alpha \exp\left(\frac{Q_R}{k_B T}\right) - c_i^\alpha c_j^\alpha \right] \pi \left(\frac{2\pi k_B T}{M} \right)^{\frac{3}{2}} \\ &\quad \left[2\pi \left(\frac{2k_B T}{\mu_{ij}} \right)^2 \Gamma(2, z_i^*) - 2\pi \left(\frac{\Xi_{ij}}{c_0} \right)^2 \left(\frac{2k_B T}{\mu_{ij}} \right) \Gamma(1, z_i^*) \right] \\ &= \sigma_{ij}^2 \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} 2\pi^2 \left(\frac{2\pi k_B T}{M} \right)^{\frac{3}{2}} \left(\frac{2k_B T}{\mu_{ij}} \right) \left[\left(\frac{\mu_{ij}}{\mu_{kl}} \right)^{\frac{1}{2}} c_k^\alpha c_l^\alpha \exp\left(\frac{Q_R}{k_B T}\right) - c_i^\alpha c_j^\alpha \right] \\ &\quad \left[\left(\frac{2k_B T}{\mu_{ij}} \right) \Gamma(2, z_i^*) - \left(\frac{\Xi_{ij}}{c_0} \right)^2 \Gamma(1, z_i^*) \right]. \end{aligned}$$

Observe that

$$\begin{aligned}
\sigma_{ij}^2 \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} 2\pi^2 \left(\frac{2\pi k_B T}{M} \right)^{\frac{3}{2}} \left(\frac{2k_B T}{\mu_{ij}} \right) &= \sigma_{ij}^2 \frac{1}{(2\pi k_B T)^{\frac{3}{2}}} 2\pi^2 \left(\frac{m_i m_j}{m_i + m_j} \right)^{\frac{3}{2}} \left(\frac{2k_B T}{\mu_{ij}} \right) \\
&= \sigma_{ij}^2 2\pi \left(\frac{\mu_{ij}}{2\pi k_B T} \right)^{\frac{3}{2}} \left(\frac{2\pi k_B T}{\mu_{ij}} \right) \\
&= \sigma_{ij}^2 \left(\frac{2\pi \mu_{ij}}{k_B T} \right)^{\frac{1}{2}}.
\end{aligned}$$

Thus

$$\begin{aligned}
\mathcal{D} = \sigma_{ij}^2 \left(\frac{2\pi \mu_{ij}}{k_B T} \right)^{\frac{1}{2}} &\left[\left(\frac{\mu_{ij}}{\mu_{kl}} \right)^{\frac{1}{2}} c_k^\alpha c_l^\alpha \exp \left(\frac{Q_R}{k_B T} \right) - c_i^\alpha c_j^\alpha \right] \\
&\times \left[\left(\frac{2k_B T}{\mu_{ij}} \right) \Gamma(2, z_i^*) - \left(\frac{\Xi_{ij}}{c_0} \right)^2 \Gamma(1, z_i^*) \right]. \quad (4.3.26)
\end{aligned}$$

Following similar steps as those used to obtain equation (4.3.26) above, one obtains that the integrals $\bar{\mathcal{E}}$ and $\mathcal{F}$ given in equation (4.3.18) both vanish. For the evaluation of the integrals $\bar{\mathcal{E}}$ and $\mathcal{F}$, see Appendix A Section A.1 and Section A.2, respectively. Therefore,

$$\begin{aligned}
\int_{\mathbb{R}^3} \tilde{J}_i^{\alpha R} d\mathbf{v}_i &= \sigma_{ij}^2 \left(\frac{2\pi \mu_{ij}}{k_B T} \right)^{\frac{1}{2}} \left[\left(\frac{\mu_{ij}}{\mu_{kl}} \right)^{\frac{1}{2}} c_k^\alpha c_l^\alpha \exp \left(\frac{Q_R}{k_B T} \right) - c_i^\alpha c_j^\alpha \right] \\
&\times \left[\left(\frac{2k_B T}{\mu_{ij}} \right) \Gamma(2, z_i^*) - \left(\frac{\Xi_{ij}}{c_0} \right)^2 \Gamma(1, z_i^*) \right]. \quad (4.3.27)
\end{aligned}$$

Finally, the fact that $\mathcal{J}_i = \lambda_i \mathcal{J}_1$, where $\lambda_1 = \lambda_2 = 1$ and $\lambda_3 = \lambda_4 = -1$ is an immediate consequence of Corollary 2.3.15 about the reactive collision operators. $\square$

Remark 4.3.2. (a) The reaction rate $\mathcal{J}_i$ given in equation (4.3.2) can be written in an equivalent form, as a phenomenological law for the chemical reaction (2.3.1):

$$\mathcal{J}_i = -\lambda_i \left(k_f c_1^\alpha c_2^\alpha - k_b c_3^\alpha c_4^\alpha \right), \quad i = 1, \dots, 4, \quad (4.3.28)$$

with k_f and k_b being the forward and backward rate constants given, respectively, by

$$k_f = \sigma_{12}^2 \sqrt{\frac{8\pi k_B T}{\mu_{12}}} \exp \left(-\frac{\zeta_1}{k_B T} \right) \quad \text{and} \quad k_b = \sigma_{34}^2 \sqrt{\frac{8\pi k_B T}{\mu_{34}}} \exp \left(-\frac{\zeta_3}{k_B T} \right), \quad (4.3.29)$$

Equation (4.3.28) expresses the reaction rate in the form used, in general, in physical applications, see [74].

(b) The reaction rate $\mathcal{J}_i$ given in equation (4.3.2) differs from the corresponding one obtained in [13], see equation (42) of [13]. This is essentially because the cross-sections of the SRS kinetic model are of hard-sphere type and the integral over $\mathbb{S}_+^2$ was explicitly evaluated, see, equation (4.3.20), whereas the cross-sections of the kinetic model studied in [13] are of Maxwell molecules type and the integral over $\mathbb{S}^2$ was not explicitly evaluated. Moreover, the

exponent $1/2$, instead of $3/2$ as in [13], is a consequence of the fact that the exponent of the term (μ_{ij}/μ_{kl}) in the reactive collision operator $J_i^{\alpha R}$ is 2, see equation (3.3.16), while in [13] it is 3.

4.4 Momentum Balance Equations

The momentum balance equations for the species in the reactive mixture can formally be derived from the scaled SRS kinetic equations given in equation (4.2.1). This is achieved by multiplying the scaled kinetic equations by the molecular velocity $\mathbf{v}_i$ and then integrate the resulting equations over all possible velocities.

Lemma 4.4.1. *The momentum balance equation for each of the species in the reactive mixture is given by*

$$\alpha^2 \frac{\partial}{\partial t} (c_i^\alpha \mathbf{u}_i^\alpha) + \frac{k_B T}{m_i} \frac{\partial c_i^\alpha}{\partial \mathbf{x}} + \alpha^2 \frac{\partial}{\partial \mathbf{x}} (c_i^\alpha \mathbf{u}_i^\alpha \otimes \mathbf{u}_i^\alpha) = \mathcal{O}_i - \mathcal{P}_i + \mathcal{Q}_i, \quad (4.4.1)$$

where

$$\mathcal{O}_i = \frac{32}{9} \sum_{\substack{s=1 \\ s \neq i}}^4 \sigma_{is}^2 \frac{m_s}{m_i + m_s} \left(\frac{2\pi k_B T}{\mu_{is}} \right)^{\frac{1}{2}} c_i^\alpha c_s^\alpha (\mathbf{u}_s^\alpha - \mathbf{u}_i^\alpha), \quad (4.4.2)$$

$$\mathcal{P}_i = \alpha^2 \sigma_{ij}^2 \frac{8\sqrt{\pi} m_j}{9M} \frac{\mu_{ij}}{k_B T} c_i^\alpha c_j^\alpha (\mathbf{u}_j^\alpha - \mathbf{u}_i^\alpha) \left[\left(\frac{2k_B T}{\mu_{ij}} \right)^{\frac{3}{2}} \Gamma(3, z_i^*) - \left(\frac{\Xi_{ij}}{c_0} \right)^3 \Gamma\left(\frac{3}{2}, z_i^*\right) \right] \quad (4.4.3)$$

$$\begin{aligned} \mathcal{Q}_i = & \alpha^2 \sigma_{ij}^2 c_k^\alpha c_l^\alpha \frac{1}{M} \left\{ \left[2 \left(\frac{2\pi k_B T}{\mu_{kl}} \right)^{\frac{1}{2}} \left(m_k \Gamma(2, z_{i*}) + \frac{2}{3} m_l \Gamma(3, z_{i*}) \right) \right. \right. \\ & - \left. \left(\frac{\Xi_{kl}}{c_0} \right)^2 \left(\frac{2\pi \mu_{kl}}{k_B T} \right)^{\frac{1}{2}} \left(m_k \Gamma(1, z_{i*}) + \frac{2}{3} m_l \Gamma(2, z_{i*}) \right) \right] \mathbf{u}_k^\alpha \\ & + \left[2 \left(\frac{2\pi k_B T}{\mu_{kl}} \right)^{\frac{1}{2}} \left(m_k \Gamma(2, z_{i*}) + \frac{2}{3} m_l \Gamma(3, z_{i*}) \right) \right. \\ & - \left. \left. \left(\frac{\Xi_{kl}}{c_0} \right)^2 \left(\frac{2\pi \mu_{kl}}{k_B T} \right)^{\frac{1}{2}} \left(m_k \Gamma(1, z_{i*}) + \frac{2}{3} m_l \Gamma(2, z_{i*}) \right) \right] \mathbf{u}_l^\alpha \right\} \\ & - \alpha^2 \sigma_{ij}^2 c_i^\alpha c_j^\alpha \frac{1}{M} \left\{ \left[2 \left(\frac{2\pi k_B T}{\mu_{ij}} \right)^{\frac{1}{2}} \left\{ m_i \Gamma(2, z_i^*) + \frac{2}{3} m_j \Gamma(3, z_i^*) \right\} \right. \right. \\ & + \left. \left(\frac{\Xi_{ij}}{c_0} \right)^2 \left(\frac{2\pi \mu_{ij}}{k_B T} \right)^{\frac{1}{2}} \left(m_i \Gamma(1, z_i^*) + \frac{2}{3} m_j \Gamma(2, z_i^*) \right) \right] \mathbf{u}_i^\alpha \\ & - \left[2 \left(\frac{2\pi k_B T}{\mu_{ij}} \right)^{\frac{1}{2}} \left\{ m_i \Gamma(2, z_i^*) + \frac{2}{3} m_j \Gamma(3, z_i^*) \right\} \right. \\ & + \left. \left. \left(\frac{\Xi_{ij}}{c_0} \right)^2 \left(\frac{2\pi \mu_{ij}}{k_B T} \right)^{\frac{1}{2}} \left(m_i \Gamma(1, z_i^*) + \frac{2}{3} m_j \Gamma(2, z_i^*) \right) \right] \mathbf{u}_j^\alpha \right\}. \end{aligned} \quad (4.4.4)$$

Proof. Multiplying both sides of the scaled SRS kintetic equations given in equation (4.2.1) by $\mathbf{v}_i$ and then integrate the resulting equation with respect $\mathbf{v}_i \in \mathbb{R}^3$, we obtain:

$$\begin{aligned} \alpha \int_{\mathbb{R}^3} \mathbf{v}_i \frac{\partial f_i^\alpha}{\partial t} d\mathbf{v}_i + \int_{\mathbb{R}^3} (\mathbf{v}_i \otimes \mathbf{v}_i) \frac{\partial f_i^\alpha}{\partial \mathbf{x}} d\mathbf{v}_i \\ = \frac{1}{\alpha} \int_{\mathbb{R}^3} \mathbf{v}_i J_i^{\alpha m E} d\mathbf{v}_i + \frac{1}{\alpha} \int_{\mathbb{R}^3} \mathbf{v}_i J_i^{\alpha b E} d\mathbf{v}_i - \alpha \int_{\mathbb{R}^3} \mathbf{v}_i \tilde{J}_{ij}^{\alpha b * E} d\mathbf{v}_i + \alpha \int_{\mathbb{R}^3} \mathbf{v}_i \tilde{J}_i^{\alpha R} d\mathbf{v}_i. \end{aligned}$$

Using the Leibniz rule for differentiation under the integral sign for the two terms on the left-hand side of the previous equation, we obtain:

$$\begin{aligned} \alpha \frac{\partial}{\partial t} \underbrace{\left(\int_{\mathbb{R}^3} \mathbf{v}_i f_i^\alpha d\mathbf{v}_i \right)}_{c_i^\alpha \mathbf{u}_i^\alpha \text{ see (4.3.11)}} + \frac{\partial}{\partial \mathbf{x}} \left(\int_{\mathbb{R}^3} (\mathbf{v}_i \otimes \mathbf{v}_i) f_i^\alpha d\mathbf{v}_i \right) \\ = \frac{1}{\alpha} \int_{\mathbb{R}^3} \mathbf{v}_i J_i^{\alpha m E} d\mathbf{v}_i + \underbrace{\frac{1}{\alpha} \int_{\mathbb{R}^3} \mathbf{v}_i J_i^{\alpha b E} d\mathbf{v}_i}_{O_i} - \underbrace{\alpha \int_{\mathbb{R}^3} \mathbf{v}_i \tilde{J}_{ij}^{\alpha b * E} d\mathbf{v}_i}_{\mathcal{P}_i} + \underbrace{\alpha \int_{\mathbb{R}^3} \mathbf{v}_i \tilde{J}_i^{\alpha R} d\mathbf{v}_i}_{\mathcal{Q}_i}. \quad (4.4.5) \end{aligned}$$

Using the definition of the distribution functions given in equation (4.2.3), we can write the second integral on the left-hand side of the previous equation as follows:

$$\int_{\mathbb{R}^3} (\mathbf{v}_i \otimes \mathbf{v}_i) f_i^\alpha d\mathbf{v}_i = c_i^\alpha \left(\frac{m_i}{2\pi k_B T} \right)^{\frac{3}{2}} \int_{\mathbb{R}^3} (\mathbf{v}_i \otimes \mathbf{v}_i) \exp \left(- \frac{m_i (\mathbf{v}_i - \alpha \mathbf{u}_i^\alpha)^2}{2k_B T} \right) d\mathbf{v}_i.$$

Using equation (4.3.7), we obtain:

$$\int_{\mathbb{R}^3} (\mathbf{v}_i \otimes \mathbf{v}_i) f_i^\alpha d\mathbf{v}_i = c_i^\alpha \left(\frac{m_i}{2\pi k_B T} \right)^{\frac{3}{2}} \int_{\mathbb{R}^3} ((\boldsymbol{\xi}_i + \alpha \mathbf{u}_i^\alpha) \otimes (\boldsymbol{\xi}_i + \alpha \mathbf{u}_i^\alpha)) \exp \left(- \frac{m_i (\boldsymbol{\xi}_i)^2}{2k_B T} \right) d\boldsymbol{\xi}_i.$$

Observe that

$$\begin{aligned} (\boldsymbol{\xi}_i + \alpha \mathbf{u}_i^\alpha) \otimes (\boldsymbol{\xi}_i + \alpha \mathbf{u}_i^\alpha) &= \boldsymbol{\xi}_i \otimes (\boldsymbol{\xi}_i + \alpha \mathbf{u}_i^\alpha) + \alpha \mathbf{u}_i^\alpha \otimes (\boldsymbol{\xi}_i + \alpha \mathbf{u}_i^\alpha) \\ &= \boldsymbol{\xi}_i \otimes \boldsymbol{\xi}_i + 2\alpha (\boldsymbol{\xi}_i \otimes \mathbf{u}_i^\alpha) + \alpha^2 (\mathbf{u}_i^\alpha \otimes \mathbf{u}_i^\alpha). \end{aligned} \quad (4.4.6)$$

Therefore,

$$\begin{aligned} \int_{\mathbb{R}^3} (\mathbf{v}_i \otimes \mathbf{v}_i) f_i^\alpha d\mathbf{v}_i &= c_i^\alpha \left(\frac{m_i}{2\pi k_B T} \right)^{\frac{3}{2}} \int_{\mathbb{R}^3} (\boldsymbol{\xi}_i \otimes \boldsymbol{\xi}_i + 2\alpha (\boldsymbol{\xi}_i \otimes \mathbf{u}_i^\alpha) + \alpha^2 (\mathbf{u}_i^\alpha \otimes \mathbf{u}_i^\alpha)) \\ &\quad \times \exp \left(- \frac{m_i (\boldsymbol{\xi}_i)^2}{2k_B T} \right) d\boldsymbol{\xi}_i. \end{aligned}$$

Expanding the previous equation gives:

$$\int_{\mathbb{R}^3} (\mathbf{v}_i \otimes \mathbf{v}_i) f_i^\alpha d\mathbf{v}_i = c_i^\alpha \left(\frac{m_i}{2\pi k_B T} \right)^{\frac{3}{2}} \int_{\mathbb{R}^3} (\boldsymbol{\xi}_i \otimes \boldsymbol{\xi}_i) \exp \left(- \frac{m_i (\boldsymbol{\xi}_i)^2}{2k_B T} \right) d\boldsymbol{\xi}_i$$

$$\begin{aligned}
& + c_i^\alpha \left(\frac{m_i}{2\pi k_B T} \right)^{\frac{3}{2}} 2\alpha \mathbf{u}_i^\alpha \otimes \underbrace{\int_{\mathbb{R}^3} \boldsymbol{\xi}_i \exp \left(-\frac{m_i(\boldsymbol{\xi}_i)^2}{2k_B T} \right) d\boldsymbol{\xi}_i}_{\mathbf{0} \text{ see (4.3.10)}} \\
& + c_i^\alpha \left(\frac{m_i}{2\pi k_B T} \right)^{\frac{3}{2}} \alpha^2 (\mathbf{u}_i^\alpha \otimes \mathbf{u}_i^\alpha) \int_{\mathbb{R}^3} \exp \left(-\frac{m_i(\boldsymbol{\xi}_i)^2}{2k_B T} \right) d\boldsymbol{\xi}_i.
\end{aligned}$$

The third term on the right-hand side of the previous equation can be written as

$$\alpha^2 (\mathbf{u}_i^\alpha \otimes \mathbf{u}_i^\alpha) c_i^\alpha \left(\frac{m_i}{2\pi k_B T} \right)^{\frac{3}{2}} \int_{\mathbb{R}^3} \exp \left(-\frac{m_i(\boldsymbol{\xi}_i)^2}{2k_B T} \right) d\boldsymbol{\xi}_i = \alpha^2 (\mathbf{u}_i^\alpha \otimes \mathbf{u}_i^\alpha) \underbrace{\int_{\mathbb{R}^3} f_i^\alpha d\mathbf{v}_i}_{c_i^\alpha \text{ see (4.3.9)}}.$$

Therefore,

$$\int_{\mathbb{R}^3} (\mathbf{v}_i \otimes \mathbf{v}_i) f_i^\alpha d\mathbf{v}_i = c_i^\alpha \left(\frac{m_i}{2\pi k_B T} \right)^{\frac{3}{2}} \int_{\mathbb{R}^3} (\boldsymbol{\xi}_i \otimes \boldsymbol{\xi}_i) \exp \left(-\frac{m_i(\boldsymbol{\xi}_i)^2}{2k_B T} \right) d\boldsymbol{\xi}_i + \alpha^2 c_i^\alpha (\mathbf{u}_i^\alpha \otimes \mathbf{u}_i^\alpha).$$

The integral on the right-hand side of the previous equation can be written as

$$\int_{\mathbb{R}^3} (\boldsymbol{\xi}_i \otimes \boldsymbol{\xi}_i) \exp \left(-\frac{m_i(\boldsymbol{\xi}_i)^2}{2k_B T} \right) d\boldsymbol{\xi}_i = \frac{1}{3} \mathbf{I} \int_{\mathbb{R}^3} (\boldsymbol{\xi}_i)^2 \exp \left(-\frac{m_i(\boldsymbol{\xi}_i)^2}{2k_B T} \right) d\boldsymbol{\xi}_i,$$

where $\mathbf{I}$ is an identity tensor. Writing the previous equation in spherical coordinates and integrating gives:

$$\begin{aligned}
\int_{\mathbb{R}^3} (\boldsymbol{\xi}_i \otimes \boldsymbol{\xi}_i) \exp \left(-\frac{m_i(\boldsymbol{\xi}_i)^2}{2k_B T} \right) d\boldsymbol{\xi}_i &= \frac{1}{3} \mathbf{I} \int_0^\infty \int_0^\pi \int_0^{2\pi} (\boldsymbol{\xi}_i)^2 \exp \left(-\frac{m_i(\boldsymbol{\xi}_i)^2}{2k_B T} \right) \xi_i^2 \sin \theta d\phi d\theta d\xi_i \\
&= \frac{1}{3} \mathbf{I} \int_0^\infty \xi_i^4 \exp \left(-\frac{m_i(\boldsymbol{\xi}_i)^2}{2k_B T} \right) d\xi_i \underbrace{\int_0^\pi \sin \theta d\theta}_2 \underbrace{\int_0^{2\pi} d\phi}_{2\pi} \\
&= \frac{4\pi}{3} \mathbf{I} \int_0^\infty \xi_i^4 \exp \left(-\frac{m_i(\boldsymbol{\xi}_i)^2}{2k_B T} \right) d\xi_i.
\end{aligned}$$

Using the integral representation of gamma function given in equation (4.3.8), we obtain:

$$\begin{aligned}
\int_{\mathbb{R}^3} (\boldsymbol{\xi}_i \otimes \boldsymbol{\xi}_i) \exp \left(-\frac{m_i(\boldsymbol{\xi}_i)^2}{2k_B T} \right) d\boldsymbol{\xi}_i &= \frac{4\pi}{3} \mathbf{I} \frac{1}{2} \Gamma \left(\frac{5}{2} \right) \left(\frac{2k_B T}{m_i} \right)^{\frac{5}{2}} \\
&= \frac{4\pi}{3} \mathbf{I} \frac{1}{2} \frac{3\sqrt{\pi}}{4} \left(\frac{2k_B T}{m_i} \right)^{\frac{5}{2}} \\
&= \mathbf{I} \frac{1}{2} \left(\frac{2\pi k_B T}{m_i} \right)^{\frac{3}{2}} \frac{2k_B T}{m_i} \\
&= \mathbf{I} \left(\frac{2\pi k_B T}{m_i} \right)^{\frac{3}{2}} \frac{k_B T}{m_i}.
\end{aligned}$$

Thus

$$\begin{aligned}
\int_{\mathbb{R}^3} (\mathbf{v}_i \otimes \mathbf{v}_i) f_i^\alpha d\mathbf{v}_i &= c_i^\alpha \left(\frac{m_i}{2\pi k_B T} \right)^{\frac{3}{2}} \mathbf{I} \left(\frac{2\pi k_B T}{m_i} \right)^{\frac{3}{2}} \frac{k_B T}{m_i} + \alpha^2 c_i^\alpha (\mathbf{u}_i^\alpha \otimes \mathbf{u}_i^\alpha) \\
&= c_i^\alpha \frac{k_B T}{m_i} + \alpha^2 c_i^\alpha (\mathbf{u}_i^\alpha \otimes \mathbf{u}_i^\alpha).
\end{aligned} \tag{4.4.7}$$

Substituting equation (4.4.7) into equation (4.4.5), we obtain:

$$\begin{aligned}
&\alpha \frac{\partial}{\partial t} (c_i^\alpha \mathbf{u}_i^\alpha) + \frac{\partial}{\partial \mathbf{x}} \left(c_i^\alpha \frac{k_B T}{m_i} + \alpha^2 c_i^\alpha (\mathbf{u}_i^\alpha \otimes \mathbf{u}_i^\alpha) \right) \\
&= \frac{1}{\alpha} \int_{\mathbb{R}^3} \mathbf{v}_i J_i^{\alpha m E} d\mathbf{v}_i + \underbrace{\frac{1}{\alpha} \int_{\mathbb{R}^3} \mathbf{v}_i J_i^{\alpha b E} d\mathbf{v}_i}_{\mathcal{O}_i} - \underbrace{\alpha \int_{\mathbb{R}^3} \mathbf{v}_i \tilde{J}_{ij}^{\alpha b * E} d\mathbf{v}_i}_{\mathcal{P}_i} + \underbrace{\alpha \int_{\mathbb{R}^3} \mathbf{v}_i \tilde{J}_i^{\alpha R} d\mathbf{v}_i}_{\mathcal{Q}_i}.
\end{aligned} \tag{4.4.8}$$

Since the properties of the scaled collision operators are similar to their un-scaled version, the first integral on the right-hand side of equation (4.4.8) vanishes, that is,

$$\int_{\mathbb{R}^3} \mathbf{v}_i J_i^{\alpha m E} d\mathbf{v}_i = 0. \tag{4.4.9}$$

See the second equation of (2.3.54) with $m_i = 1$.

To evaluate the integral $\mathcal{O}_i$ given in equation (4.4.8), we substitute equation (3.3.14) into the integral $\mathcal{O}_i$ and use equation (2.3.38) of Lemma 2.3.8 with $\varphi(\mathbf{v}_i) = \mathbf{v}_i$ to obtain:

$$\mathcal{O}_i = \frac{1}{\alpha} \sum_{\substack{s=1 \\ s \neq i}}^4 \sigma_{is}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} (\mathbf{v}'_i - \mathbf{v}_i) f_i^\alpha f_s^\alpha \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_s \rangle d\boldsymbol{\epsilon} d\mathbf{v}_s d\mathbf{v}_i$$

since the properties of the scaled collision operators are similar to their un-scaled version. Observe that from the definition of elastic post-collision velocity given in equation (2.3.8), we can write:

$$\begin{aligned}
\mathbf{v}'_i - \mathbf{v}_i &= -\frac{2\mu_{is}}{m_i} \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_s \rangle \boldsymbol{\epsilon} \\
&= -\frac{2m_i m_s}{(m_i + m_s)m_i} \|\mathbf{v}_i - \mathbf{v}_s\| \cos \theta \frac{\mathbf{v}_i - \mathbf{v}_s}{\|\mathbf{v}_i - \mathbf{v}_s\|} \\
&= \frac{2m_s}{m_i + m_s} (\mathbf{v}_s - \mathbf{v}_i) \cos \theta.
\end{aligned} \tag{4.4.10}$$

Therefore,

$$\begin{aligned}
\mathcal{O}_i &= \frac{1}{\alpha} \sum_{\substack{s=1 \\ s \neq i}}^4 \sigma_{is}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} \frac{2m_s}{m_i + m_s} (\mathbf{v}_s - \mathbf{v}_i) \cos \theta f_i^\alpha f_s^\alpha \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_s \rangle d\boldsymbol{\epsilon} d\mathbf{v}_s d\mathbf{v}_i \\
&= \frac{1}{\alpha} \sum_{\substack{s=1 \\ s \neq i}}^4 \sigma_{is}^2 \frac{2m_s}{m_i + m_s} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_0^\pi \int_0^{2\pi} (\mathbf{v}_s - \mathbf{v}_i) \cos \theta f_i^\alpha f_s^\alpha \|\mathbf{v}_i - \mathbf{v}_s\| \cos \theta \sin \theta d\phi d\theta d\mathbf{v}_s d\mathbf{v}_i \\
&= \frac{1}{\alpha} \sum_{\substack{s=1 \\ s \neq i}}^4 \sigma_{is}^2 \frac{2m_s}{m_i + m_s} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} (\mathbf{v}_s - \mathbf{v}_i) f_i^\alpha f_s^\alpha \|\mathbf{v}_i - \mathbf{v}_s\| d\mathbf{v}_s d\mathbf{v}_i \underbrace{\int_0^\pi \sin \theta \cos^2 \theta d\theta}_{\frac{1}{3}} \underbrace{\int_0^{2\pi} d\phi}_{2\pi}
\end{aligned}$$

$$= \frac{4\pi}{3\alpha} \sum_{\substack{s=1 \\ s \neq i}}^4 \sigma_{is}^2 \frac{m_s}{m_i + m_s} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} (\mathbf{v}_s - \mathbf{v}_i) f_i^\alpha f_s^\alpha \|\mathbf{v}_i - \mathbf{v}_s\| d\mathbf{v}_s d\mathbf{v}_i.$$

Substituting equation (4.3.15) with j replaced by s into the last equality of the previous equation, then expand the resulting equation and neglect the terms of order α^2 , that is, the term with coefficient $(\mathbf{a}_i \cdot \mathbf{v}_i)(\mathbf{a}_j \cdot \mathbf{v}_j)$, we obtain:

$$\begin{aligned} \mathcal{O}_i &= \frac{4\pi}{3\alpha} \sum_{\substack{s=1 \\ s \neq i}}^4 \sigma_{is}^2 \frac{m_s}{m_i + m_s} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} (\mathbf{v}_s - \mathbf{v}_i) M_i^\alpha M_s^\alpha \|\mathbf{v}_i - \mathbf{v}_s\| d\mathbf{v}_s d\mathbf{v}_i \\ &+ \frac{4\pi}{3\alpha} \sum_{\substack{s=1 \\ s \neq i}}^4 \sigma_{is}^2 \frac{m_s}{m_i + m_s} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} (\mathbf{v}_s - \mathbf{v}_i) M_i^\alpha M_s^\alpha (\mathbf{a}_i \cdot \mathbf{v}_i) \|\mathbf{v}_i - \mathbf{v}_s\| d\mathbf{v}_s d\mathbf{v}_i \\ &+ \frac{4\pi}{3\alpha} \sum_{\substack{s=1 \\ s \neq i}}^4 \sigma_{is}^2 \frac{m_s}{m_i + m_s} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} (\mathbf{v}_s - \mathbf{v}_i) M_i^\alpha M_s^\alpha (\mathbf{a}_s \cdot \mathbf{v}_s) \|\mathbf{v}_i - \mathbf{v}_s\| d\mathbf{v}_s d\mathbf{v}_i \\ &= \frac{4\pi}{3\alpha} \sum_{\substack{s=1 \\ s \neq i}}^4 \sigma_{is}^2 \frac{m_s}{m_i + m_s} c_i^\alpha c_s^\alpha \frac{(m_i m_s)^{\frac{3}{2}}}{(2\pi k_B T)^3} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} (\mathbf{v}_s - \mathbf{v}_i) \exp\left(-\frac{m_i(\mathbf{v}_i)^2 + m_s(\mathbf{v}_s)^2}{2k_B T}\right) \\ &\quad \times \|\mathbf{v}_i - \mathbf{v}_s\| d\mathbf{v}_s d\mathbf{v}_i \\ &+ \frac{4\pi}{3\alpha} \sum_{\substack{s=1 \\ s \neq i}}^4 \sigma_{is}^2 \frac{m_s}{m_i + m_s} c_i^\alpha c_s^\alpha \frac{(m_i m_s)^{\frac{3}{2}}}{(2\pi k_B T)^3} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} (\mathbf{v}_s - \mathbf{v}_i) \exp\left(-\frac{m_i(\mathbf{v}_i)^2 + m_s(\mathbf{v}_s)^2}{2k_B T}\right) \\ &\quad \times (\mathbf{a}_i \cdot \mathbf{v}_i) \|\mathbf{v}_i - \mathbf{v}_s\| d\mathbf{v}_s d\mathbf{v}_i \\ &+ \frac{4\pi}{3\alpha} \sum_{\substack{s=1 \\ s \neq i}}^4 \sigma_{is}^2 \frac{m_s}{m_i + m_s} c_i^\alpha c_s^\alpha \frac{(m_i m_s)^{\frac{3}{2}}}{(2\pi k_B T)^3} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} (\mathbf{v}_s - \mathbf{v}_i) \exp\left(-\frac{m_i(\mathbf{v}_i)^2 + m_s(\mathbf{v}_s)^2}{2k_B T}\right) \\ &\quad \times (\mathbf{a}_s \cdot \mathbf{v}_s) \|\mathbf{v}_i - \mathbf{v}_s\| d\mathbf{v}_s d\mathbf{v}_i. \end{aligned}$$

It will be convenient to transform the above six fold integrals to the centre of mass velocity

$$\mathbf{X}_* = \frac{m_i \mathbf{v}_i + m_s \mathbf{v}_s}{m_i + m_s}, \quad (4.4.11)$$

and relative velocity

$$\mathbf{V}_* = \mathbf{v}_s - \mathbf{v}_i. \quad (4.4.12)$$

Following the steps used to obtain equations (2.4.10), (2.4.11) and (2.4.12), we obtain:

$$\mathbf{v}_i = \mathbf{X}_* - \frac{m_s \mathbf{V}_*}{m_i + m_s}, \quad (4.4.13)$$

$$\mathbf{v}_s = \mathbf{X}_* + \frac{m_i \mathbf{V}_*}{m_i + m_s}, \quad (4.4.14)$$

$$m_i(\mathbf{v}_i)^2 + m_s(\mathbf{v}_s)^2 = (m_i + m_s)X_*^2 + \mu_{is}V_*^2, \quad (4.4.15)$$

respectively, where $X_* = ||\mathbf{X}_*|| = |\mathbf{X}_*|$ and $V_* = ||\mathbf{V}_*|| = |\mathbf{V}_*| = |\mathbf{v}_s - \mathbf{v}_i| = |\mathbf{v}_i - \mathbf{v}_s|$. Using equations (4.4.12), (4.4.13), (4.4.14) and (4.4.15) together with the fact that the Jacobian of the transformation $(\mathbf{v}_i, \mathbf{v}_s) \rightarrow (\mathbf{X}_*, \mathbf{V}_*)$ has absolute value of unity, which implies that

$$d\mathbf{v}_i d\mathbf{v}_s = d\mathbf{X}_* d\mathbf{V}_*, \quad (4.4.16)$$

we can rewrite the integral $\mathcal{O}_i$ as follows:

$$\begin{aligned} \mathcal{O}_i = & \frac{4\pi}{3\alpha} \sum_{\substack{s=1 \\ s \neq i}}^4 \sigma_{is}^2 \frac{m_s}{m_i + m_s} c_i^\alpha c_s^\alpha \frac{(m_i m_s)^{\frac{3}{2}}}{(2\pi k_B T)^3} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \mathbf{V}_* \exp \left(-\frac{M_{is} X_*^2 + \mu_{is} V_*^2}{2k_B T} \right) V_* d\mathbf{X}_* d\mathbf{V}_* \\ & + \frac{4\pi}{3\alpha} \sum_{\substack{s=1 \\ s \neq i}}^4 \sigma_{is}^2 \frac{m_s}{m_i + m_s} c_i^\alpha c_s^\alpha \frac{(m_i m_s)^{\frac{3}{2}}}{(2\pi k_B T)^3} \\ & \quad \times \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \mathbf{V}_* \exp \left(-\frac{M_{is} X_*^2 + \mu_{is} V_*^2}{2k_B T} \right) \mathbf{a}_i \cdot \left(\mathbf{X}_* - \frac{m_s \mathbf{V}_*}{M_{is}} \right) V_* d\mathbf{X}_* d\mathbf{V}_* \\ & + \frac{4\pi}{3\alpha} \sum_{\substack{s=1 \\ s \neq i}}^4 \sigma_{is}^2 \frac{m_s}{m_i + m_s} c_i^\alpha c_s^\alpha \frac{(m_i m_s)^{\frac{3}{2}}}{(2\pi k_B T)^3} \\ & \quad \times \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \mathbf{V}_* \exp \left(-\frac{M_{is} X_*^2 + \mu_{is} V_*^2}{2k_B T} \right) \mathbf{a}_s \cdot \left(\mathbf{X}_* + \frac{m_i \mathbf{V}_*}{M_{is}} \right) V_* d\mathbf{X}_* d\mathbf{V}_*, \end{aligned}$$

where the notation $m_i + m_s = M_{is}$ have been used. Expanding the previous equation gives:

$$\begin{aligned} \mathcal{O}_i = & \frac{4\pi}{3\alpha} \sum_{\substack{s=1 \\ s \neq i}}^4 \sigma_{is}^2 \frac{m_s}{m_i + m_s} c_i^\alpha c_s^\alpha \frac{(m_i m_s)^{\frac{3}{2}}}{(2\pi k_B T)^3} \\ & \quad \times \int_{\mathbb{R}^3} \exp \left(-\frac{M_{is} X_*^2}{2k_B T} \right) d\mathbf{X}_* \int_{\mathbb{R}^3} \mathbf{V}_* \exp \left(-\frac{\mu_{is} V_*^2}{2k_B T} \right) V_* d\mathbf{V}_* \\ & + \frac{4\pi}{3\alpha} \sum_{\substack{s=1 \\ s \neq i}}^4 \sigma_{is}^2 \frac{m_s}{m_i + m_s} c_i^\alpha c_s^\alpha \frac{(m_i m_s)^{\frac{3}{2}}}{(2\pi k_B T)^3} \\ & \quad \times \int_{\mathbb{R}^3} (\mathbf{a}_i \cdot \mathbf{X}_*) \exp \left(-\frac{M_{is} X_*^2}{2k_B T} \right) d\mathbf{X}_* \int_{\mathbb{R}^3} \mathbf{V}_* \exp \left(-\frac{\mu_{is} V_*^2}{2k_B T} \right) V_* d\mathbf{V}_* \\ & - \frac{4\pi}{3\alpha} \sum_{\substack{s=1 \\ s \neq i}}^4 \sigma_{is}^2 \frac{m_s}{m_i + m_s} c_i^\alpha c_s^\alpha \frac{(m_i m_s)^{\frac{3}{2}}}{(2\pi k_B T)^3} \\ & \quad \times \int_{\mathbb{R}^3} \exp \left(-\frac{M_{is} X_*^2}{2k_B T} \right) d\mathbf{X}_* \frac{m_s}{M_{is}} \int_{\mathbb{R}^3} \mathbf{V}_* (\mathbf{a}_i \cdot \mathbf{V}_*) \exp \left(-\frac{\mu_{is} V_*^2}{2k_B T} \right) V_* d\mathbf{V}_* \\ & + \frac{4\pi}{3\alpha} \sum_{\substack{s=1 \\ s \neq i}}^4 \sigma_{is}^2 \frac{m_s}{m_i + m_s} c_i^\alpha c_s^\alpha \frac{(m_i m_s)^{\frac{3}{2}}}{(2\pi k_B T)^3} \end{aligned}$$

$$\begin{aligned}
& \times \int_{\mathbb{R}^3} (\mathbf{a}_s \cdot \mathbf{X}_*) \exp \left(-\frac{M_{is} X_*^2}{2k_B T} \right) d\mathbf{X}_* \int_{\mathbb{R}^3} \mathbf{V}_* \exp \left(-\frac{\mu_{is} V_*^2}{2k_B T} \right) V_* d\mathbf{V}_* \\
& + \frac{4\pi}{3\alpha} \sum_{\substack{s=1 \\ s \neq i}}^4 \sigma_{is}^2 \frac{m_s}{m_i + m_s} c_i^\alpha c_s^\alpha \frac{(m_i m_s)^{\frac{3}{2}}}{(2\pi k_B T)^3} \\
& \times \int_{\mathbb{R}^3} \exp \left(-\frac{M_{is} X_*^2}{2k_B T} \right) d\mathbf{X}_* \frac{m_i}{M_{is}} \int_{\mathbb{R}^3} \mathbf{V}_* (\mathbf{a}_s \cdot \mathbf{V}_*) \exp \left(-\frac{\mu_{is} V_*^2}{2k_B T} \right) V_* d\mathbf{V}_*.
\end{aligned}$$

Rearranging, we obtain:

$$\begin{aligned}
\mathcal{O}_i &= \frac{4\pi}{3\alpha} \sum_{\substack{s=1 \\ s \neq i}}^4 \sigma_{is}^2 \frac{m_s}{m_i + m_s} c_i^\alpha c_s^\alpha \frac{(m_i m_s)^{\frac{3}{2}}}{(2\pi k_B T)^3} \\
& \left\{ \underbrace{\int_{\mathbb{R}^3} \exp \left(-\frac{M_{is} X_*^2}{2k_B T} \right) d\mathbf{X}_*}_{\mathcal{Z}_1} \underbrace{\int_{\mathbb{R}^3} \mathbf{V}_* \exp \left(-\frac{\mu_{is} V_*^2}{2k_B T} \right) V_* d\mathbf{V}_*}_{\mathcal{Z}_2} \right. \\
& + (\mathbf{a}_i + \mathbf{a}_s) \cdot \underbrace{\int_{\mathbb{R}^3} \mathbf{X}_* \exp \left(-\frac{M_{is} X_*^2}{2k_B T} \right) d\mathbf{X}_*}_{\mathcal{Z}_3} \underbrace{\left(\int_{\mathbb{R}^3} \mathbf{V}_* \exp \left(-\frac{\mu_{is} V_*^2}{2k_B T} \right) V_* d\mathbf{V}_* \right)}_{\mathcal{Z}_2} \\
& + \underbrace{\int_{\mathbb{R}^3} \exp \left(-\frac{M_{is} X_*^2}{2k_B T} \right) d\mathbf{X}_*}_{\mathcal{Z}_1} \underbrace{\frac{m_i}{M_{is}} \int_{\mathbb{R}^3} \mathbf{V}_* (\mathbf{a}_s \cdot \mathbf{V}_*) \exp \left(-\frac{\mu_{is} V_*^2}{2k_B T} \right) V_* d\mathbf{V}_*}_{\mathcal{Z}_4} \\
& \left. - \underbrace{\int_{\mathbb{R}^3} \exp \left(-\frac{M_{is} X_*^2}{2k_B T} \right) d\mathbf{X}_*}_{\mathcal{Z}_1} \underbrace{\frac{m_s}{M_{is}} \int_{\mathbb{R}^3} \mathbf{V}_* (\mathbf{a}_i \cdot \mathbf{V}_*) \exp \left(-\frac{\mu_{is} V_*^2}{2k_B T} \right) V_* d\mathbf{V}_*}_{\mathcal{Z}_5} \right\}.
\end{aligned}$$

The integral $\mathcal{Z}_1$ is similar to the integral evaluated in equation (4.3.22). Therefore following similar procedure, one has that

$$\int_{\mathbb{R}^3} \exp \left(-\frac{M_{is} X_*^2}{2k_B T} \right) d\mathbf{X}_* = \left(\frac{2\pi k_B T}{M_{is}} \right)^{\frac{3}{2}}. \quad (4.4.17)$$

The integral $\mathcal{Z}_2$ can be written as

$$\int_{\mathbb{R}^3} \mathbf{V}_* \exp \left(-\frac{\mu_{is} V_*^2}{2k_B T} \right) V_* d\mathbf{V}_* = \int_{\mathbb{R}^3} V_* \vec{v} \exp \left(-\frac{\mu_{is} V_*^2}{2k_B T} \right) V_* d\mathbf{V}_*,$$

where the fact that any vector $\mathbf{V}_*$ can be written in terms of a unit vector as $\mathbf{V}_* = V_* \vec{v}$, with $V_* = \|\mathbf{V}_*\|$ and $\vec{v}$ a unit vector have been used. Writing the previous integral in spherical coordinates and evaluating gives:

$$\int_{\mathbb{R}^3} V_* \vec{v} \exp \left(-\frac{\mu_{is} V_*^2}{2k_B T} \right) V_* d\mathbf{V}_*$$

$$\begin{aligned}
&= \int_0^\infty \int_0^\pi \int_0^{2\pi} V_*^2 (\hat{\mathbf{x}} \sin \theta \cos \phi + \hat{\mathbf{y}} \sin \theta \sin \phi + \hat{\mathbf{z}} \cos \theta) \exp\left(-\frac{\mu_{is} V_*^2}{2k_B T}\right) V_*^2 \sin \theta d\phi d\theta dV_* \\
&= \int_0^\infty V_*^4 \exp\left(-\frac{\mu_{is} V_*^2}{2k_B T}\right) dV_* \left(\underbrace{\hat{\mathbf{x}} \int_0^\pi \sin^2 \theta d\theta}_{\frac{\pi}{2}} \underbrace{\int_0^{2\pi} \cos \phi d\phi}_0 + \underbrace{\hat{\mathbf{y}} \int_0^\pi \sin^2 \theta d\theta}_{\frac{\pi}{2}} \underbrace{\int_0^{2\pi} \sin \phi d\phi}_0 \right. \\
&\quad \left. + \underbrace{\hat{\mathbf{z}} \int_0^\pi \cos \theta \sin \theta}_{0} + \underbrace{\int_0^{2\pi} d\phi}_{2\pi} \right),
\end{aligned}$$

where $\hat{\mathbf{x}}, \hat{\mathbf{y}}, \hat{\mathbf{z}}$ are the Cartesian unit vectors in $\mathbb{R}^3$. The integral in V_* can be evaluated using the integral representation of gamma function given in Eq. (4.3.8) as given below:

$$\begin{aligned}
\int_0^\infty V_*^4 \exp\left(-\frac{\mu_{is} V_*^2}{2k_B T}\right) dV_* &= \frac{1}{2} \Gamma\left(\frac{5}{2}\right) \left(\frac{2k_B T}{\mu_{is}}\right)^{\frac{5}{2}} \\
&= \frac{1}{2} \frac{3\sqrt{\pi}}{4} \left(\frac{2k_B T}{\mu_{is}}\right)^{\frac{5}{2}} \\
&= \frac{3\sqrt{\pi}}{8} \left(\frac{2k_B T}{\mu_{is}}\right)^{\frac{5}{2}}. \tag{4.4.18}
\end{aligned}$$

Therefore,

$$\int_{\mathbb{R}^3} \mathbf{V}_* \exp\left(-\frac{\mu_{is} V_*^2}{2k_B T}\right) V_* d\mathbf{V}_* = \frac{3\sqrt{\pi}}{8} \left(\frac{2k_B T}{\mu_{is}}\right)^{\frac{5}{2}} [\hat{\mathbf{x}}(0) + \hat{\mathbf{y}}(0) + \hat{\mathbf{z}}(0)] = \mathbf{0}. \tag{4.4.19}$$

The integral $\mathcal{Z}_3$ is similar to the integral evaluated in equation (4.3.10). Therefore, following similar steps, one has that

$$\int_{\mathbb{R}^3} \mathbf{X}_* \exp\left(-\frac{M_{is} X_*^2}{2k_B T}\right) d\mathbf{X}_* = \mathbf{0}. \tag{4.4.20}$$

The integral $\mathcal{Z}_4$ can be written as

$$\begin{aligned}
\int_{\mathbb{R}^3} \mathbf{V}_* (\mathbf{a}_s \cdot \mathbf{V}_*) \exp\left(-\frac{\mu_{is} V_*^2}{2k_B T}\right) V_* d\mathbf{V}_* &= \int_{\mathbb{R}^3} V_* \vec{\mathbf{v}} (a_s V_* \cos \theta) \exp\left(-\frac{\mu_{is} V_*^2}{2k_B T}\right) V_* d\mathbf{V}_* \\
&= a_s \int_{\mathbb{R}^3} V_* \vec{\mathbf{v}} \exp\left(-\frac{\mu_{is} V_*^2}{2k_B T}\right) V_*^2 \cos \theta d\mathbf{V}_*,
\end{aligned}$$

where the fact that any vector $\mathbf{V}_*$ can be written in terms of a unit vector as $\mathbf{V}_* = V_* \vec{\mathbf{v}}$, with $V_* = \|\mathbf{V}_*\|$, $\vec{\mathbf{v}}$ a unit vector and $a_s = \|\mathbf{a}_s\| = |\mathbf{a}_s|$ have been used. Writing the previous integral in spherical coordinates and integrating, gives:

$$\begin{aligned}
&a_s \int_{\mathbb{R}^3} V_* \vec{\mathbf{v}} \exp\left(-\frac{\mu_{is} V_*^2}{2k_B T}\right) V_*^2 \cos \theta d\mathbf{V}_* \\
&= a_s \int_0^\infty \int_0^\pi \int_0^{2\pi} V_* (\hat{\mathbf{x}} \sin \theta \cos \phi + \hat{\mathbf{y}} \sin \theta \sin \phi + \hat{\mathbf{z}} \cos \theta) \exp\left(-\frac{\mu_{is} V_*^2}{2k_B T}\right)
\end{aligned}$$

$$\begin{aligned}
& \times V_*^2 \cos \theta V_*^2 \sin \theta d\phi d\theta dV_* \\
& = a_s \int_0^\infty V_*^5 \exp\left(-\frac{\mu_{is} V_*^2}{2k_B T}\right) dV_* \left(\underbrace{\hat{\mathbf{x}} \int_0^\pi \sin^2 \theta \cos \theta d\theta}_0 \underbrace{\int_0^{2\pi} \cos \phi d\phi}_0 \right. \\
& \quad \left. + \underbrace{\hat{\mathbf{y}} \int_0^\pi \sin^2 \theta \cos \theta d\theta}_0 \underbrace{\int_0^{2\pi} \sin \phi d\phi}_0 + \underbrace{\hat{\mathbf{z}} \int_0^\pi \sin \theta \cos^2 \theta d\theta}_{\frac{2}{3}} \underbrace{\int_0^{2\pi} d\phi}_{2\pi} \right),
\end{aligned}$$

where $\hat{\mathbf{x}}, \hat{\mathbf{y}}, \hat{\mathbf{z}}$ are the Cartesian unit vectors in $\mathbb{R}^3$. The integral in V_* above can be evaluated using the integral representation of gamma function given in equation (4.3.8) as given below:

$$\int_0^\infty V_*^5 \exp\left(-\frac{\mu_{is} V_*^2}{2k_B T}\right) dV_* = \frac{1}{2} \Gamma(3) \left(\frac{2k_B T}{\mu_{is}}\right)^3 = \frac{1}{2} 2! \left(\frac{2k_B T}{\mu_{is}}\right)^3 = \left(\frac{2k_B T}{\mu_{is}}\right)^3. \quad (4.4.21)$$

Therefore,

$$\int_{\mathbb{R}^3} \mathbf{V}_* (\mathbf{a}_s \cdot \mathbf{V}_*) \exp\left(-\frac{\mu_{is} V_*^2}{2k_B T}\right) V_* d\mathbf{V}_* = a_s \left(\frac{2k_B T}{\mu_{is}}\right)^3 \hat{\mathbf{z}} \frac{4\pi}{3} = \mathbf{a}_s \frac{4\pi}{3} \left(\frac{2k_B T}{\mu_{is}}\right)^3. \quad (4.4.22)$$

Similarly, following the same steps as those used in the evaluation of the integral $\mathcal{Z}_4$, we obtain that the integral $\mathcal{Z}_5$ is given by:

$$\int_{\mathbb{R}^3} \mathbf{V}_* (\mathbf{a}_i \cdot \mathbf{V}_*) \exp\left(-\frac{\mu_{is} V_*^2}{2k_B T}\right) V_* d\mathbf{V}_* = \mathbf{a}_i \frac{4\pi}{3} \left(\frac{2k_B T}{\mu_{is}}\right)^3. \quad (4.4.23)$$

Now substituting equations (4.4.17), (4.4.19), (4.4.20), (4.4.22) and (4.4.23) into $\mathcal{O}_i$ gives:

$$\begin{aligned}
\mathcal{O}_i &= \frac{4\pi}{3\alpha} \sum_{\substack{s=1 \\ s \neq i}}^4 \sigma_{is}^2 \frac{m_s}{m_i + m_s} c_i^\alpha c_s^\alpha \frac{(m_i m_s)^{\frac{3}{2}}}{(2\pi k_B T)^3} \left\{ \left(\frac{2\pi k_B T}{M_{is}}\right)^{\frac{3}{2}} \times \mathbf{0} + ((\mathbf{a}_i + \mathbf{a}_s) \cdot \mathbf{0}) \mathbf{0} \right. \\
& \quad \left. + \left(\frac{2\pi k_B T}{M_{is}}\right)^{\frac{3}{2}} \frac{m_i}{M_{is}} \mathbf{a}_s \frac{4\pi}{3} \left(\frac{2k_B T}{\mu_{is}}\right)^3 - \left(\frac{2\pi k_B T}{M_{is}}\right)^{\frac{3}{2}} \frac{m_s}{M_{is}} \mathbf{a}_i \frac{4\pi}{3} \left(\frac{2k_B T}{\mu_{is}}\right)^3 \right\} \\
&= \frac{4\pi}{3\alpha} \sum_{\substack{s=1 \\ s \neq i}}^4 \sigma_{is}^2 \frac{m_s}{m_i + m_s} c_i^\alpha c_s^\alpha \frac{(m_i m_s)^{\frac{3}{2}}}{(2\pi k_B T)^3} \left\{ \left(\frac{2\pi k_B T}{M_{is}}\right)^{\frac{3}{2}} \frac{m_i}{M_{is}} \mathbf{a}_s \frac{4\pi}{3} \left(\frac{2k_B T}{\mu_{is}}\right)^3 \right. \\
& \quad \left. - \left(\frac{2\pi k_B T}{M_{is}}\right)^{\frac{3}{2}} \frac{m_s}{M_{is}} \mathbf{a}_i \frac{4\pi}{3} \left(\frac{2k_B T}{\mu_{is}}\right)^3 \right\} \\
&= \frac{16\pi^2}{9\alpha} \sum_{\substack{s=1 \\ s \neq i}}^4 \sigma_{is}^2 \frac{m_s}{m_i + m_s} c_i^\alpha c_s^\alpha \frac{(m_i m_s)^{\frac{3}{2}}}{(2\pi k_B T)^3} \left(\frac{2\pi k_B T}{M_{is}}\right)^{\frac{3}{2}} \left(\frac{2k_B T}{\mu_{is}}\right)^3 \left\{ \frac{m_i}{M_{is}} \frac{\alpha m_s \mathbf{u}_s^\alpha}{k_B T} - \frac{m_s}{M_{is}} \frac{\alpha m_i \mathbf{u}_i^\alpha}{k_B T} \right\} \\
&= \frac{16\pi^2}{9} \sum_{\substack{s=1 \\ s \neq i}}^4 \sigma_{is}^2 \frac{m_s}{m_i + m_s} c_i^\alpha c_s^\alpha \frac{(m_i m_s)^{\frac{3}{2}}}{(2\pi k_B T)^3} \left(\frac{2\pi k_B T}{M_{is}}\right)^{\frac{3}{2}} \left(\frac{2k_B T}{\mu_{is}}\right)^3 \left\{ \frac{\mu_{is} \mathbf{u}_s^\alpha}{k_B T} - \frac{\mu_{is} \mathbf{u}_i^\alpha}{k_B T} \right\}
\end{aligned}$$

$$= \frac{16\pi^2}{9} \sum_{\substack{s=1 \\ s \neq i}}^4 \sigma_{is}^2 \frac{m_s}{m_i + m_s} c_i^\alpha c_s^\alpha \frac{(m_i m_s)^{\frac{3}{2}}}{(2\pi k_B T)^3} \left(\frac{2\pi k_B T}{M_{is}} \right)^{\frac{3}{2}} \left(\frac{2k_B T}{\mu_{is}} \right)^3 \frac{\mu_{is}}{k_B T} (\mathbf{u}_s^\alpha - \mathbf{u}_i^\alpha),$$

where the definition of $\mathbf{a}_i$ given in equation (4.3.14) have been used and $\mathbf{a}_s$ is similarly defined. Observe that

$$\begin{aligned} & \frac{16\pi^2}{9} \sum_{\substack{s=1 \\ s \neq i}}^4 \sigma_{is}^2 \frac{m_s}{m_i + m_s} c_i^\alpha c_s^\alpha \frac{(m_i m_s)^{\frac{3}{2}}}{(2\pi k_B T)^3} \left(\frac{2\pi k_B T}{M_{is}} \right)^{\frac{3}{2}} \left(\frac{2k_B T}{\mu_{is}} \right)^3 \frac{\mu_{is}}{k_B T} \\ &= \frac{16}{9} \sum_{\substack{s=1 \\ s \neq i}}^4 \sigma_{is}^2 \frac{m_s}{m_i + m_s} c_i^\alpha c_s^\alpha \frac{1}{(2\pi k_B T)^{\frac{3}{2}}} \left(\frac{m_i m_s}{M_{is}} \right)^{\frac{3}{2}} \left(\frac{2\pi k_B T}{\mu_{is}} \right)^2 \left(\frac{2k_B T}{\mu_{is}} \right) \frac{\mu_{is}}{k_B T} \\ &= \frac{32}{9} \sum_{\substack{s=1 \\ s \neq i}}^4 \sigma_{is}^2 \frac{m_s}{m_i + m_s} c_i^\alpha c_s^\alpha \left(\frac{\mu_{is}}{2\pi k_B T} \right)^{\frac{3}{2}} \left(\frac{2\pi k_B T}{\mu_{is}} \right)^2 \\ &= \frac{32}{9} \sum_{\substack{s=1 \\ s \neq i}}^4 \sigma_{is}^2 \frac{m_s}{m_i + m_s} c_i^\alpha c_s^\alpha \left(\frac{2\pi k_B T}{\mu_{is}} \right)^{\frac{1}{2}}. \end{aligned}$$

Therefore,

$$\mathcal{O}_i = \frac{32}{9} \sum_{\substack{s=1 \\ s \neq i}}^4 \sigma_{is}^2 \frac{m_s}{m_i + m_s} \left(\frac{2\pi k_B T}{\mu_{is}} \right)^{\frac{1}{2}} c_i^\alpha c_s^\alpha (\mathbf{u}_s^\alpha - \mathbf{u}_i^\alpha) \quad (4.4.24)$$

Next let us evaluate the third integral on the right-hand side of equation (4.4.8). To do this, we substitute equation (3.3.17) into the integral $\mathcal{P}_i$ and use equation (2.3.49) of Lemma 2.3.10 with $\varphi(\mathbf{v}_i) = \mathbf{v}_i$ to obtain:

$$\mathcal{P}_i = \alpha \sigma_{ij}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} (\mathbf{v}'_i - \mathbf{v}_i) f_i^\alpha f_j^\alpha \Theta(\langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_j \rangle - \Xi_{ij}) \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_j \rangle d\boldsymbol{\epsilon} d\mathbf{v}_j d\mathbf{v}_i,$$

since the properties of the scaled collision operators are similar to their un-scaled version. Substituting equation (4.3.15) into the previous equation, expanding and neglecting the term of order α^2 , that is, the term with coefficient $(\mathbf{a}_i \cdot \mathbf{v}_i)(\mathbf{a}_j \cdot \mathbf{v}_j)$ gives:

$$\begin{aligned} \mathcal{P}_i &= \alpha \sigma_{ij}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} (\mathbf{v}'_i - \mathbf{v}_i) M_i^\alpha M_j^\alpha \Theta(\langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_j \rangle - \Xi_{ij}) \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_j \rangle d\boldsymbol{\epsilon} d\mathbf{v}_j d\mathbf{v}_i \\ &\quad + \alpha \sigma_{ij}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} (\mathbf{v}'_i - \mathbf{v}_i) M_i^\alpha M_j^\alpha (\mathbf{a}_i \cdot \mathbf{v}_i) \\ &\quad \quad \quad \times \Theta(\langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_j \rangle - \Xi_{ij}) \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_j \rangle d\boldsymbol{\epsilon} d\mathbf{v}_j d\mathbf{v}_i \\ &\quad + \alpha \sigma_{ij}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} (\mathbf{v}'_i - \mathbf{v}_i) M_i^\alpha M_j^\alpha (\mathbf{a}_j \cdot \mathbf{v}_j) \\ &\quad \quad \quad \times \Theta(\langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_j \rangle - \Xi_{ij}) \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_j \rangle d\boldsymbol{\epsilon} d\mathbf{v}_j d\mathbf{v}_i. \end{aligned} \quad (4.4.25)$$

Using equation (4.4.10) with s replaced by j , we obtain:

$$\begin{aligned}
\mathcal{P}_i &= \alpha \sigma_{ij}^2 \frac{2m_j}{m_i + m_j} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} (\mathbf{v}_j - \mathbf{v}_i) \cos \theta M_i^\alpha M_j^\alpha \\
&\quad \times \Theta(\langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_j \rangle - \Xi_{ij}) \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_j \rangle d\boldsymbol{\epsilon} d\mathbf{v}_j d\mathbf{v}_i \\
&= \alpha \sigma_{ij}^2 \frac{2m_j}{m_i + m_j} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} (\mathbf{v}_j - \mathbf{v}_i) \cos \theta M_i^\alpha M_j^\alpha (\mathbf{a}_i \cdot \mathbf{v}_i) \\
&\quad \times \Theta(\langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_j \rangle - \Xi_{ij}) \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_j \rangle d\boldsymbol{\epsilon} d\mathbf{v}_j d\mathbf{v}_i \\
&= \alpha \sigma_{ij}^2 \frac{2m_j}{m_i + m_j} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} (\mathbf{v}_j - \mathbf{v}_i) \cos \theta M_i^\alpha M_j^\alpha (\mathbf{a}_s \cdot \mathbf{v}_s) \\
&\quad \times \Theta(\langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_j \rangle - \Xi_{ij}) \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_j \rangle d\boldsymbol{\epsilon} d\mathbf{v}_j d\mathbf{v}_i.
\end{aligned}$$

Observe that

$$\begin{aligned}
&\int_{\mathbb{S}_+^2} \cos \theta \Theta(\langle \boldsymbol{\epsilon}, c_0 \mathbf{v}_i - c_0 \mathbf{v}_j \rangle - \Xi_{ij}) \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_j \rangle d\boldsymbol{\epsilon} \\
&= \int_{\mathbb{S}_+^2} \cos \theta \Theta(c_0 \|\mathbf{v}_i - \mathbf{v}_j\| \cos \theta - \Xi_{ij}) \|\mathbf{v}_i - \mathbf{v}_j\| \cos \theta d\boldsymbol{\epsilon} \\
&= \int_0^{\frac{\pi}{2}} \int_0^{2\pi} \cos \theta \Theta(c_0 \|\mathbf{v}_i - \mathbf{v}_j\| \cos \theta - \Xi_{ij}) \|\mathbf{v}_i - \mathbf{v}_j\| \cos \theta \sin \theta d\phi d\theta \\
&= 2\pi \int_0^{\frac{\pi}{2}} \Theta(c_0 \|\mathbf{v}_i - \mathbf{v}_j\| \cos \theta - \Xi_{ij}) \|\mathbf{v}_i - \mathbf{v}_j\| \cos^2 \theta \sin \theta d\theta \\
&= 2\pi \int_0^{\arccos\left(\frac{\Xi_{ij}}{c_0 \|\mathbf{v}_i - \mathbf{v}_j\|}\right)} \Theta\left(\|\mathbf{v}_i - \mathbf{v}_j\| - \frac{\Xi_{ij}}{c_0}\right) \|\mathbf{v}_i - \mathbf{v}_j\| \cos^2 \theta \sin \theta d\theta \\
&= 2\pi \Theta\left(\|\mathbf{v}_i - \mathbf{v}_j\| - \frac{\Xi_{ij}}{c_0}\right) \|\mathbf{v}_i - \mathbf{v}_j\| \int_0^{\arccos\left(\frac{\Xi_{ij}}{c_0 \|\mathbf{v}_i - \mathbf{v}_j\|}\right)} \cos^2 \theta \sin \theta d\theta \\
&= 2\pi \Theta\left(\|\mathbf{v}_i - \mathbf{v}_j\| - \frac{\Xi_{ij}}{c_0}\right) \|\mathbf{v}_i - \mathbf{v}_j\| \left[-\frac{\cos^3 \theta}{3}\right]_0^{\arccos\left(\frac{\Xi_{ij}}{c_0 \|\mathbf{v}_i - \mathbf{v}_j\|}\right)} \\
&= \frac{2\pi}{3} \Theta\left(\|\mathbf{v}_i - \mathbf{v}_j\| - \frac{\Xi_{ij}}{c_0}\right) \|\mathbf{v}_i - \mathbf{v}_j\| \left[1 - \left(\frac{\Xi_{ij}}{c_0 \|\mathbf{v}_i - \mathbf{v}_j\|}\right)^3\right]. \quad (4.4.26)
\end{aligned}$$

Substituting equation (4.4.26) into the integral $\mathcal{P}_i$ above and using equation (2.4.7) together with the fact that

$$\|\mathbf{v}_i - \mathbf{v}_j\| = \|-(\mathbf{v}_j - \mathbf{v}_i)\| = |-1| \|\mathbf{v}_j - \mathbf{v}_i\| = \|\mathbf{V}^*\| = V^*, \quad (4.4.27)$$

we obtain that the integral $\mathcal{P}_i$ can be written as given below:

$$\begin{aligned}
\mathcal{P}_i &= \alpha \sigma_{ij}^2 \frac{4\pi m_j}{3(m_i + m_j)} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \mathbf{V}^* M_i^\alpha M_j^\alpha \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) V^* \left[1 - \left(\frac{\Xi_{ij}}{c_0 V^*}\right)^3\right] d\mathbf{v}_j d\mathbf{v}_i \\
&\quad + \alpha \sigma_{ij}^2 \frac{4\pi m_j}{3(m_i + m_j)} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \mathbf{V}^* M_i^\alpha M_j^\alpha (\mathbf{a}_i \cdot \mathbf{v}_i) \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) V^* \left[1 - \left(\frac{\Xi_{ij}}{c_0 V^*}\right)^3\right] d\mathbf{v}_j d\mathbf{v}_i
\end{aligned}$$

$$\begin{aligned}
& + \alpha \sigma_{ij}^2 \frac{4\pi m_j}{3(m_i + m_j)} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \mathbf{V}^* M_i^\alpha M_j^\alpha (\mathbf{a}_j \cdot \mathbf{v}_j) \Theta \left(V^* - \frac{\Xi_{ij}}{c_0} \right) V^* \left[1 - \left(\frac{\Xi_{ij}}{c_0 V^*} \right)^3 \right] d\mathbf{v}_j d\mathbf{v}_i \\
& = \alpha \sigma_{ij}^2 \frac{4\pi m_j}{3(m_i + m_j)} \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_j^\alpha \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \mathbf{V}^* \exp \left(- \frac{m_i (\mathbf{v}_i)^2 + m_j (\mathbf{v}_j)^2}{2k_B T} \right) \\
& \quad \times \Theta \left(V^* - \frac{\Xi_{ij}}{c_0} \right) V^* \left[1 - \left(\frac{\Xi_{ij}}{c_0 V^*} \right)^3 \right] d\mathbf{v}_j d\mathbf{v}_i \\
& + \alpha \sigma_{ij}^2 \frac{4\pi m_j}{3(m_i + m_j)} \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_j^\alpha \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \mathbf{V}^* \exp \left(- \frac{m_i (\mathbf{v}_i)^2 + m_j (\mathbf{v}_j)^2}{2k_B T} \right) (\mathbf{a}_i \cdot \mathbf{v}_i) \\
& \quad \times \Theta \left(V^* - \frac{\Xi_{ij}}{c_0} \right) V^* \left[1 - \left(\frac{\Xi_{ij}}{c_0 V^*} \right)^3 \right] d\mathbf{v}_j d\mathbf{v}_i \\
& + \alpha \sigma_{ij}^2 \frac{4\pi m_j}{3(m_i + m_j)} \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_j^\alpha \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \mathbf{V}^* \exp \left(- \frac{m_i (\mathbf{v}_i)^2 + m_j (\mathbf{v}_j)^2}{2k_B T} \right) (\mathbf{a}_j \cdot \mathbf{v}_j) \\
& \quad \times \Theta \left(V^* - \frac{\Xi_{ij}}{c_0} \right) V^* \left[1 - \left(\frac{\Xi_{ij}}{c_0 V^*} \right)^3 \right] d\mathbf{v}_j d\mathbf{v}_i.
\end{aligned}$$

Next we transform the above six fold integrals from $\mathbf{v}_i$ and $\mathbf{v}_j$ to the centre of mass velocity $\mathbf{X}^*$ and relative velocity $\mathbf{V}^*$, respectively given in equations (2.4.6) and (2.4.7). To do this, we use equations (2.4.10), (2.4.11) and (2.4.12) with $(m_i + m_j) = M$ together with equation (4.3.21), and obtain:

$$\begin{aligned}
\mathcal{P}_i & = \alpha \sigma_{ij}^2 \frac{4\pi m_j}{3(m_i + m_j)} \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_j^\alpha \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \mathbf{V}^* \exp \left(- \frac{M X^{*2} + \mu_{ij} V^{*2}}{2k_B T} \right) \\
& \quad \times \Theta \left(V^* - \frac{\Xi_{ij}}{c_0} \right) V^* \left[1 - \left(\frac{\Xi_{ij}}{c_0 V^*} \right)^3 \right] d\mathbf{X}^* d\mathbf{V}^* \\
& + \alpha \sigma_{ij}^2 \frac{4\pi m_j}{3(m_i + m_j)} \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_j^\alpha \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \mathbf{V}^* \exp \left(- \frac{M X^{*2} + \mu_{ij} V^{*2}}{2k_B T} \right) \\
& \quad \times \mathbf{a}_i \cdot \left(\mathbf{X}^* - \frac{m_j \mathbf{V}^*}{M} \right) \Theta \left(V^* - \frac{\Xi_{ij}}{c_0} \right) V^* \left[1 - \left(\frac{\Xi_{ij}}{c_0 V^*} \right)^3 \right] d\mathbf{X}^* d\mathbf{V}^* \\
& + \alpha \sigma_{ij}^2 \frac{4\pi m_j}{3(m_i + m_j)} \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_j^\alpha \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \mathbf{V}^* \exp \left(- \frac{M X^{*2} + \mu_{ij} V^{*2}}{2k_B T} \right) \\
& \quad \times \mathbf{a}_j \cdot \left(\mathbf{X}^* + \frac{m_i \mathbf{V}^*}{M} \right) \Theta \left(V^* - \frac{\Xi_{ij}}{c_0} \right) V^* \left[1 - \left(\frac{\Xi_{ij}}{c_0 V^*} \right)^3 \right] d\mathbf{X}^* d\mathbf{V}^* \\
& = \alpha \sigma_{ij}^2 \frac{4\pi m_j}{3(m_i + m_j)} \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_j^\alpha \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \mathbf{V}^* \exp \left(- \frac{M X^{*2} + \mu_{ij} V^{*2}}{2k_B T} \right) \\
& \quad \times \Theta \left(V^* - \frac{\Xi_{ij}}{c_0} \right) V^* d\mathbf{X}^* d\mathbf{V}^* \\
& - \alpha \sigma_{ij}^2 \frac{4\pi m_j}{3(m_i + m_j)} \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_j^\alpha \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \mathbf{V}^* \exp \left(- \frac{M X^{*2} + \mu_{ij} V^{*2}}{2k_B T} \right)
\end{aligned}$$

$$\begin{aligned}
& \times \Theta \left(V^* - \frac{\Xi_{ij}}{c_0} \right) V^* \left(\frac{\Xi_{ij}}{c_0 V^*} \right)^3 d\mathbf{X}^* d\mathbf{V}^* \\
& + \alpha \sigma_{ij}^2 \frac{4\pi m_j}{3(m_i + m_j)} \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_j^\alpha \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \mathbf{V}^* \exp \left(- \frac{MX^{*2} + \mu_{ij} V^{*2}}{2k_B T} \right) \\
& \quad \times \mathbf{a}_i \cdot \left(\mathbf{X}^* - \frac{m_j \mathbf{V}^*}{M} \right) \Theta \left(V^* - \frac{\Xi_{ij}}{c_0} \right) V^* d\mathbf{X}^* d\mathbf{V}^* \\
& - \alpha \sigma_{ij}^2 \frac{4\pi m_j}{3(m_i + m_j)} \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_j^\alpha \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \mathbf{V}^* \exp \left(- \frac{MX^{*2} + \mu_{ij} V^{*2}}{2k_B T} \right) \\
& \quad \times \mathbf{a}_i \cdot \left(\mathbf{X}^* - \frac{m_j \mathbf{V}^*}{M} \right) \Theta \left(V^* - \frac{\Xi_{ij}}{c_0} \right) V^* \left(\frac{\Xi_{ij}}{c_0 V^*} \right)^3 d\mathbf{X}^* d\mathbf{V}^* \\
& + \alpha \sigma_{ij}^2 \frac{4\pi m_j}{3(m_i + m_j)} \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_j^\alpha \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \mathbf{V}^* \exp \left(- \frac{MX^{*2} + \mu_{ij} V^{*2}}{2k_B T} \right) \\
& \quad \times \mathbf{a}_j \cdot \left(\mathbf{X}^* + \frac{m_i \mathbf{V}^*}{M} \right) \Theta \left(V^* - \frac{\Xi_{ij}}{c_0} \right) V^* d\mathbf{X}^* d\mathbf{V}^* \\
& - \alpha \sigma_{ij}^2 \frac{4\pi m_j}{3(m_i + m_j)} \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_j^\alpha \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \mathbf{V}^* \exp \left(- \frac{MX^{*2} + \mu_{ij} V^{*2}}{2k_B T} \right) \\
& \quad \times \mathbf{a}_j \cdot \left(\mathbf{X}^* + \frac{m_i \mathbf{V}^*}{M} \right) \Theta \left(V^* - \frac{\Xi_{ij}}{c_0} \right) V^* \left(\frac{\Xi_{ij}}{c_0 V^*} \right)^3 d\mathbf{X}^* d\mathbf{V}^*.
\end{aligned}$$

Expanding gives:

$$\begin{aligned}
\mathcal{P}_i &= \alpha \sigma_{ij}^2 \frac{4\pi m_j}{3(m_i + m_j)} \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_j^\alpha \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \mathbf{V}^* \exp \left(- \frac{MX^{*2} + \mu_{ij} V^{*2}}{2k_B T} \right) \\
& \quad \times \Theta \left(V^* - \frac{\Xi_{ij}}{c_0} \right) V^* d\mathbf{X}^* d\mathbf{V}^* \\
& - \alpha \sigma_{ij}^2 \frac{4\pi m_j}{3(m_i + m_j)} \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_j^\alpha \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \mathbf{V}^* \exp \left(- \frac{MX^{*2} + \mu_{ij} V^{*2}}{2k_B T} \right) \\
& \quad \times \Theta \left(V^* - \frac{\Xi_{ij}}{c_0} \right) V^* \left(\frac{\Xi_{ij}}{c_0 V^*} \right)^3 d\mathbf{X}^* d\mathbf{V}^* \\
& + \alpha \sigma_{ij}^2 \frac{4\pi m_j}{3(m_i + m_j)} \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_j^\alpha \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \mathbf{V}^* \exp \left(- \frac{MX^{*2} + \mu_{ij} V^{*2}}{2k_B T} \right) \\
& \quad \times (\mathbf{a}_i \cdot \mathbf{X}^*) \Theta \left(V^* - \frac{\Xi_{ij}}{c_0} \right) V^* d\mathbf{X}^* d\mathbf{V}^* \\
& - \alpha \sigma_{ij}^2 \frac{4\pi m_j}{3(m_i + m_j)} \frac{m_j}{M} \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_j^\alpha \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \mathbf{V}^* \exp \left(- \frac{MX^{*2} + \mu_{ij} V^{*2}}{2k_B T} \right) \\
& \quad \times (\mathbf{a}_i \cdot \mathbf{V}^*) \Theta \left(V^* - \frac{\Xi_{ij}}{c_0} \right) V^* d\mathbf{X}^* d\mathbf{V}^* \\
& - \alpha \sigma_{ij}^2 \frac{4\pi m_j}{3(m_i + m_j)} \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_j^\alpha \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \mathbf{V}^* \exp \left(- \frac{MX^{*2} + \mu_{ij} V^{*2}}{2k_B T} \right)
\end{aligned}$$

$$\begin{aligned}
& \times (\mathbf{a}_i \cdot \mathbf{X}^*) \Theta \left(V^* - \frac{\Xi_{ij}}{c_0} \right) V^* \left(\frac{\Xi_{ij}}{c_0 V^*} \right)^3 d\mathbf{X}^* d\mathbf{V}^* \\
& + \alpha \sigma_{ij}^2 \frac{4\pi m_j}{3(m_i + m_j)} \frac{m_j}{M} \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_j^\alpha \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \mathbf{V}^* \exp \left(- \frac{MX^{*2} + \mu_{ij} V^{*2}}{2k_B T} \right) \\
& \quad \times (\mathbf{a}_i \cdot \mathbf{V}^*) \Theta \left(V^* - \frac{\Xi_{ij}}{c_0} \right) V^* \left(\frac{\Xi_{ij}}{c_0 V^*} \right)^3 d\mathbf{X}^* d\mathbf{V}^* \\
& + \alpha \sigma_{ij}^2 \frac{4\pi m_j}{3(m_i + m_j)} \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_j^\alpha \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \mathbf{V}^* \exp \left(- \frac{MX^{*2} + \mu_{ij} V^{*2}}{2k_B T} \right) \\
& \quad \times (\mathbf{a}_j \cdot \mathbf{X}^*) \Theta \left(V^* - \frac{\Xi_{ij}}{c_0} \right) V^* d\mathbf{X}^* d\mathbf{V}^* \\
& + \alpha \sigma_{ij}^2 \frac{4\pi m_j}{3(m_i + m_j)} \frac{m_i}{M} \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_j^\alpha \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \mathbf{V}^* \exp \left(- \frac{MX^{*2} + \mu_{ij} V^{*2}}{2k_B T} \right) \\
& \quad \times (\mathbf{a}_j \cdot \mathbf{V}^*) \Theta \left(V^* - \frac{\Xi_{ij}}{c_0} \right) V^* d\mathbf{X}^* d\mathbf{V}^* \\
& - \alpha \sigma_{ij}^2 \frac{4\pi m_j}{3(m_i + m_j)} \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_j^\alpha \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \mathbf{V}^* \exp \left(- \frac{MX^{*2} + \mu_{ij} V^{*2}}{2k_B T} \right) \\
& \quad \times (\mathbf{a}_j \cdot \mathbf{X}^*) \Theta \left(V^* - \frac{\Xi_{ij}}{c_0} \right) V^* \left(\frac{\Xi_{ij}}{c_0 V^*} \right)^3 d\mathbf{X}^* d\mathbf{V}^* \\
& - \alpha \sigma_{ij}^2 \frac{4\pi m_j}{3(m_i + m_j)} \frac{m_i}{M} \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_j^\alpha \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \mathbf{V}^* \exp \left(- \frac{MX^{*2} + \mu_{ij} V^{*2}}{2k_B T} \right) \\
& \quad \times (\mathbf{a}_j \cdot \mathbf{V}^*) \Theta \left(V^* - \frac{\Xi_{ij}}{c_0} \right) V^* \left(\frac{\Xi_{ij}}{c_0 V^*} \right)^3 d\mathbf{X}^* d\mathbf{V}^*.
\end{aligned}$$

The integral $\mathcal{P}_i$ above can equivalently be written as follows:

$$\begin{aligned}
\mathcal{P}_i &= \alpha \sigma_{ij}^2 \frac{4\pi m_j}{3(m_i + m_j)} \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_j^\alpha \\
& \left\{ \int_{\mathbb{R}^3} \exp \left(- \frac{MX^{*2}}{2k_B T} \right) d\mathbf{X}^* \underbrace{\int_{\mathbb{R}^3} \mathbf{V}^* \exp \left(- \frac{\mu_{ij} V^{*2}}{2k_B T} \right) \Theta \left(V^* - \frac{\Xi_{ij}}{c_0} \right) V^* d\mathbf{V}^*}_{\mathcal{Y}_1} \right. \\
& - \int_{\mathbb{R}^3} \exp \left(- \frac{MX^{*2}}{2k_B T} \right) d\mathbf{X}^* \underbrace{\int_{\mathbb{R}^3} \mathbf{V}^* \exp \left(- \frac{\mu_{ij} V^{*2}}{2k_B T} \right) \Theta \left(V^* - \frac{\Xi_{ij}}{c_0} \right) V^* \left(\frac{\Xi_{ij}}{c_0 V^*} \right)^3 d\mathbf{V}^*}_{\mathcal{Y}_2} \\
& + \mathbf{a}_i \cdot \int_{\mathbb{R}^3} \mathbf{X}^* \exp \left(- \frac{MX^{*2}}{2k_B T} \right) d\mathbf{X}^* \underbrace{\int_{\mathbb{R}^3} \mathbf{V}^* \exp \left(- \frac{\mu_{ij} V^{*2}}{2k_B T} \right) \Theta \left(V^* - \frac{\Xi_{ij}}{c_0} \right) V^* d\mathbf{V}^*}_{\mathcal{Y}_1} \\
& \left. - \int_{\mathbb{R}^3} \exp \left(- \frac{MX^{*2}}{2k_B T} \right) d\mathbf{X}^* \frac{m_j}{M} \underbrace{\int_{\mathbb{R}^3} \mathbf{V}^* \exp \left(- \frac{\mu_{ij} V^{*2}}{2k_B T} \right) (\mathbf{a}_i \cdot \mathbf{V}^*) \Theta \left(V^* - \frac{\Xi_{ij}}{c_0} \right) V^* d\mathbf{V}^*}_{\mathcal{Y}_3} \right\}
\end{aligned}$$

$$\begin{aligned}
& -\mathbf{a}_i \cdot \int_{\mathbb{R}^3} \mathbf{X}^* \exp\left(-\frac{MX^{*2}}{2k_B T}\right) d\mathbf{X}^* \underbrace{\int_{\mathbb{R}^3} \mathbf{V}^* \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) V^* \left(\frac{\Xi_{ij}}{c_0 V^*}\right)^3 d\mathbf{V}^*}_{\mathcal{Y}_2} \\
& + \int_{\mathbb{R}^3} \exp\left(-\frac{MX^{*2}}{2k_B T}\right) d\mathbf{X}^* \frac{m_j}{M} \underbrace{\int_{\mathbb{R}^3} \mathbf{V}^* \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) (\mathbf{a}_i \cdot \mathbf{V}^*) \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) V^* \left(\frac{\Xi_{ij}}{c_0 V^*}\right)^3 d\mathbf{V}^*}_{\mathcal{Y}_4} \\
& + \mathbf{a}_j \cdot \int_{\mathbb{R}^3} \mathbf{X}^* \exp\left(-\frac{MX^{*2}}{2k_B T}\right) d\mathbf{X}^* \underbrace{\int_{\mathbb{R}^3} \mathbf{V}^* \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) V^* d\mathbf{V}^*}_{\mathcal{Y}_1} \\
& + \int_{\mathbb{R}^3} \exp\left(-\frac{MX^{*2}}{2k_B T}\right) d\mathbf{X}^* \frac{m_i}{M} \underbrace{\int_{\mathbb{R}^3} \mathbf{V}^* \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) (\mathbf{a}_j \cdot \mathbf{V}^*) \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) V^* d\mathbf{V}^*}_{\mathcal{Y}_5} \\
& - \mathbf{a}_j \cdot \int_{\mathbb{R}^3} \mathbf{X}^* \exp\left(-\frac{MX^{*2}}{2k_B T}\right) d\mathbf{X}^* \underbrace{\int_{\mathbb{R}^3} \mathbf{V}^* \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) V^* \left(\frac{\Xi_{ij}}{c_0 V^*}\right)^3 d\mathbf{V}^*}_{\mathcal{Y}_2} \\
& - \int_{\mathbb{R}^3} \exp\left(-\frac{MX^{*2}}{2k_B T}\right) d\mathbf{X}^* \frac{m_i}{M} \underbrace{\int_{\mathbb{R}^3} \mathbf{V}^* \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) (\mathbf{a}_j \cdot \mathbf{V}^*) \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) V^* \left(\frac{\Xi_{ij}}{c_0 V^*}\right)^3 d\mathbf{V}^*}_{\mathcal{Y}_6} \Bigg\}.
\end{aligned}$$

The value of the last integrals in $\mathbf{X}^*$ on the right-hand side of the previous equation is given in equation (4.3.22). The second to the last integral in $\mathbf{X}^*$ on the right-hand side of the previous equation is similar to that given in equation (4.4.20). Therefore,

$$\int_{\mathbb{R}^3} \exp\left(-\frac{MX^{*2}}{2k_B T}\right) d\mathbf{X}^* = \left(\frac{2\pi k_B T}{M}\right)^{\frac{3}{2}} \quad \text{and} \quad \int_{\mathbb{R}^3} \mathbf{X}^* \exp\left(-\frac{MX^{*2}}{2k_B T}\right) d\mathbf{X}^* = \mathbf{0}. \quad (4.4.28)$$

Now let us evaluate the integrals in $\mathbf{V}^*$. Using the fact that any vector $\mathbf{V}_*$ can be written in terms of a unit vector as $\mathbf{V}_* = V_* \vec{v}$, with $V_* = \|\mathbf{V}_*\|$ and $\vec{v}$ a unit vector, the integrals in $\mathbf{V}^*$ can be evaluated in spherical coordinates as given below. The integral $\mathcal{Y}_1$ is evaluated as follows:

$$\begin{aligned}
& \int_{\mathbb{R}^3} \mathbf{V}^* \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) V^* d\mathbf{V}^* \\
& = \int_{\mathbb{R}^3} V^* \vec{v} \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) V^* \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) d\mathbf{V}^* \\
& = \int_0^\infty \int_0^\pi \int_0^{2\pi} V^{*2} \{\hat{x} \sin \theta \cos \phi + \hat{y} \sin \theta \sin \phi + \hat{z} \cos \theta\} \\
& \quad \times \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) V^{*2} \sin \theta d\phi d\theta dV^* \\
& = \int_{V^* \geq \frac{\Xi_{ij}}{c_0}}^\infty V^{*4} \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) dV^* \left(\underbrace{\hat{x} \int_0^\pi \sin^2 \theta d\theta}_{\frac{\pi}{2}} \underbrace{\int_0^{2\pi} \cos \phi d\phi}_0 \right)
\end{aligned}$$

$$+ \hat{\mathbf{y}} \underbrace{\int_0^\pi \sin^2 \theta d\theta}_{\frac{\pi}{2}} \underbrace{\int_0^{2\pi} \sin \phi d\phi}_0 + \hat{\mathbf{z}} \underbrace{\int_0^\pi \sin \theta \cos \theta d\theta}_0 \underbrace{\int_0^{2\pi} d\phi}_{2\pi} \Bigg),$$

where $\hat{\mathbf{x}}, \hat{\mathbf{y}}, \hat{\mathbf{z}}$ are the Cartesian unit vectors in $\mathbb{R}^3$. The integral in V^* can be evaluated using the change of variables given in equation (4.3.23) together equations (4.3.24) and (4.3.25), to obtain:

$$\begin{aligned} \int_{V^* \geq \frac{\Xi_{ij}}{c_0}}^\infty V^{*4} \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) dV^* &= \int_{z_i^*}^\infty z^2 \left(\frac{2k_B T}{\mu_{ij}}\right)^2 \exp(-z) \frac{1}{2z^{\frac{1}{2}}} \left(\frac{2k_B T}{\mu_{ij}}\right)^{\frac{1}{2}} dz \\ &= \frac{1}{2} \left(\frac{2k_B T}{\mu_{ij}}\right)^{\frac{5}{2}} \int_{z_i^*}^\infty z^{\frac{3}{2}} \exp(-z) dz. \end{aligned}$$

Using the incomplete Euler gamma function (4.3.3) with $\eta - 1 = \frac{3}{2}$, i.e., $\eta = \frac{5}{2}$, we obtain:

$$\int_{V^* \geq \frac{\Xi_{ij}}{c_0}}^\infty V^{*4} \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) dV^* = \frac{1}{2} \left(\frac{2k_B T}{\mu_{ij}}\right)^{\frac{5}{2}} \Gamma\left(\frac{5}{2}, z_i^*\right). \quad (4.4.29)$$

Therefore,

$$\begin{aligned} \int_{\mathbb{R}^3} \mathbf{V}^* \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) V^* d\mathbf{V}^* \\ = \frac{1}{2} \left(\frac{2k_B T}{\mu_{ij}}\right)^{\frac{5}{2}} \Gamma\left(\frac{5}{2}, z_i^*\right) [\hat{\mathbf{x}}(0) + \hat{\mathbf{y}}(0) + \hat{\mathbf{z}}(0)] \\ = \frac{1}{2} \left(\frac{2k_B T}{\mu_{ij}}\right)^{\frac{5}{2}} \Gamma\left(\frac{5}{2}, z_i^*\right) \times \mathbf{0} \\ = \mathbf{0}. \end{aligned} \quad (4.4.30)$$

The integral $\mathcal{Y}_2$ is evaluated as given below:

$$\begin{aligned} \int_{\mathbb{R}^3} \mathbf{V}^* \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) V^* \left(\frac{\Xi_{ij}}{c_0 V^*}\right)^3 d\mathbf{V}^* \\ = \int_{\mathbb{R}^3} V^* \vec{\mathbf{v}} \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) V^* \left(\frac{\Xi_{ij}}{c_0 V^*}\right)^3 d\mathbf{V}^* \\ = \int_0^\infty \int_0^\pi \int_0^{2\pi} V^* \{\hat{\mathbf{x}} \sin \theta \cos \phi + \hat{\mathbf{y}} \sin \theta \sin \phi + \hat{\mathbf{z}} \cos \theta\} \\ \times \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) V^* \left(\frac{\Xi_{ij}}{c_0 V^*}\right)^3 V^{*2} \sin \theta d\phi d\theta dV \\ = \left(\frac{\Xi_{ij}}{c_0}\right)^3 \int_{V^* \geq \frac{\Xi_{ij}}{c_0}}^\infty V^* \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) dV^* \left(\underbrace{\hat{\mathbf{x}} \int_0^\pi \sin^2 \theta d\theta}_{\frac{\pi}{2}} \underbrace{\int_0^{2\pi} \cos \phi d\phi}_0 \right. \\ \left. + \hat{\mathbf{y}} \underbrace{\int_0^\pi \sin^2 \theta d\theta}_{\frac{\pi}{2}} \underbrace{\int_0^{2\pi} \sin \phi d\phi}_0 + \hat{\mathbf{z}} \underbrace{\int_0^\pi \sin \theta \cos \theta d\theta}_0 \underbrace{\int_0^{2\pi} d\phi}_{2\pi} \right), \end{aligned}$$

where $\hat{\mathbf{x}}, \hat{\mathbf{y}}, \hat{\mathbf{z}}$ are the Cartesian unit vectors in $\mathbb{R}^3$. The integral in V^* can be evaluated using the change of variables given in equation (4.3.23) together equations (4.3.24) and (4.3.25), to obtain:

$$\begin{aligned} \int_{V^* \geq \frac{\Xi_{ij}}{c_0}}^{\infty} V^* \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) dV^* &= \int_{z_i^*}^{\infty} z^{\frac{1}{2}} \left(\frac{2k_B T}{\mu_{ij}}\right)^{\frac{1}{2}} \exp(-z) \frac{1}{2z^{\frac{1}{2}}} \left(\frac{2k_B T}{\mu_{ij}}\right)^{\frac{1}{2}} dz \\ &= \frac{1}{2} \left(\frac{2k_B T}{\mu_{ij}}\right) \int_{z_i^*}^{\infty} \exp(-z) dz. \end{aligned}$$

Using the incomplete Euler gamma function given in equation (4.3.3) with $\eta - 1 = 0$, i.e., $\eta = 1$, we obtain:

$$\int_{V^* \geq \frac{\Xi_{ij}}{c_0}}^{\infty} V^* \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) dV^* = \frac{1}{2} \left(\frac{2k_B T}{\mu_{ij}}\right) \Gamma(1, z_i^*). \quad (4.4.31)$$

Therefore,

$$\begin{aligned} \int_{\mathbb{R}^3} \mathbf{V}^* \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) V^* \left(\frac{\Xi_{ij}}{c_0 V^*}\right)^3 d\mathbf{V}^* \\ = \frac{1}{2} \left(\frac{\Xi_{ij}}{c_0}\right)^3 \left(\frac{2k_B T}{\mu_{ij}}\right) \Gamma(1, z_i^*) [\hat{\mathbf{x}}(0) + \hat{\mathbf{y}}(0) + \hat{\mathbf{z}}(0)] \\ = \frac{1}{2} \left(\frac{\Xi_{ij}}{c_0}\right)^3 \left(\frac{2k_B T}{\mu_{ij}}\right) \Gamma(1, z_i^*) \times \mathbf{0} \\ = \mathbf{0}. \end{aligned} \quad (4.4.32)$$

The integral $\mathcal{J}_3$ can be evaluated as given below:

$$\begin{aligned} \int_{\mathbb{R}^3} \mathbf{V}^* \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) (\mathbf{a}_i \cdot \mathbf{V}^*) \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) V^* d\mathbf{V}^* \\ = \int_{\mathbb{R}^3} V^* \vec{v} \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) (a_i V^* \cos \theta) \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) V^* d\mathbf{V}^* \\ = \int_0^{\infty} \int_0^{\pi} \int_0^{2\pi} V^* \{\hat{\mathbf{x}} \sin \theta \cos \phi + \hat{\mathbf{y}} \sin \theta \sin \phi + \hat{\mathbf{z}} \cos \theta\} \exp\left(-\frac{\mu_{ij} V^2}{2k_B T}\right) \\ \times (a_i V^* \cos \theta) V^* \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) V^{*2} \sin \theta d\phi d\theta dV^* \\ = a_i \int_{V^* \geq \frac{\Xi_{ij}}{c_0}}^{\infty} V^{*5} \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) dV^* \left(\hat{\mathbf{x}} \underbrace{\int_0^{\pi} \sin^2 \theta \cos \theta d\theta}_0 \underbrace{\int_0^{2\pi} \cos \phi d\phi}_0 \right. \\ \left. + \hat{\mathbf{y}} \underbrace{\int_0^{\pi} \sin^2 \theta \cos \theta d\theta}_0 \underbrace{\int_0^{2\pi} \sin \phi d\phi}_0 + \hat{\mathbf{z}} \underbrace{\int_0^{\pi} \sin \theta \cos^2 \theta d\theta}_{\frac{2}{3}} \underbrace{\int_0^{2\pi} d\phi}_{2\pi} \right), \end{aligned}$$

where $\hat{\mathbf{x}}, \hat{\mathbf{y}}, \hat{\mathbf{z}}$ are the Cartesian unit vectors in $\mathbb{R}^3$ and $a_i = ||\mathbf{a}_i|| = |\mathbf{a}_i|$. The integral in V^* can be evaluated using the change of variables given in equation (4.3.23) together equations (4.3.24) and (4.3.25), as given below:

$$\begin{aligned}
\int_{V^* \geq \frac{\Xi_{ij}}{c_0}}^{\infty} V^{*5} \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) dV^* &= \int_{z_i^*}^{\infty} z^{\frac{5}{2}} \left(\frac{2k_B T}{\mu_{ij}}\right)^{\frac{5}{2}} \exp(-z) \frac{1}{2z^{\frac{1}{2}}} \left(\frac{2k_B T}{\mu_{ij}}\right)^{\frac{1}{2}} dz \\
&= \frac{1}{2} \left(\frac{2k_B T}{\mu_{ij}}\right)^3 \int_{z_i^*}^{\infty} z^2 \exp(-z) dz.
\end{aligned}$$

Using the incomplete Euler gamma function given in equation (4.3.3) with $\eta - 1 = 2$, i.e., $\eta = 3$, we obtain:

$$\int_{V^* \geq \frac{\Xi_{ij}}{c_0}}^{\infty} V^{*5} \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) dV^* = \frac{1}{2} \left(\frac{2k_B T}{\mu_{ij}}\right)^3 \Gamma\left(3, z_i^*\right). \quad (4.4.33)$$

Therefore,

$$\begin{aligned}
&\int_{\mathbb{R}^3} \mathbf{V}^* \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) (\mathbf{a}_i \cdot \mathbf{V}^*) \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) V^* d\mathbf{V}^* \\
&= a_i \frac{1}{2} \left(\frac{2k_B T}{\mu_{ij}}\right)^3 \Gamma\left(3, z_i^*\right) \left[\hat{\mathbf{x}}(0 \times 0) + \hat{\mathbf{y}}(0 \times 0) + \hat{\mathbf{z}}\left(\frac{2}{3} \times 2\pi\right)\right] \\
&= a_i \frac{1}{2} \left(\frac{2k_B T}{\mu_{ij}}\right)^3 \Gamma\left(3, z_i^*\right) \hat{\mathbf{z}}\left(\frac{4\pi}{3}\right) \\
&= \mathbf{a}_i \frac{2\pi}{3} \left(\frac{2k_B T}{\mu_{ij}}\right)^3 \Gamma\left(3, z_i^*\right). \quad (4.4.34)
\end{aligned}$$

The integral $\mathcal{Y}_4$ can be evaluated as given below:

$$\begin{aligned}
&\int_{\mathbb{R}^3} \mathbf{V}^* \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) (\mathbf{a}_i \cdot \mathbf{V}^*) \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) V^* \left(\frac{\Xi_{ij}}{c_0 V^*}\right)^3 d\mathbf{V}^* \\
&= \int_{\mathbb{R}^3} V^* \vec{\mathbf{v}} \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) (a_i V^* \cos \theta) \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) V^* \left(\frac{\Xi_{ij}}{c_0 V^*}\right)^3 d\mathbf{V}^* \\
&= \int_0^{\infty} \int_0^{\pi} \int_0^{2\pi} V^* \{\hat{\mathbf{x}} \sin \theta \cos \phi + \hat{\mathbf{y}} \sin \theta \sin \phi + \hat{\mathbf{z}} \cos \theta\} \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) \\
&\quad \times (a_i V^* \cos \theta) \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) V^* \left(\frac{\Xi_{ij}}{c_0 V^*}\right)^3 V^{*2} \sin \theta d\phi d\theta dV^* \\
&= a_i \left(\frac{\Xi_{ij}}{c_0}\right)^3 \int_{V^* \geq \frac{\Xi_{ij}}{c_0}}^{\infty} V^{*2} \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) dV^* \left(\underbrace{\int_0^{\pi} \sin^2 \theta \cos \theta d\theta}_0 \underbrace{\int_0^{2\pi} \cos \phi d\phi}_0\right. \\
&\quad \left.+ \underbrace{\hat{\mathbf{y}} \int_0^{\pi} \sin^2 \theta \cos \theta d\theta}_0 \underbrace{\int_0^{2\pi} \sin \phi d\phi}_0 + \underbrace{\hat{\mathbf{z}} \int_0^{\pi} \sin \theta \cos^2 \theta d\theta}_{\frac{2}{3}} \underbrace{\int_0^{2\pi} d\phi}_{2\pi}\right).
\end{aligned}$$

where $\hat{\mathbf{x}}, \hat{\mathbf{y}}, \hat{\mathbf{z}}$ are the Cartesian unit vectors in $\mathbb{R}^3$ and $a_i = ||\mathbf{a}_i|| = |\mathbf{a}_i|$. The integral in V^* can be evaluated using the change of variables given in equation (4.3.23) together equations (4.3.24) and (4.3.25), as given below:

$$\begin{aligned}
\int_{V^* \geq \frac{\Xi_{ij}}{c_0}}^{\infty} V^{*2} \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) dV^* &= \int_{z^*}^{\infty} z \left(\frac{2k_B T}{\mu_{ij}}\right) \exp(-z) \frac{1}{2z^{\frac{1}{2}}} \left(\frac{2k_B T}{\mu_{ij}}\right)^{\frac{1}{2}} dz \\
&= \frac{1}{2} \left(\frac{2k_B T}{\mu_{ij}}\right)^{\frac{3}{2}} \int_{z^*}^{\infty} z^{\frac{1}{2}} \exp(-z) dz.
\end{aligned}$$

Using the incomplete Euler gamma function given in equation (4.3.3) with $\eta-1 = \frac{1}{2}$, i.e., $\eta = \frac{3}{2}$, we obtain:

$$\int_{V^* \geq \frac{\Xi_{ij}}{c_0}}^{\infty} V^{*2} \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) dV^* = \frac{1}{2} \left(\frac{2k_B T}{\mu_{ij}}\right)^{\frac{3}{2}} \Gamma\left(\frac{3}{2}, z_i^*\right). \quad (4.4.35)$$

Therefore,

$$\begin{aligned}
&\int_{\mathbb{R}^3} \mathbf{V}^* \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) (\mathbf{a}_i \cdot \mathbf{V}^*) \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) V^* \left(\frac{\Xi_{ij}}{c_0 V^*}\right)^3 d\mathbf{V}^* \\
&= a_i \left(\frac{\Xi_{ij}}{c_0}\right)^3 \frac{1}{2} \left(\frac{2k_B T}{\mu_{ij}}\right)^{\frac{3}{2}} \Gamma\left(\frac{3}{2}, z_i^*\right) \left[\hat{\mathbf{x}}(0 \times 0) + \hat{\mathbf{y}}(0 \times 0) + \hat{\mathbf{z}}\left(\frac{2}{3} \times 2\pi\right)\right] \\
&= a_i \left(\frac{\Xi_{ij}}{c_0}\right)^3 \frac{1}{2} \left(\frac{2k_B T}{\mu_{ij}}\right)^{\frac{3}{2}} \Gamma\left(\frac{3}{2}, z_i^*\right) \hat{\mathbf{z}}\left(\frac{4\pi}{3}\right) \\
&= \mathbf{a}_i \frac{2\pi}{3} \left(\frac{\Xi_{ij}}{c_0}\right)^3 \left(\frac{2k_B T}{\mu_{ij}}\right)^{\frac{3}{2}} \Gamma\left(\frac{3}{2}, z_i^*\right). \quad (4.4.36)
\end{aligned}$$

The integrals $\mathcal{Y}_5$ and $\mathcal{Y}_6$ are similar to the integrals $\mathcal{Y}_3$ and $\mathcal{Y}_4$, respectively. More precisely, replacing $\mathbf{a}_i$ with $\mathbf{a}_j$ in the integrals $\mathcal{Y}_3$ and $\mathcal{Y}_4$, one obtains the integrals $\mathcal{Y}_5$ and $\mathcal{Y}_6$, respectively. Therefore, following exactly the same procedures as those used in the the computation of the integrals $\mathcal{Y}_3$ and $\mathcal{Y}_4$, respectively, we obtain:

$$\int_{\mathbb{R}^3} \mathbf{V}^* \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) (\mathbf{a}_j \cdot \mathbf{V}^*) \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) V^* d\mathbf{V}^* = \mathbf{a}_j \frac{2\pi}{3} \left(\frac{2k_B T}{\mu_{ij}}\right)^3 \Gamma(3, z_i^*), \quad (4.4.37)$$

$$\begin{aligned}
&\int_{\mathbb{R}^3} \mathbf{V}^* \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) (\mathbf{a}_j \cdot \mathbf{V}^*) \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) V^* \left(\frac{\Xi_{ij}}{c_0 V^*}\right)^3 d\mathbf{V}^* \\
&= \mathbf{a}_j \frac{2\pi}{3} \left(\frac{\Xi_{ij}}{c_0}\right)^3 \left(\frac{2k_B T}{\mu_{ij}}\right)^{\frac{3}{2}} \Gamma\left(\frac{3}{2}, z_i^*\right). \quad (4.4.38)
\end{aligned}$$

Substituting Eqs. (4.4.28), (4.4.30), (4.4.32), (4.4.34), (4.4.36), (4.4.37) and (4.4.38) into $\mathcal{P}_i$ gives:

$$\begin{aligned}
\mathcal{P}_i &= \alpha \sigma_{ij}^2 \frac{4\pi m_j}{3(m_i + m_j)} \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_j^\alpha \\
&\left\{ -\left(\frac{2\pi k_B T}{M}\right)^{\frac{3}{2}} \frac{m_j}{M} \mathbf{a}_i \frac{2\pi}{3} \left(\frac{2k_B T}{\mu_{ij}}\right)^3 \Gamma(3, z_i^*) + \left(\frac{2\pi k_B T}{M}\right)^{\frac{3}{2}} \frac{m_j}{M} \mathbf{a}_i \left(\frac{\Xi_{ij}}{c_0}\right)^3 \frac{2\pi}{3} \left(\frac{2k_B T}{\mu_{ij}}\right)^{\frac{3}{2}} \Gamma\left(\frac{3}{2}, z_i^*\right) \right. \\
&\left. + \left(\frac{2\pi k_B T}{M}\right)^{\frac{3}{2}} \frac{m_i}{M} \mathbf{a}_j \frac{2\pi}{3} \left(\frac{2k_B T}{\mu_{ij}}\right)^3 \Gamma(3, z_i^*) - \left(\frac{2\pi k_B T}{M}\right)^{\frac{3}{2}} \frac{m_i}{M} \mathbf{a}_j \left(\frac{\Xi_{ij}}{c_0}\right)^3 \frac{2\pi}{3} \left(\frac{2k_B T}{\mu_{ij}}\right)^{\frac{3}{2}} \Gamma\left(\frac{3}{2}, z_i^*\right) \right\}.
\end{aligned}$$

Factorising, we obtain:

$$\begin{aligned}
\mathcal{P}_i &= \alpha \sigma_{ij}^2 \frac{8\pi^2 m_j}{9(m_i + m_j)} \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_j^\alpha \left(\frac{2\pi k_B T}{M} \right)^{\frac{3}{2}} \left(\frac{2k_B T}{\mu_{ij}} \right)^3 \Gamma(3, z_i^*) \left\{ \frac{m_i}{M} \mathbf{a}_j - \frac{m_j}{M} \mathbf{a}_i \right\} \\
&+ \alpha \frac{8\pi^2 \sigma_{ij}^2 m_j}{9(m_i + m_j)} \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_j^\alpha \left(\frac{2\pi k_B T}{M} \right)^{\frac{3}{2}} \left(\frac{\Xi_{ij}}{c_0} \right)^3 \left(\frac{2k_B T}{\mu_{ij}} \right)^{\frac{3}{2}} \Gamma\left(\frac{3}{2}, z_i^*\right) \left\{ \frac{m_j}{M} \mathbf{a}_i - \frac{m_i}{M} \mathbf{a}_j \right\} \\
&= \alpha \sigma_{ij}^2 \frac{8\pi^2 m_j}{9(m_i + m_j)} \left(\frac{1}{2\pi k_B T} \right)^{\frac{3}{2}} c_i^\alpha c_j^\alpha \left(\frac{m_i m_j}{M} \right)^{\frac{3}{2}} \left(\frac{2k_B T}{\mu_{ij}} \right)^3 \Gamma(3, z_i^*) \left\{ \frac{m_i}{M} \mathbf{a}_j - \frac{m_j}{M} \mathbf{a}_i \right\} \\
&+ \alpha \frac{8\pi^2 \sigma_{ij}^2 m_j}{9(m_i + m_j)} \left(\frac{1}{2\pi k_B T} \right)^{\frac{3}{2}} c_i^\alpha c_j^\alpha \left(\frac{m_i m_j}{M} \right)^{\frac{3}{2}} \left(\frac{\Xi_{ij}}{c_0} \right)^3 \left(\frac{2k_B T}{\mu_{ij}} \right)^{\frac{3}{2}} \Gamma\left(\frac{3}{2}, z_i^*\right) \left\{ \frac{m_j}{M} \mathbf{a}_i - \frac{m_i}{M} \mathbf{a}_j \right\} \\
&= \alpha \sigma_{ij}^2 \frac{8m_j}{9(m_i + m_j)} \left(\frac{\mu_{ij}}{2\pi k_B T} \right)^{\frac{3}{2}} c_i^\alpha c_j^\alpha \left(\frac{2\pi k_B T}{\mu_{ij}} \right)^2 \left(\frac{2k_B T}{\mu_{ij}} \right) \Gamma(3, z_i^*) \left\{ \frac{\mu_{ij} \alpha \mathbf{u}_j^\alpha}{k_B T} - \frac{\mu_{ij} \alpha \mathbf{u}_i^\alpha}{k_B T} \right\} \\
&+ \alpha \frac{8\sqrt{\pi} \sigma_{ij}^2 m_j}{9(m_i + m_j)} \left(\frac{\mu_{ij}}{2\pi k_B T} \right)^{\frac{3}{2}} c_i^\alpha c_j^\alpha \left(\frac{\Xi_{ij}}{c_0} \right)^3 \left(\frac{2\pi k_B T}{\mu_{ij}} \right)^{\frac{3}{2}} \Gamma\left(\frac{3}{2}, z_i^*\right) \left\{ \frac{\mu_{ij} \alpha \mathbf{u}_i^\alpha}{k_B T} - \frac{\mu_{ij} \alpha \mathbf{u}_j^\alpha}{k_B T} \right\},
\end{aligned}$$

where the definition of $\mathbf{a}_i$ given in equation (4.3.14) have been used and $\mathbf{a}_s$ is similarly defined. The previous equation can be rewritten as:

$$\begin{aligned}
\mathcal{P}_i &= \alpha^2 \sigma_{ij}^2 \frac{8\sqrt{\pi} m_j}{9(m_i + m_j)} c_i^\alpha c_j^\alpha \left(\frac{2k_B T}{\mu_{ij}} \right)^{\frac{1}{2}} \left(\frac{2k_B T}{\mu_{ij}} \right) \Gamma(3, z_i^*) \frac{\mu_{ij}}{k_B T} (\mathbf{u}_j^\alpha - \mathbf{u}_i^\alpha) \\
&- \alpha^2 \sigma_{ij}^2 \frac{8\sqrt{\pi} m_j}{9(m_i + m_j)} c_i^\alpha c_j^\alpha \left(\frac{\Xi_{ij}}{c_0} \right)^3 \Gamma\left(\frac{3}{2}, z_i^*\right) \frac{\mu_{ij}}{k_B T} (\mathbf{u}_j^\alpha - \mathbf{u}_i^\alpha) \\
&= \alpha^2 \sigma_{ij}^2 \frac{8\sqrt{\pi} m_j}{9M} c_i^\alpha c_j^\alpha \left(\frac{2k_B T}{\mu_{ij}} \right)^{\frac{3}{2}} \Gamma(3, z_i^*) \frac{\mu_{ij}}{k_B T} (\mathbf{u}_j^\alpha - \mathbf{u}_i^\alpha) \\
&- \alpha^2 \sigma_{ij}^2 \frac{8\sqrt{\pi} m_j}{9M} c_i^\alpha c_j^\alpha \left(\frac{\Xi_{ij}}{c_0} \right)^3 \Gamma\left(\frac{3}{2}, z_i^*\right) \frac{\mu_{ij}}{k_B T} (\mathbf{u}_j^\alpha - \mathbf{u}_i^\alpha).
\end{aligned}$$

Therefore,

$$\mathcal{P}_i = \alpha^2 \sigma_{ij}^2 \frac{8\sqrt{\pi} m_j}{9M} c_i^\alpha c_j^\alpha \frac{\mu_{ij}}{k_B T} (\mathbf{u}_j^\alpha - \mathbf{u}_i^\alpha) \left[\left(\frac{2k_B T}{\mu_{ij}} \right)^{\frac{3}{2}} \Gamma(3, z_i^*) - \left(\frac{\Xi_{ij}}{c_0} \right)^3 \Gamma\left(\frac{3}{2}, z_i^*\right) \right]. \quad (4.4.39)$$

Finally, let us evaluate the last integral on the right-hand side of equation (4.4.8). To do this, we substitute the definition of $\tilde{J}_i^{\alpha R}$ given in equation (3.3.18) into the integral $\mathcal{Q}_i$. Then using equation (4.3.17) and expanding, we obtain that the integral $\mathcal{Q}_i$ can be written as follows:

$$\begin{aligned}
\mathcal{Q}_i &= \alpha \sigma_{ij}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} \mathbf{v}_i \left[\left(\frac{\mu_{ij}}{\mu_{kl}} \right)^2 M_k^{\alpha\circ} M_l^{\alpha\circ} - M_i^\alpha M_j^\alpha \right] \\
&\quad \times \Theta(\langle \boldsymbol{\epsilon}, c_0 \mathbf{v}_i - c_0 \mathbf{v}_j \rangle - \Xi_{ij}) \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_j \rangle d\boldsymbol{\epsilon} d\mathbf{v}_j d\mathbf{v}_i \Bigg\} \mathcal{Q}_i^{(1)} \\
&+ \alpha \sigma_{ij}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} \mathbf{v}_i \left[\left(\frac{\mu_{ij}}{\mu_{kl}} \right)^2 M_k^{\alpha\circ} M_l^{\alpha\circ} (\mathbf{a}_k \cdot \mathbf{v}_k^\circ + \mathbf{a}_l \cdot \mathbf{v}_l^\circ) - M_i^\alpha M_j^\alpha (\mathbf{a}_i \cdot \mathbf{v}_i + \mathbf{a}_j \cdot \mathbf{v}_j) \right] \\
&\quad \times \Theta(\langle \boldsymbol{\epsilon}, c_0 \mathbf{v}_i - c_0 \mathbf{v}_j \rangle - \Xi_{ij}) \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_j \rangle d\boldsymbol{\epsilon} d\mathbf{v}_j d\mathbf{v}_i \Bigg\} \mathcal{Q}_i^{(2)}
\end{aligned} \quad (4.4.40)$$

The integral $\mathcal{Q}_i^{(1)}$ vanishes upon evaluation. That is

$$\mathcal{Q}_i^{(1)} = 0, \quad (4.4.41)$$

see Appendix A section A.3 for the details of the computation. Let us now evaluate the integral $\mathcal{Q}_i^{(2)}$. Expanding it, we obtain:

$$\begin{aligned} \mathcal{Q}_i^{(2)} = & \left. \alpha \sigma_{ij}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} \mathbf{v}_i \left(\frac{\mu_{ij}}{\mu_{kl}} \right)^2 M_k^{\alpha\circ} M_l^{\alpha\circ} (\mathbf{a}_k \cdot \mathbf{v}_k^\circ) \right. \\ & \times \Theta(\langle \boldsymbol{\epsilon}, c_0 \mathbf{v}_i - c_0 \mathbf{v}_j \rangle - \Xi_{ij}) \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_j \rangle d\boldsymbol{\epsilon} d\mathbf{v}_j d\mathbf{v}_i \left. \right\} \mathcal{R}_1 \\ & + \left. \alpha \sigma_{ij}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} \mathbf{v}_i \left(\frac{\mu_{ij}}{\mu_{kl}} \right)^2 M_k^{\alpha\circ} M_l^{\alpha\circ} (\mathbf{a}_l \cdot \mathbf{v}_l^\circ) \right. \\ & \times \Theta(\langle \boldsymbol{\epsilon}, c_0 \mathbf{v}_i - c_0 \mathbf{v}_j \rangle - \Xi_{ij}) \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_j \rangle d\boldsymbol{\epsilon} d\mathbf{v}_j d\mathbf{v}_i \left. \right\} \mathcal{R}_2 \\ & - \underbrace{\alpha \sigma_{ij}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} \mathbf{v}_i M_i^\alpha M_j^\alpha (\mathbf{a}_i \cdot \mathbf{v}_i) \Theta(\langle \boldsymbol{\epsilon}, c_0 \mathbf{v}_i - c_0 \mathbf{v}_j \rangle - \Xi_{ij}) \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_j \rangle d\boldsymbol{\epsilon} d\mathbf{v}_j d\mathbf{v}_i}_{\mathcal{R}_3} \\ & - \underbrace{\alpha \sigma_{ij}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} \mathbf{v}_i M_i^\alpha M_j^\alpha (\mathbf{a}_j \cdot \mathbf{v}_j) \Theta(\langle \boldsymbol{\epsilon}, c_0 \mathbf{v}_i - c_0 \mathbf{v}_j \rangle - \Xi_{ij}) \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_j \rangle d\boldsymbol{\epsilon} d\mathbf{v}_j d\mathbf{v}_i}_{\mathcal{R}_4}. \end{aligned}$$

It will be convenient to transform the integrals $\mathcal{R}_1$ and $\mathcal{R}_2$ from $(\mathbf{v}_i, \mathbf{v}_j)$ to $(\mathbf{v}_k^\circ, \mathbf{v}_l^\circ)$. To do this, we use the fact that the Jacobian of this transformation is

$$\left(\frac{\mu_{kl}}{\mu_{ij}} \right)^{\frac{3}{2}} \frac{\langle \boldsymbol{\epsilon}, \mathbf{v}_k^\circ - \mathbf{v}_l^\circ \rangle}{\omega^+}, \quad (4.4.42)$$

see equation (2.3.23)₁. This implies that

$$d\mathbf{v}_i d\mathbf{v}_j = \left(\frac{\mu_{kl}}{\mu_{ij}} \right)^{\frac{3}{2}} \frac{\langle \boldsymbol{\epsilon}, \mathbf{v}_k^\circ - \mathbf{v}_l^\circ \rangle}{\omega^+} d\mathbf{v}_k^\circ d\mathbf{v}_l^\circ. \quad (4.4.43)$$

Now using equation (4.4.43) above together with equation (2.3.20), we obtain that the integrals $\mathcal{R}_1$ and $\mathcal{R}_2$ can be rewritten as follows:

$$\begin{aligned} \mathcal{R}_1 = & \alpha \sigma_{ij}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} \mathbf{v}_k^\circ \left(\frac{\mu_{ij}}{\mu_{kl}} \right)^2 M_k^{\alpha\circ} M_l^{\alpha\circ} (\mathbf{a}_k \cdot \mathbf{v}_k^\circ) \Theta(\langle \boldsymbol{\epsilon}, c_0 \mathbf{v}_k^\circ - c_0 \mathbf{v}_l^\circ \rangle - \Xi_{kl}) \\ & \times \left(\frac{\mu_{kl}}{\mu_{ij}} \right)^{\frac{1}{2}} \omega^+ \left(\frac{\mu_{kl}}{\mu_{ij}} \right)^{\frac{3}{2}} \frac{\langle \boldsymbol{\epsilon}, \mathbf{v}_k^\circ - \mathbf{v}_l^\circ \rangle}{\omega^+} d\boldsymbol{\epsilon} d\mathbf{v}_k^\circ d\mathbf{v}_l^\circ \\ = & \alpha \sigma_{ij}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} \mathbf{v}_k^\circ M_k^{\alpha\circ} M_l^{\alpha\circ} (\mathbf{a}_k \cdot \mathbf{v}_k^\circ) \\ & \times \Theta(\langle \boldsymbol{\epsilon}, c_0 \mathbf{v}_k^\circ - c_0 \mathbf{v}_l^\circ \rangle - \Xi_{kl}) \langle \boldsymbol{\epsilon}, \mathbf{v}_k^\circ - \mathbf{v}_l^\circ \rangle d\boldsymbol{\epsilon} d\mathbf{v}_k^\circ d\mathbf{v}_l^\circ, \\ \mathcal{R}_2 = & \alpha \sigma_{ij}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} \mathbf{v}_k^\circ \left(\frac{\mu_{ij}}{\mu_{kl}} \right)^2 M_k^{\alpha\circ} M_l^{\alpha\circ} (\mathbf{a}_l \cdot \mathbf{v}_l^\circ) \Theta(\langle \boldsymbol{\epsilon}, c_0 \mathbf{v}_k^\circ - c_0 \mathbf{v}_l^\circ \rangle - \Xi_{kl}) \end{aligned}$$

$$\begin{aligned}
& \times \left(\frac{\mu_{kl}}{\mu_{ij}} \right)^{\frac{1}{2}} \omega^+ \left(\frac{\mu_{kl}}{\mu_{ij}} \right)^{\frac{3}{2}} \frac{\langle \boldsymbol{\epsilon}, \mathbf{v}_k^\circ - \mathbf{v}_l^\circ \rangle}{\omega^+} d\boldsymbol{\epsilon} d\mathbf{v}_k^\circ d\mathbf{v}_l^\circ \\
& = \alpha \sigma_{ij}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} \mathbf{v}_k^\circ M_k^{\alpha\circ} M_l^{\alpha\circ} (\mathbf{a}_l \cdot \mathbf{v}_l^\circ) \\
& \quad \times \Theta(\langle \boldsymbol{\epsilon}, c_0 \mathbf{v}_k^\circ - c_0 \mathbf{v}_l^\circ \rangle - \Xi_{kl}) \langle \boldsymbol{\epsilon}, \mathbf{v}_k^\circ - \mathbf{v}_l^\circ \rangle d\boldsymbol{\epsilon} d\mathbf{v}_k^\circ d\mathbf{v}_l^\circ.
\end{aligned}$$

Therefore, the integral $\mathcal{Q}_i^{(2)}$ can be rewritten as given below:

$$\begin{aligned}
\mathcal{Q}_i^{(2)} &= \underbrace{\alpha \sigma_{ij}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} \mathbf{v}_k^\circ M_k^{\alpha\circ} M_l^{\alpha\circ} (\mathbf{a}_k \cdot \mathbf{v}_k^\circ) \Theta(\langle \boldsymbol{\epsilon}, c_0 \mathbf{v}_k^\circ - c_0 \mathbf{v}_l^\circ \rangle - \Xi_{kl}) \langle \boldsymbol{\epsilon}, \mathbf{v}_k^\circ - \mathbf{v}_l^\circ \rangle d\boldsymbol{\epsilon} d\mathbf{v}_k^\circ d\mathbf{v}_l^\circ}_{\mathcal{R}_1} \\
&+ \underbrace{\alpha \sigma_{ij}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} \mathbf{v}_k^\circ M_k^{\alpha\circ} M_l^{\alpha\circ} (\mathbf{a}_l \cdot \mathbf{v}_l^\circ) \Theta(\langle \boldsymbol{\epsilon}, c_0 \mathbf{v}_k^\circ - c_0 \mathbf{v}_l^\circ \rangle - \Xi_{kl}) \langle \boldsymbol{\epsilon}, \mathbf{v}_k^\circ - \mathbf{v}_l^\circ \rangle d\boldsymbol{\epsilon} d\mathbf{v}_k^\circ d\mathbf{v}_l^\circ}_{\mathcal{R}_2} \\
&- \underbrace{\alpha \sigma_{ij}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} \mathbf{v}_i M_i^\alpha M_j^\alpha (\mathbf{a}_i \cdot \mathbf{v}_i) \Theta(\langle \boldsymbol{\epsilon}, c_0 \mathbf{v}_i - c_0 \mathbf{v}_j \rangle - \Xi_{ij}) \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_j \rangle d\boldsymbol{\epsilon} d\mathbf{v}_j d\mathbf{v}_i}_{\mathcal{R}_3} \\
&- \underbrace{\alpha \sigma_{ij}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} \mathbf{v}_i M_i^\alpha M_j^\alpha (\mathbf{a}_j \cdot \mathbf{v}_j) \Theta(\langle \boldsymbol{\epsilon}, c_0 \mathbf{v}_i - c_0 \mathbf{v}_j \rangle - \Xi_{ij}) \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_j \rangle d\boldsymbol{\epsilon} d\mathbf{v}_j d\mathbf{v}_i}_{\mathcal{R}_4}.
\end{aligned}$$

The integrals $\mathcal{R}_1$, $\mathcal{R}_2$, $\mathcal{R}_3$ and $\mathcal{R}_4$ above are similar to the second and third terms on the right-hand side of equation (4.4.25). Therefore, using similar steps as those used in their computation, we obtain:

$$\begin{aligned}
\mathcal{Q}_i^{(2)} &= 2\alpha^2 \sigma_{ij}^2 \frac{1}{M} c_k^\alpha c_l^\alpha \mathbf{u}_k^\alpha \left(\frac{2\pi k_B T}{\mu_{kl}} \right)^{\frac{1}{2}} \left[m_k \Gamma(2, z_{i*}) + \frac{2m_l}{3} \Gamma(3, z_{i*}) \right] \\
&\quad - \alpha^2 \sigma_{ij}^2 \frac{1}{M} c_k^\alpha c_l^\alpha \mathbf{u}_k^\alpha \left(\frac{2\pi \mu_{kl}}{k_B T} \right)^{\frac{1}{2}} \left(\frac{\Xi_{kl}}{c_0} \right)^2 \left[m_k \Gamma(1, z_{i*}) + \frac{2m_l}{3} \Gamma(2, z_{i*}) \right] \Bigg\} \mathcal{R}_1 \\
&+ 2\alpha^2 \sigma_{ij}^2 \frac{1}{M} c_k^\alpha c_l^\alpha m_l \mathbf{u}_l^\alpha \left(\frac{2\pi k_B T}{\mu_{kl}} \right)^{\frac{1}{2}} \left[\Gamma(2, z_{i*}) - \frac{2}{3} \Gamma(3, z_{i*}) \right] \\
&\quad - \alpha^2 \sigma_{ij}^2 \frac{1}{M} c_k^\alpha c_l^\alpha m_l \mathbf{u}_l^\alpha \left(\frac{\Xi_{kl}}{c_0} \right)^2 \left(\frac{2\pi \mu_{kl}}{k_B T} \right)^{\frac{1}{2}} \left[\Gamma(1, z_{i*}) - \frac{2}{3} \Gamma(2, z_{i*}) \right] \Bigg\} \mathcal{R}_2 \\
&- 2\alpha^2 \sigma_{ij}^2 c_i^\alpha c_j^\alpha \frac{1}{M} \mathbf{u}_i^\alpha \left(\frac{2\pi k_B T}{\mu_{ij}} \right)^{\frac{1}{2}} \left[m_i \Gamma(2, z_i^*) + \frac{2}{3} m_j \Gamma(3, z_i^*) \right] \\
&\quad + \alpha^2 \sigma_{ij}^2 c_i^\alpha c_j^\alpha \frac{1}{M} \mathbf{u}_i^\alpha \left(\frac{\Xi_{ij}}{c_0} \right)^2 \left(\frac{2\pi \mu_{ij}}{k_B T} \right)^{\frac{1}{2}} \left[m_i \Gamma(1, z_i^*) + \frac{2}{3} m_j \Gamma(2, z_i^*) \right] \Bigg\} \mathcal{R}_3 \\
&- 2\alpha^2 \sigma_{ij}^2 c_i^\alpha c_j^\alpha m_i \mathbf{u}_j^\alpha \left(\frac{2\pi k_B T}{\mu_{ij}} \right)^{\frac{1}{2}} \frac{1}{M} \left[\Gamma(2, z_i^*) - \frac{2}{3} \Gamma(3, z_i^*) \right] \\
&\quad + \alpha^2 \sigma_{ij}^2 c_i^\alpha c_j^\alpha m_i \mathbf{u}_j^\alpha \left(\frac{\Xi_{ij}}{c_0} \right)^2 \left(\frac{2\pi \mu_{ij}}{k_B T} \right)^{\frac{1}{2}} \frac{1}{M} \left[\Gamma(1, z_i^*) - \frac{2}{3} \Gamma(2, z_i^*) \right], \Bigg\} \mathcal{R}_4
\end{aligned} \tag{4.4.44}$$

where M and z_i^* are as defined equations (2.4.3) and (4.3.25), respectively, while

$$z_{i*} = \frac{\mu_{kl}}{2k_B T} \left(\frac{\Xi_{kl}}{c_0} \right)^2. \quad (4.4.45)$$

Therefore, putting together equations (4.4.41) and (4.4.44) gives:

$$\mathcal{Q}_i = 0 + \mathcal{Q}_i^{(2)} = \mathcal{Q}_i^{(2)}. \quad (4.4.46)$$

Substituting equations (4.4.9), (4.4.24), (4.4.39) and (4.4.46) into equation (4.4.8) gives the desired result. Therefore the proof is complete. $\square$

4.5 Macroscopic Equations and Formal Asymptotics

The main result of this chapter is given in this in this section. In particular, using equation (4.3.1) given in Lemma 4.3.1 and equation (4.4.1) given in Lemma 4.4.1, the reaction-diffusion system of MS type is formally derived as the hydrodynamic asymptotic limit of the scaled SRS kinetic system given in equation (4.2.1). The connection between the two systems is based on the fact that the scaled Maxwellians given in equation (4.2.3) solve the scaled kinetic equations if the macroscopic parameters c_i^α and $\mathbf{u}_i^\alpha$ characterising such Maxwellians solve the approximate equations (4.3.1) and (4.4.1). The conclusion is obtained by taking the limit as $\alpha \rightarrow 0$ together with an assumption that the parameters c_i^α , $\mathbf{u}_i^\alpha$ converge point-wise to c_i , $\mathbf{u}_i$, for $t \geq 0$ and $\mathbf{x} \in \Omega$.

Theorem 4.5.1. (i) *Given the scaled SRS kinetic equations defined in equation (4.2.1) accompanied by the boundary condition*

$$\nu \cdot \mathbf{J}_i = 0, \quad \mathbf{x} \in \partial\Omega, \quad t > 0, \quad i = 1, 2, 3, 4. \quad (4.5.1)$$

The Maxwellians defined in equation (4.2.3) are solutions of the initial boundary value problem for the scaled SRS kinetic equations (4.2.1) with initial conditions (4.2.2) if for $i = 1, 2, 3, 4$, the parameters c_i^α and $\mathbf{u}_i^\alpha$ solve the approximate system

$$\begin{cases} \frac{\partial c_i^\alpha}{\partial t} + \frac{\partial}{\partial \mathbf{x}}(c_i^\alpha \mathbf{u}_i^\alpha) = \mathcal{J}_i, \\ \alpha^2 \frac{\partial}{\partial t}(c_i^\alpha \mathbf{u}_i^\alpha) + \frac{k_B T}{m_i} \frac{\partial c_i^\alpha}{\partial \mathbf{x}} + \alpha^2 \frac{\partial}{\partial \mathbf{x}}(c_i^\alpha \mathbf{u}_i^\alpha \otimes \mathbf{u}_i^\alpha) = \mathcal{O}_i - \mathcal{P}_i + \mathcal{Q}_i, \end{cases} \quad (4.5.2)$$

where the reaction rate $\mathcal{J}_i$ is defined in equation (4.3.2) and the production terms $\mathcal{O}_i$, $\mathcal{P}_i$ and $\mathcal{Q}_i$ are defined in equations (4.4.2), (4.4.3) and (4.4.4), respectively.

(ii) *Moreover, in the limit as $\alpha \rightarrow 0$, the system of equations (4.5.2) reduces to*

$$\begin{cases} \frac{\partial c_i}{\partial t} + \frac{\partial \mathbf{J}_i}{\partial \mathbf{x}} = \sigma_{ij}^2 \left(\frac{2\pi\mu_{ij}}{k_B T} \right)^{\frac{1}{2}} \left[\left(\frac{\mu_{ij}}{\mu_{kl}} \right)^{\frac{1}{2}} c_k c_l \exp\left(\frac{Q_R}{k_B T} \right) - c_i c_j \right] \\ \quad \times \left[\frac{2k_B T}{\mu_{ij}} \Gamma(2, z_i^*) - \left(\frac{\Xi_{ij}}{c_0} \right)^2 \Gamma(1, z_i^*) \right], \\ \frac{\partial c_i}{\partial \mathbf{x}} = \frac{32}{9} \sum_{\substack{s=1 \\ s \neq i}}^4 \sigma_{is}^2 \left(\frac{2\pi\mu_{ij}}{k_B T} \right)^{\frac{1}{2}} (c_i \mathbf{J}_s - c_s \mathbf{J}_i), \end{cases} \quad (4.5.3)$$

whose unknowns are the concentrations c_i and the molar diffusion fluxes $\mathbf{J}_i$.

Proof. The statement in item (i) follows from Lemma 4.3.1 and Lemma 4.4.1.

Concerning item (ii), we define the molar diffusion flux in this case as:

$$\mathbf{J}_i^\alpha = c_i^\alpha (\mathbf{u}_i^\alpha - \mathbf{u}^\alpha) \iff c_i^\alpha \mathbf{u}_i^\alpha = \mathbf{J}_i^\alpha + c_i^\alpha \mathbf{u}^\alpha \quad (4.5.4)$$

where

$$\mathbf{u}^\alpha := \mathbf{u}^\alpha(t, \mathbf{x}) = \frac{\sum_{i=1}^4 \int_{\mathbb{R}^3} m_i \mathbf{v}_i f_i^\alpha(t, \mathbf{x}, \mathbf{v}_i) d\mathbf{v}_i}{\sum_{i=1}^4 \int_{\mathbb{R}^3} m_i f_i^\alpha(t, \mathbf{x}, \mathbf{v}_i) d\mathbf{v}_i} \quad (4.5.5)$$

Substituting equation (4.5.4) into equation (4.5.2) and then let $\alpha \rightarrow 0$ in the resulting equation, and assume that the limits

$$c_i = \lim_{\alpha \rightarrow 0} c_i^\alpha, \quad \mathbf{J}_i = \lim_{\alpha \rightarrow 0} \mathbf{J}_i^\alpha, \quad \mathbf{u} = \lim_{\alpha \rightarrow 0} \mathbf{u}^\alpha,$$

exist pointwise for any $t > 0$, $\mathbf{x} \in \Omega$, as well as using assumption (c) given in subsection 4.2.2 which implies that $\frac{\partial}{\partial \mathbf{x}}(c_i \mathbf{u}) = 0$, we obtain system (4.5.3). $\square$

Observe that summing the first and second equations of equation (4.5.3) over all species, we obtain that c is uniform in space and constant in time. Therefore, the second equation of the system of equations (4.5.3) can be rewritten as

$$\frac{\partial c_i}{\partial \mathbf{x}} = \frac{1}{c} \sum_{\substack{s=1 \\ s \neq i}}^4 \frac{c_i \mathbf{J}_s - c_s \mathbf{J}_i}{D_{is}}, \quad (4.5.6)$$

where

$$D_{is} = \frac{9}{32} \left(\frac{k_B T}{2\pi\mu_{is}} \right)^{\frac{1}{2}} \frac{1}{c \sigma_{is}^2} \quad (4.5.7)$$

are the diffusion coefficients, i.e, the Maxwell-Stefan diffusion coefficients.

Consequently, for $i = 1, 2, 3, 4$, putting together equation (4.5.3) with the second equation replaced by equation (4.5.6), the constraint law given in equation (3.1.11) which in this case translates to

$$\sum_{i=1}^4 m_i \mathbf{J}_i = 0$$

and the boundary conditions given in equation (4.5.1) for the diffusive fluxes $\mathbf{J}_i$, we obtain:

$$\left\{ \begin{array}{l} \frac{\partial c_i}{\partial t} + \frac{\partial \mathbf{J}_i}{\partial \mathbf{x}} = \mathcal{J}_i, \quad \mathbf{x} \in \Omega, \quad t > 0, \\ \frac{\partial c_i}{\partial \mathbf{x}} = -\frac{1}{c} \sum_{\substack{s=1 \\ s \neq i}}^4 \frac{c_s \mathbf{J}_i - c_i \mathbf{J}_s}{D_{is}}, \quad \mathbf{x} \in \Omega, \quad t > 0, \\ \sum_{i=1}^4 m_i \mathbf{J}_i = 0, \quad \mathbf{x} \in \Omega, \quad t > 0, \\ \nu \cdot \mathbf{J}_i = 0, \quad \mathbf{x} \in \partial\Omega, \quad t > 0. \end{array} \right. \quad (4.5.8)$$

The System of equations given in equation (4.5.8) constitutes a boundary value problem referred to as the reaction-diffusion system of Maxwell-Stefan type.

Remark 4.5.2. *It is important to underline that the expansion of the distribution function given in equation (4.2.4) was used for the explicit computation of the integrals appearing on the right-hand side of the concentration and momentum balance equations (see equations (4.3.1), (4.4.1) respectively). In addition, the terms of α^2 neglected in the computation of the production terms in the mass and momentum balance equations would not have affected the result obtained. This is because they would vanish in the limit as $\alpha \rightarrow 0$.*

Furthermore, note that a system of Maxwell-Stefan type with the same general structure as the one in equation (4.5.3) can be derived from the SRS kinetic model if we do not use the expansion of the distribution function given in equation (4.2.4). $\square$

4.6 Conclusion

In this chapter, a reaction-diffusion system where the diffusion process is modelled by the MS equations was formally derived as the hydrodynamic limit of the SRS kinetic model. This derivation was achieved by considering a scaling of the SRS kinetic equations in which elastic collisions play a dominant role in the evolution of the species while chemical reactions are slow.

An important aspect in the computations presented in this chapter is the fact that a first order correction to the Maxwellian distribution was used for the computation of both the elastic and reactive production terms. Moreover, the first order correction to the Maxwellian distribution used coincides with the one used by Stefan in his celebrated work from 1872 to derive the diffusion coefficients in a mixture of gases.

In the quoted literature about the hydrodynamic limits of kinetic models for reactive mixtures, the derivation of the reaction-diffusion system of MS type had not yet been considered. The work developed in this chapter provides the first result in this direction. Therefore, the work developed in this chapter complements the works developed in [26, 28, 29, 68] in the context of non-reactive mixtures.

Still in connection with the works developed in [26, 28, 29, 68] for non-reactive mixtures, it worth mentioning that when the chemical reaction is turn off in the SRS kinetic model (i.e., if the mixture is

made up of four non-reactive species), the limiting system of equations (4.5.8) reduces to the Maxwell-Stefan diffusion system for hard sphere cross-sections obtained in [4], but for N non-reactive species and is similar to the one in [28] for N non-reactive species with Maxwellian molecules.

The fact that a reactive mixture was analysed in this chapter allows for the consideration of many interesting problems concerning the derivation of the MS equations from reactive Maxwell-Boltzmann type equations. Among the most interesting problems, are the following.

The first problem is the introduction of chemical potentials as the main agent in the definition of the driving forces of the MS equations and then study the passage to hydrodynamic limit by removing the isothermal assumption. This will certainly lead to a very rich setting from the physical and mathematical point of view.

The second problem concerns the possibility of studying different time scales associated to the chemical reaction. In particular, studying different chemical regimes and obtaining the influence of chemical reaction in the limiting MS equations. This problem has been studied in [7] and will be presented in Chapter 5.

In fact, the scaling of slow chemical reaction studied in this chapter is the sole reason why the limit equations for the momentum of the species do not include contributions from the reactive pair with sufficient amount of energy to produce a chemical reaction. This can be seen from equation (4.4.1) of Lemma 4.4.1, where clearly they are contributions from collisions with enough energy to produce a chemical reaction, but they are of order of α^2 , due to the scaling, and hence go to zero in the limit as $\alpha \rightarrow 0$.

Additionally, when studying different time scales associated to the chemical reaction, especially those chemical regimes in which reactive collisions are treated on a par with elastic ones, the SRS model results to be appropriate because of the inclusion of the correction term in the elastic operator. This correction term as mentioned before singles out those pre-collision states that are energetic enough to result in a chemical reaction, therefore preventing double counting of these collisions in the elastic and reactive operators. In this sense, the correction term leads to non anomalous results.

Finally, since it is well known that physically meaningful chemical processes often involve gases with polyatomic structure, it will be useful to extend the present analysis to polyatomic models. This problem will be addressed in chapter 6.

Chapter 5

On the formal derivation of the reactive Maxwell-Stefan equations from the kinetic theory

This chapter contains the results published in EPL, 2020, in collaboration with Patrícia Gonçalves and Ana Jacinta Soares.

5.1 Introduction

The equations nowadays referred to as the Maxwell-Stefan (MS) equations were first derived from the kinetic theory of gases by Maxwell in his renowned work [83], where a binary mixture of non-reactive gases was considered. Few years later, Stefan presented in [105] a continuum mechanical derivation of the same equations, but valid for a mixture of several non-reactive species. The MS equations have successfully been used by many applied and experimental researchers to model diffusion in multicomponent mixtures [77]. This is because they provide a more consistent and complete approach than the standard description of diffusion given by Fick in [52, 53]. In fact, the MS equations can be used to describe non-typical diffusion phenomena like osmotic diffusion, uphill or reverse diffusion and diffusion barrier observed experimentally in multi-species mixtures, [30, 47, 77].

Several contributions have been made at the level of both the mathematical analysis [26, 32, 70, 71] and numerical studies [26, 50, 54] of MS type diffusion models. Furthermore, several works have been published about the derivation of the MS equations from the MBEs for non-reactive mixtures, under a diffusive scaling, see for example, [29, 69]. In these papers, the MS equations were obtained through the passage from the kinetic dynamics, in a proper scaling, to the hydrodynamic limit. More precisely, the MS equations were obtained from the momentum balance equation of the species, in the limit, as the scaling parameter tends to zero. In the same spirit, chemically reactive mixtures of monatomic and polyatomic gases have been considered in [5, 6], under isothermal and non-isothermal conditions, respectively. In both papers, a chemical regime, in which mechanical collisions are dominant and chemical reactions

are less frequent, was considered. The corresponding MS equations have been derived from the species momentum balance equations, in the hydrodynamic limit, but they do not contain diffusion terms resulting from chemical interactions.

The aim of this chapter is the formidable task of extending the approach of [5, 6] and derive the MS equations in a regime, where chemical interactions between the species play a relevant role and influences the dynamics of the reactive mixture. To this end, the SRS kinetic model given in [93] and described in section 2.3 will be considered for the derivation presented in this chapter. The starting point of this derivation is a scaling of the kinetic equations in which both mechanical collisions and chemical reactions have comparable relaxation times. The MS equations obtained from the momentum balance equations of the species in the hydrodynamic limit, contain additional diffusion terms resulting from chemical interactions. For this reason, the present extension will be referred to as the reactive MS equations. As a particular case, the isothermal reactive MS equations is obtained when the temperature of the mixture is constant in time and uniform in space.

The rest of this chapter is organised as follows. In the next section, the main results of this chapter is presented. In section 5.3, the scaling of kinetic equations to be studied is introduced. This will be followed by the assumptions that will be needed to obtain the results presented in this chapter and some properties of the collision operators which are consequences of one of the assumptions. In section 5.4, the momentum balance equations for the species are obtained. In section 5.5, the prove the main results of this chapter is given. The last section is dedicated to the conclusions about the results obtained and some discussion about new perspectives in connection with the reactive MS equations.

5.2 The main results

Let $\Omega \subset \mathbb{R}^3$ be an open bounded domain with regular boundary. Consider a reactive mixture of four monatomic-like gases, A_1, A_2, A_3 and A_4 , participating in the bi-molecular reversible chemical reaction described in equation (2.3.1) that evolves in Ω . This reactive mixture is described by the SRS kinetic model given in section 2.3. Furthermore, let the temperature and the molar average velocity of the mixture: $T = T(t, \mathbf{x})$ and $\mathbf{u} = \mathbf{u}(t, \mathbf{x})$, respectively be as defined in equations (2.3.63c) and (2.3.63b). For each species A_i , with $i = 1, 2, 3, 4$, let $\mathbf{u}_i = \mathbf{u}_i(t, \mathbf{x})$ be the molar average velocity, m_i the molecular mass, $c_i = c_i(t, \mathbf{x})$ the molar concentration defined as given in equation (2.3.63a) and $\mathbf{J}_i = \mathbf{J}_i(t, \mathbf{x})$ the molar diffusion flux defined as given in equation (3.1.6).

The scaling of the SRS kinetic model considered in this chapter describes a physical situation in which both mechanical collisions and chemical reactions have comparable relaxation times, which are much smaller than the characteristic times of the flow. By passing to the corresponding hydrodynamic limit under isothermal and non-isothermal conditions, respectively, the reactive MS equations are deduced from the momentum balance equations of the species with explicit expressions for the diffusion coefficients.

The main results of this chapter are presented in the theorem and corollary given below.

Theorem 5.2.1. *The non-isothermal reactive MS equations are given by*

$$\frac{\partial}{\partial \mathbf{x}}(c_i T) = - \sum_{\substack{s=1 \\ s \neq i}}^4 \left(\frac{c_s \mathbf{J}_i - c_i \mathbf{J}_s}{D_{is}} \right) + \frac{c_j \mathbf{J}_i - c_i \mathbf{J}_j}{D_{ij}} + \frac{c_l \mathbf{J}_k}{D_k} + \frac{c_k \mathbf{J}_l}{D_l} - \frac{c_j \mathbf{J}_i}{D_i} - \frac{c_i \mathbf{J}_j}{D_j}, \quad (5.2.1)$$

where D_{is} , D_{ij} , D_k , D_l , D_i , D_j are diffusion coefficients respectively defined as follows:

$$\begin{aligned} D_{is} &= \frac{9}{32\sigma_{is}^2} \left(\frac{k_B}{2\pi\mu_{is}T} \right)^{\frac{1}{2}} \\ D_{ij} &= \frac{9k_B^2 T}{8\sqrt{\pi}\sigma_{ij}^2\beta_{ij}\mu_{ij} \left[\left(\frac{2k_B T}{\mu_{ij}} \right)^{\frac{3}{2}} \Gamma(3, z_i^*) - \left(\frac{\Xi_{ij}}{c_0} \right)^3 \Gamma\left(\frac{3}{2}, z_i^*\right) \right]} \\ D_k &= \left\{ \sigma_{ij}^2\beta_{ij}m_k \left[2 \left(\frac{2\pi k_B T}{\mu_{kl}} \right)^{\frac{1}{2}} \left(m_k \Gamma(2, z_{i*}) + \frac{2}{3} m_l \Gamma(3, z_{i*}) \right) \right. \right. \\ &\quad \left. \left. - \left(\frac{\Xi_{kl}}{c_0} \right)^2 \left(\frac{2\pi\mu_{kl}}{k_B T} \right)^{\frac{1}{2}} \left(m_k \Gamma(1, z_{i*}) + \frac{2}{3} m_l \Gamma(2, z_{i*}) \right) \right] \right\}^{-1} M k_B \\ D_l &= \left\{ \sigma_{ij}^2\beta_{ij}\mu_{kl} \left[2 \left(\frac{2\pi k_B T}{\mu_{kl}} \right)^{\frac{1}{2}} \left(\Gamma(2, z_{i*}) - \frac{2}{3} \Gamma(3, z_{i*}) \right) \right. \right. \\ &\quad \left. \left. - \left(\frac{\Xi_{kl}}{c_0} \right)^2 \left(\frac{2\pi\mu_{kl}}{k_B T} \right)^{\frac{1}{2}} \left(\Gamma(1, z_{i*}) - \frac{2}{3} \Gamma(2, z_{i*}) \right) \right] \right\}^{-1} k_B, \\ D_i &= \left\{ \sigma_{ij}^2\beta_{ij}m_i \left[2 \left(\frac{2\pi k_B T}{\mu_{ij}} \right)^{\frac{1}{2}} \left(m_i \Gamma(2, z_i^*) + \frac{2}{3} m_j \Gamma(3, z_i^*) \right) \right. \right. \\ &\quad \left. \left. - \left(\frac{\Xi_{ij}}{c_0} \right)^2 \left(\frac{2\pi\mu_{ij}}{k_B T} \right)^{\frac{1}{2}} \left(m_i \Gamma(1, z_i^*) + \frac{2}{3} m_j \Gamma(2, z_i^*) \right) \right] \right\}^{-1} M k_B, \\ D_j &= \left\{ \sigma_{ij}^2\beta_{ij}\mu_{ij} \left[2 \left(\frac{2\pi k_B T}{\mu_{ij}} \right)^{\frac{1}{2}} \left(\Gamma(2, z_i^*) - \frac{2}{3} \Gamma(3, z_i^*) \right) \right. \right. \\ &\quad \left. \left. - \left(\frac{\Xi_{ij}}{c_0} \right)^2 \left(\frac{2\pi\mu_{ij}}{k_B T} \right)^{\frac{1}{2}} \left(\Gamma(1, z_i^*) - \frac{2}{3} \Gamma(2, z_i^*) \right) \right] \right\}^{-1} k_B, \end{aligned}$$

with $\Gamma(.,.)$ the incomplete Euler gamma function defined as given in equation (4.3.3), z_{i*} , z_i^* and M are as defined in equations (4.3.4), (4.4.45) and (2.4.3), respectively.

The following corollary is an immediate consequence of Theorem 5.2.1 above.

Corollary 5.2.2. *If the mixture temperature T is constant in time and uniform in space, then the isothermal reactive MS equations are given by*

$$\frac{\partial c_i}{\partial \mathbf{x}} = - \sum_{\substack{s=1 \\ s \neq i}}^4 \left(\frac{c_s \mathbf{J}_i - c_i \mathbf{J}_s}{\mathbb{D}_{is}} \right) + \frac{(c_j \mathbf{J}_i - c_i \mathbf{J}_j)}{\mathbb{D}_{ij}} + \frac{c_l \mathbf{J}_k}{\mathbb{D}_k} + \frac{c_k \mathbf{J}_l}{\mathbb{D}_l} - \frac{c_j \mathbf{J}_i}{\mathbb{D}_i} - \frac{c_i \mathbf{J}_j}{\mathbb{D}_j}, \quad (5.2.2)$$

where $\mathbb{D}_{is} = T D_{is}$, $\mathbb{D}_{ij} = T D_{ij}$, $\mathbb{D}_k = T D_k$, $\mathbb{D}_l = T D_l$, $\mathbb{D}_i = T D_i$ and $\mathbb{D}_j = T D_j$, with the coefficients D_{is} , D_{ij} , D_k , D_l , D_i and D_j given as in Theorem 5.2.1.

5.3 Scaled Equations Assumptions and Properties

In this section, the scaling of the SRS kinetic equations to be considered in this chapter will be presented. Furthermore, the assumptions and the properties of the collision operators that will be useful to prove the main results of this chapter (that is, Theorem 5.2.1 and Corollary 5.2.2) will be given.

5.3.1 Scaled Kinetic Equations

In the previous chapter, a scaling of the SRS kinetic equations that describe a physical situation where the dominant role in the evolution of the species is played by mechanical interactions, while chemical reactions are assumed to be slow thus resulting to isothermal condition was considered.

In this chapter, a scaling that describe a physical situation where both mechanical collisions and chemical reactions have comparable relaxation times, which are much smaller than the characteristic times of the flow will be considered. This scaling is achieved by setting $p = q = 1$ in equation (3.3.12) to obtain:

$$\alpha \frac{\partial f_i^\alpha}{\partial t} + \mathbf{v}_i \cdot \frac{\partial f_i^\alpha}{\partial \mathbf{x}} = \frac{1}{\alpha} J_i^{\alpha m E} + \frac{1}{\alpha} J_i^{\alpha b E} - \frac{1}{\alpha} J_i^{\alpha b^* E} + \frac{1}{\alpha} J_i^{\alpha R}, \quad i = 1, 2, 3, 4, \quad (5.3.1)$$

The equations given in equation (5.3.1) above defines a regime in which both mechanical and reactive interactions are of the same relevance. In this regime, as we shall see, the MS equations obtained contain terms associated with the effects of the chemical reaction.

The aim is to derive from the momentum balance equations of the species, the reactive MS equations in the hydrodynamic limit for $\alpha \rightarrow 0$. The starting point of this derivation is the kinetic formulation of the transport equations for the species, given by

$$\begin{aligned} \alpha \int_{\mathbb{R}^3} \varphi_i \frac{\partial f_i^\alpha}{\partial t} d\mathbf{v}_i + \int_{\mathbb{R}^3} \varphi_i \mathbf{v}_i \cdot \frac{\partial f_i^\alpha}{\partial \mathbf{x}} d\mathbf{v}_i \\ = \frac{1}{\alpha} \int_{\mathbb{R}^3} \varphi_i J_i^{\alpha m E} d\mathbf{v}_i + \frac{1}{\alpha} \int_{\mathbb{R}^3} \varphi_i J_i^{\alpha b E} d\mathbf{v}_i - \frac{1}{\alpha} \int_{\mathbb{R}^3} \varphi_i J_{ij}^{\alpha b^* E} d\mathbf{v}_i + \frac{1}{\alpha} \int_{\mathbb{R}^3} \varphi_i J_i^{\alpha R} d\mathbf{v}_i, \end{aligned} \quad (5.3.2)$$

for $i = 1, 2, 3, 4$, where φ_i is a weight function of the species velocities. Equation (5.3.2) above was obtained by multiplying equation (5.3.1) by φ_i and integrating the resulting equation with respect to

5.3.2 Assumptions

Besides the scaling regime of comparable relaxation times for both elastic and reactive collisions, the central assumptions that will be used to derive the reactive MS equations from the scaled kinetic equations given in equation (5.3.1) are the following.

- (a) The bulk velocity of the mixture is small and goes to zero as the scaling parameter α goes to 0.

- (b) The distribution functions are local Maxwellians centred at the species average velocity $\alpha \mathbf{u}_i$, with species temperature $T + \alpha T_i^\alpha$, such that, for $i = 1, 2, 3, 4$,

$$f_i^\alpha(t, \mathbf{x}, \mathbf{v}_i) = c_i^\alpha(t, \mathbf{x}) \left(\frac{m_i}{2\pi k_B (T(t, \mathbf{x}) + \alpha T_i^\alpha(t, \mathbf{x}))} \right)^{\frac{3}{2}} \times \exp \left(- \frac{m_i (\mathbf{v}_i - \alpha \mathbf{u}_i^\alpha(t, \mathbf{x}))^2}{2k_B (T(t, \mathbf{x}) + \alpha T_i^\alpha(t, \mathbf{x}))} \right), \quad (5.3.3)$$

where $\mathbf{x} \in \Omega$, $\mathbf{v}_i \in \mathbb{R}^3$, $t \in \mathbb{R}_+$ and $c_i^\alpha, T, T_i^\alpha: \mathbb{R}_+ \times \Omega \rightarrow \mathbb{R}_+$, $\mathbf{u}_i^\alpha: \mathbb{R}_+ \times \Omega \rightarrow \mathbb{R}^3$.

Assumption (a) above implies that convective effects are negligible, whereas diffusion and chemical reaction are relevant. Assumption (b) above indicates that the system evolves not far away from equilibrium. The Taylor expansion of equation (5.3.3) around equilibrium will be crucial for the explicit computation of the elastic and reactive production terms that appear in the momentum balance equation of the species.

5.3.3 Some Consequences of the Assumptions

In this subsection, some properties of the collision operators that will be used in the analysis of the scaled kinetic equations given in equation (5.3.1) is given. These properties of the collision operators are consequences of assumption (b) above.

Proposition 5.3.1. *If the distribution functions are as given in equation (5.3.3), then the following properties holds:*

$$(a) \ f_i^{\alpha'} f_j^{\alpha'} - f_i^\alpha f_j^\alpha = \alpha M_i^\alpha M_j^\alpha \left[\mathbf{a}_{ij} \cdot (\mathbf{v}_i' - \mathbf{v}_i) + \frac{T_i^\alpha - T_j^\alpha}{k_B T^2} \left(\frac{m_i (\mathbf{v}_i')^2}{2} - \frac{m_i (\mathbf{v}_i)^2}{2} \right) \right] + O(\alpha^2), \quad (5.3.4)$$

$$(b) \ \left(\frac{\mu_{ij}}{\mu_{kl}} \right)^2 f_k^{\alpha\circ} f_l^{\alpha\circ} - f_i^\alpha f_j^\alpha = \left[\left(\frac{\mu_{ij}}{\mu_{kl}} \right)^2 M_k^{\alpha\circ} M_l^{\alpha\circ} - M_i^\alpha M_j^\alpha \right] + \alpha \left(\frac{\mu_{ij}}{\mu_{kl}} \right)^2 M_k^{\alpha\circ} M_l^{\alpha\circ} \times \left[(\mathbf{a}_k \cdot \mathbf{v}_k^\circ + \mathbf{a}_l \cdot \mathbf{v}_l^\circ) + (b_k + b_l) - \frac{3}{2T} (T_k^\alpha + T_l^\alpha) \right] - \alpha M_i^\alpha M_j^\alpha \left[(\mathbf{a}_i \cdot \mathbf{v}_i + \mathbf{a}_j \cdot \mathbf{v}_j) + (b_i + b_j) - \frac{3}{2T} (T_i^\alpha + T_j^\alpha) \right] + O(\alpha^2), \quad (5.3.5)$$

where M_i^α is as given in equation (4.2.5) and M_j^α , $M_k^{\alpha\circ}$, $M_l^{\alpha\circ}$ are similarly defined. Furthermore,

$$\mathbf{a}_{ij} = \frac{m_i (\mathbf{u}_i^\alpha - \mathbf{u}_j^\alpha)}{k_B T}, \quad \mathbf{a}_i = \frac{m_i \mathbf{u}_i^\alpha}{k_B T}, \quad b_i = \frac{m_i T_i^\alpha (\mathbf{v}_i)^2}{2k_B T^2}. \quad (5.3.6)$$

Proof. Observe that

$$\begin{aligned}
& \exp\left(-\frac{m_i(\mathbf{v}_i - \alpha \mathbf{u}_i^\alpha)^2}{2k_B(T + \alpha T_i^\alpha)}\right) \\
&= \exp\left[-\frac{m_i}{2k_B(T + \alpha T_i^\alpha)}\left((\mathbf{v}_i)^2 - 2\alpha \mathbf{u}_i^\alpha \cdot \mathbf{v}_i + (\alpha \mathbf{u}_i^\alpha)^2\right)\right] \\
&= \exp\left(-\frac{m_i(\mathbf{v}_i)^2}{2k_B(T + \alpha T_i^\alpha)}\right) \exp\left(\frac{m_i \alpha \mathbf{u}_i^\alpha \cdot \mathbf{v}_i}{k_B(T + \alpha T_i^\alpha)}\right) \exp\left(-\frac{m_i(\alpha \mathbf{u}_i^\alpha)^2}{2k_B(T + \alpha T_i^\alpha)}\right).
\end{aligned}$$

Taylor expanding the above exponentials with respect to α gives:

$$\begin{aligned}
\exp\left(-\frac{m_i(\mathbf{v}_i)^2}{2k_B(T + \alpha T_i^\alpha)}\right) &= \exp\left(-\frac{m_i(\mathbf{v}_i)^2}{2k_B T}\right) + \alpha \frac{m_i T_i^\alpha (\mathbf{v}_i)^2}{2k_B T^2} \exp\left(-\frac{m_i(\mathbf{v}_i)^2}{2k_B T}\right) \\
&\quad + \alpha^2 \frac{m_i (T_i^\alpha)^2 (\mathbf{v}_i)^2}{8k_B^2 T^4} \exp\left(-\frac{m_i(\mathbf{v}_i)^2}{2k_B T}\right) (m_i(\mathbf{v}_i)^2 - 4k_B T) + O(\alpha^3) \\
&= \exp\left(-\frac{m_i(\mathbf{v}_i)^2}{2k_B T}\right) \left(1 + \alpha \frac{m_i T_i^\alpha (\mathbf{v}_i)^2}{2k_B T^2} + O(\alpha^2)\right), \\
\exp\left(\frac{m_i \alpha \mathbf{u}_i^\alpha \cdot \mathbf{v}_i}{k_B(T + \alpha T_i^\alpha)}\right) &= 1 + \alpha \frac{m_i \mathbf{u}_i^\alpha \cdot \mathbf{v}_i}{k_B T} + \alpha^2 \frac{m_i \mathbf{u}_i^\alpha \cdot \mathbf{v}_i (m_i \mathbf{u}_i^\alpha \cdot \mathbf{v}_i - 2T_i^\alpha k_B)}{2k_B^2 T^2} + O(\alpha^3), \\
\exp\left(-\frac{m_i(\alpha \mathbf{u}_i^\alpha)^2}{2k_B(T + \alpha T_i^\alpha)}\right) &= 1 - \alpha^2 \frac{m_i (\mathbf{u}_i^\alpha)^2}{2k_B T} + \alpha^3 \frac{m_i (\mathbf{u}_i^\alpha)^2 T_i^\alpha}{2k_B T^2} + O(\alpha^4).
\end{aligned}$$

Therefore,

$$\begin{aligned}
& \exp\left(-\frac{m_i(\mathbf{v}_i - \alpha \mathbf{u}_i^\alpha)^2}{2k_B(T + \alpha T_i^\alpha)}\right) \\
&= \exp\left(-\frac{m_i(\mathbf{v}_i)^2}{2k_B T}\right) \left(1 + \alpha \frac{m_i \mathbf{u}_i^\alpha \cdot \mathbf{v}_i}{k_B T} + \alpha \frac{m_i T_i^\alpha (\mathbf{v}_i)^2}{2k_B T^2} + O(\alpha^2)\right). \quad (5.3.7)
\end{aligned}$$

Also, Taylor expanding the term with exponent $\frac{3}{2}$ in equation (5.3.3) with respect to α gives:

$$\begin{aligned}
\left(\frac{m_i}{2\pi k_B(T + \alpha T_i^\alpha)}\right)^{\frac{3}{2}} &= \left(\frac{m_i}{2\pi k_B T}\right)^{\frac{3}{2}} - \alpha \frac{3T_i}{2T} \left(\frac{m_i}{2\pi k_B T}\right)^{\frac{3}{2}} + O(\alpha^2) \\
&= \left(\frac{m_i}{2\pi k_B T}\right)^{\frac{3}{2}} \left(1 - \alpha \frac{3T_i}{2T} + O(\alpha^2)\right). \quad (5.3.8)
\end{aligned}$$

Taking the product of equations (5.3.7) and (5.3.8) gives:

$$\left(\frac{m_i}{2\pi k_B T}\right)^{\frac{3}{2}} \exp\left(-\frac{m_i(\mathbf{v}_i)^2}{2k_B T}\right) \left(1 + \alpha \frac{m_i (\mathbf{u}_i^\alpha \cdot \mathbf{v}_i)}{k_B T} + \alpha \frac{m_i T_i^\alpha (\mathbf{v}_i)^2}{2k_B T^2} - \alpha \frac{3T_i^\alpha}{2T} + O(\alpha^2)\right).$$

Therefore, the distribution functions given in equation (5.3.3) can be written as follows:

$$f_i^\alpha = c_i^\alpha \left(\frac{m_i}{2\pi k_B T}\right)^{\frac{3}{2}} \exp\left(-\frac{m_i(\mathbf{v}_i)^2}{2k_B T}\right) \left(1 + \alpha \frac{m_i (\mathbf{u}_i^\alpha \cdot \mathbf{v}_i)}{k_B T} + \alpha \frac{m_i T_i^\alpha (\mathbf{v}_i)^2}{2k_B T^2} - \alpha \frac{3T_i^\alpha}{2T} + O(\alpha^2)\right)$$

$$= M_i^\alpha \left(1 + \alpha \frac{m_i(\mathbf{u}_i^\alpha \cdot \mathbf{v}_i)}{k_B T} + \alpha \frac{m_i T_i^\alpha(\mathbf{v}_i)^2}{2k_B T^2} - \alpha \frac{3T_i^\alpha}{2T} + O(\alpha^2) \right), \quad (5.3.9)$$

where M_i^α is as defined in equation (4.2.5).

Equation (5.3.9) will be referred to as the expanded form of the distribution function. Similarly, expansion like the one given in equation (5.3.9) can be obtained for the distribution functions f_j^α , $f_i^{\alpha'}$, $f_j^{\alpha'}$, $f_k^{\alpha\circ}$ and $f_l^{\alpha\circ}$.

To prove part (a), observe that using the expanded form of the distribution functions gives:

$$f_i^\alpha f_j^\alpha = M_i^\alpha M_j^\alpha \left(1 + \alpha \frac{m_i(\mathbf{u}_i^\alpha \cdot \mathbf{v}_i)}{k_B T} + \alpha \frac{m_i T_i^\alpha(\mathbf{v}_i)^2}{2k_B T^2} + \alpha \frac{m_j(\mathbf{u}_j^\alpha \cdot \mathbf{v}_j)}{k_B T} + \alpha \frac{m_j T_j^\alpha(\mathbf{v}_j)^2}{2k_B T^2} - \alpha \frac{3T_i^\alpha}{2T} - \alpha \frac{3T_j^\alpha}{2T} + O(\alpha^2) \right), \quad (5.3.10)$$

$$f_i^{\alpha'} f_j^{\alpha'} = M_i^{\alpha'} M_j^{\alpha'} \left(1 + \alpha \frac{m_i(\mathbf{u}_i^{\alpha'} \cdot \mathbf{v}_i')}{k_B T} + \alpha \frac{m_i T_i^{\alpha'}(\mathbf{v}_i')^2}{2k_B T^2} + \alpha \frac{m_j(\mathbf{u}_j^{\alpha'} \cdot \mathbf{v}_j')}{k_B T} + \alpha \frac{m_j T_j^{\alpha'}(\mathbf{v}_j')^2}{2k_B T^2} - \alpha \frac{3T_i^{\alpha'}}{2T} - \alpha \frac{3T_j^{\alpha'}}{2T} + O(\alpha^2) \right). \quad (5.3.11)$$

Also, observe that

$$M_i^{\alpha'} M_j^{\alpha'} = c_i^\alpha \left(\frac{m_i}{2\pi k_B T} \right)^{\frac{3}{2}} c_j^\alpha \left(\frac{m_j}{2\pi k_B T} \right)^{\frac{3}{2}} \exp \left(-\frac{m_i(\mathbf{v}_i')^2 + m_j(\mathbf{v}_j')^2}{2k_B T} \right).$$

Using the conservation of kinetic energy for elastic collisions given in equation (2.3.7) with s replaced by j , we obtain:

$$M_i^{\alpha'} M_j^{\alpha'} = c_i^\alpha \left(\frac{m_i}{2\pi k_B T} \right)^{\frac{3}{2}} c_j^\alpha \left(\frac{m_j}{2\pi k_B T} \right)^{\frac{3}{2}} \exp \left(-\frac{m_i(\mathbf{v}_i)^2 + m_j(\mathbf{v}_j)^2}{2k_B T} \right) = M_i^\alpha M_j^\alpha. \quad (5.3.12)$$

Therefore, equation (5.3.11) can be rewritten as follows:

$$f_i^{\alpha'} f_j^{\alpha'} = M_i^\alpha M_j^\alpha \left(1 + \alpha \frac{m_i(\mathbf{u}_i^{\alpha'} \cdot \mathbf{v}_i')}{k_B T} + \alpha \frac{m_i T_i^{\alpha'}(\mathbf{v}_i')^2}{2k_B T^2} + \alpha \frac{m_j(\mathbf{u}_j^{\alpha'} \cdot \mathbf{v}_j')}{k_B T} + \alpha \frac{m_j T_j^{\alpha'}(\mathbf{v}_j')^2}{2k_B T^2} - \alpha \frac{3T_i^{\alpha'}}{2T} - \alpha \frac{3T_j^{\alpha'}}{2T} + O(\alpha^2) \right). \quad (5.3.13)$$

Using equations (5.3.10) and (5.3.13), we can write

$$\begin{aligned} f_i^{\alpha'} f_j^{\alpha'} - f_i^\alpha f_j^\alpha &= M_i^\alpha M_j^\alpha \left(1 + \alpha \frac{m_i(\mathbf{u}_i^{\alpha'} \cdot \mathbf{v}_i')}{k_B T} + \alpha \frac{m_i T_i^{\alpha'}(\mathbf{v}_i')^2}{2k_B T^2} + \alpha \frac{m_j(\mathbf{u}_j^{\alpha'} \cdot \mathbf{v}_j')}{k_B T} + \alpha \frac{m_j T_j^{\alpha'}(\mathbf{v}_j')^2}{2k_B T^2} \right. \\ &\quad \left. - \alpha \frac{3T_i^{\alpha'}}{2T} - \alpha \frac{3T_j^{\alpha'}}{2T} + O(\alpha^2) \right) - M_i^\alpha M_j^\alpha \left(1 + \alpha \frac{m_i(\mathbf{u}_i^\alpha \cdot \mathbf{v}_i)}{k_B T} + \alpha \frac{m_i T_i^\alpha(\mathbf{v}_i)^2}{2k_B T^2} \right. \\ &\quad \left. + \alpha \frac{m_j(\mathbf{u}_j^\alpha \cdot \mathbf{v}_j)}{k_B T} + \alpha \frac{m_j T_j^\alpha(\mathbf{v}_j)^2}{2k_B T^2} - \alpha \frac{3T_i^\alpha}{2T} - \alpha \frac{3T_j^\alpha}{2T} + O(\alpha^2) \right). \end{aligned}$$

Putting together terms of the same order in α gives:

$$\begin{aligned}
f_i^{\alpha'} f_j^{\alpha'} - f_i^{\alpha} f_j^{\alpha} &= \left(M_i^{\alpha} M_j^{\alpha} - M_i^{\alpha} M_j^{\alpha} \right) + \alpha M_i^{\alpha} M_j^{\alpha} \left(\frac{m_i(\mathbf{u}_i^{\alpha} \cdot \mathbf{v}_i')}{k_B T} - \frac{m_i(\mathbf{u}_i^{\alpha} \cdot \mathbf{v}_i)}{k_B T} \right. \\
&\quad + \frac{m_i T_i^{\alpha}(\mathbf{v}_i')^2}{2k_B T^2} - \frac{m_i T_i^{\alpha}(\mathbf{v}_i)^2}{2k_B T^2} + \frac{m_j(\mathbf{u}_j^{\alpha} \cdot \mathbf{v}_j')}{k_B T} - \frac{m_j(\mathbf{u}_j^{\alpha} \cdot \mathbf{v}_j)}{k_B T} + \frac{m_j T_j^{\alpha}(\mathbf{v}_j')^2}{2k_B T^2} \\
&\quad \left. - \frac{m_j T_j^{\alpha}(\mathbf{v}_j)^2}{2k_B T^2} - \frac{3T_i^{\alpha}}{2T} + \frac{3T_i^{\alpha}}{2T} - \frac{3T_j^{\alpha}}{2T} + \frac{3T_j^{\alpha}}{2T} \right) + O(\alpha^2) \\
&= \alpha M_i^{\alpha} M_j^{\alpha} \left(\frac{m_i(\mathbf{u}_i^{\alpha} \cdot \mathbf{v}_i')}{k_B T} - \frac{m_i(\mathbf{u}_i^{\alpha} \cdot \mathbf{v}_i)}{k_B T} + \frac{m_i T_i^{\alpha}(\mathbf{v}_i')^2}{2k_B T^2} - \frac{m_i T_i^{\alpha}(\mathbf{v}_i)^2}{2k_B T^2} \right. \\
&\quad \left. + \frac{m_j(\mathbf{u}_j^{\alpha} \cdot \mathbf{v}_j')}{k_B T} - \frac{m_j(\mathbf{u}_j^{\alpha} \cdot \mathbf{v}_j)}{k_B T} + \frac{m_j T_j^{\alpha}(\mathbf{v}_j')^2}{2k_B T^2} - \frac{m_j T_j^{\alpha}(\mathbf{v}_j)^2}{2k_B T^2} \right) + O(\alpha^2) \\
&= \alpha M_i^{\alpha} M_j^{\alpha} \left[\frac{m_i \mathbf{u}_i^{\alpha} \cdot (\mathbf{v}_i' - \mathbf{v}_i)}{k_B T} + \frac{m_j \mathbf{u}_j^{\alpha} \cdot (\mathbf{v}_j' - \mathbf{v}_j)}{k_B T} + \frac{T_i^{\alpha}}{k_B T^2} \left(\frac{m_i(\mathbf{v}_i')^2}{2} - \frac{m_i(\mathbf{v}_i)^2}{2} \right) \right. \\
&\quad \left. + \frac{T_j^{\alpha}}{k_B T^2} \left(\frac{m_j(\mathbf{v}_j')^2}{2} - \frac{m_j(\mathbf{v}_j)^2}{2} \right) \right] + O(\alpha^2).
\end{aligned}$$

Using the conservation laws of linear momentum and kinetic energy for elastic collisions given in equations (2.3.6) and (2.3.7), respectively with s replaced by j , but rewritten as:

$$m_i(\mathbf{v}_i' - \mathbf{v}_i) = -m_j(\mathbf{v}_j' - \mathbf{v}_j), \quad \frac{1}{2}m_i(\mathbf{v}_i')^2 - \frac{1}{2}m_i(\mathbf{v}_i)^2 = \frac{1}{2}m_j(\mathbf{v}_j)^2 - \frac{1}{2}m_j(\mathbf{v}_j')^2,$$

we obtain:

$$\begin{aligned}
f_i^{\alpha'} f_j^{\alpha'} - f_i^{\alpha} f_j^{\alpha} &= \alpha M_i^{\alpha} M_j^{\alpha} \left[\frac{m_i \mathbf{u}_i^{\alpha} \cdot (\mathbf{v}_i' - \mathbf{v}_i)}{k_B T} - \frac{m_i \mathbf{u}_j^{\alpha} \cdot (\mathbf{v}_i' - \mathbf{v}_i)}{k_B T} + \frac{T_i^{\alpha}}{k_B T^2} \left(\frac{m_i(\mathbf{v}_i')^2}{2} - \frac{m_i(\mathbf{v}_i)^2}{2} \right) \right. \\
&\quad \left. - \frac{T_j^{\alpha}}{k_B T^2} \left(\frac{m_i(\mathbf{v}_i')^2}{2} - \frac{m_i(\mathbf{v}_i)^2}{2} \right) \right] + O(\alpha^2) \\
&= \alpha M_i^{\alpha} M_j^{\alpha} \left[\frac{m_i(\mathbf{v}_i' - \mathbf{v}_i) \cdot (\mathbf{u}_i^{\alpha} - \mathbf{u}_j^{\alpha})}{k_B T} + \frac{T_i^{\alpha} - T_j^{\alpha}}{k_B T^2} \left(\frac{m_i(\mathbf{v}_i')^2}{2} - \frac{m_i(\mathbf{v}_i)^2}{2} \right) \right] + O(\alpha^2).
\end{aligned}$$

Thus part (a) is proven.

To prove part (b), observe that using the expanded form of the distribution functions gives :

$$\begin{aligned}
f_k^{\alpha\circ} f_l^{\alpha\circ} &= M_k^{\alpha\circ} M_l^{\alpha\circ} \left(1 + \alpha \frac{m_k(\mathbf{u}_k^{\alpha} \cdot \mathbf{v}_k^{\circ})}{k_B T} + \alpha \frac{m_k T_k^{\alpha}(\mathbf{v}_k^{\circ})^2}{2k_B T^2} + \alpha \frac{m_l(\mathbf{u}_l^{\alpha} \cdot \mathbf{v}_l^{\circ})}{k_B T} \right. \\
&\quad \left. + \alpha \frac{m_l T_l^{\alpha}(\mathbf{v}_l^{\circ})^2}{2k_B T^2} - \alpha \frac{3T_k^{\alpha}}{2T} - \alpha \frac{3T_l^{\alpha}}{2T} + O(\alpha^2) \right). \tag{5.3.14}
\end{aligned}$$

Using equations (5.3.14) and (5.3.10), we can write

$$\begin{aligned}
\left(\frac{\mu_{ij}}{\mu_{kl}} \right)^2 f_k^{\alpha\circ} f_l^{\alpha\circ} - f_i^{\alpha} f_j^{\alpha} &= \left(\frac{\mu_{ij}}{\mu_{kl}} \right)^2 M_k^{\alpha\circ} M_l^{\alpha\circ} \left(1 + \alpha \frac{m_k(\mathbf{u}_k^{\alpha} \cdot \mathbf{v}_k^{\circ})}{k_B T} + \alpha \frac{m_k T_k^{\alpha}(\mathbf{v}_k^{\circ})^2}{2k_B T^2} \right. \\
&\quad \left. + \alpha \frac{m_l(\mathbf{u}_l^{\alpha} \cdot \mathbf{v}_l^{\circ})}{k_B T} + \alpha \frac{m_l T_l^{\alpha}(\mathbf{v}_l^{\circ})^2}{2k_B T^2} - \alpha \frac{3T_k^{\alpha}}{2T} - \alpha \frac{3T_l^{\alpha}}{2T} + O(\alpha^2) \right) \\
&\quad - M_i^{\alpha} M_j^{\alpha} \left(1 + \alpha \frac{m_i(\mathbf{u}_i^{\alpha} \cdot \mathbf{v}_i)}{k_B T} + \alpha \frac{m_i T_i^{\alpha}(\mathbf{v}_i)^2}{2k_B T^2} + \alpha \frac{m_j(\mathbf{u}_j^{\alpha} \cdot \mathbf{v}_j)}{k_B T} \right.
\end{aligned}$$

$$+ \alpha \frac{m_j T_j^\alpha (\mathbf{v}_j)^2}{2k_B T^2} - \alpha \frac{3T_i^\alpha}{2T} - \alpha \frac{3T_j^\alpha}{2T} + O(\alpha^2) \Bigg).$$

Putting together terms of the same order in α gives:

$$\begin{aligned} & \left(\frac{\mu_{ij}}{\mu_{kl}} \right)^2 f_k^{\alpha\circ} f_l^{\alpha\circ} - f_i^\alpha f_j^\alpha \\ &= \left(\frac{\mu_{ij}}{\mu_{kl}} \right)^2 M_k^{\alpha\circ} M_l^{\alpha\circ} - M_i^\alpha M_j^\alpha + \alpha \left(\frac{\mu_{ij}}{\mu_{kl}} \right)^2 M_k^{\alpha\circ} M_l^{\alpha\circ} \left(\frac{m_k (\mathbf{u}_k^\alpha \cdot \mathbf{v}_k^\circ)}{k_B T} + \frac{m_l (\mathbf{u}_l^\alpha \cdot \mathbf{v}_l^\circ)}{k_B T} \right. \\ &+ \frac{m_k T_k^\alpha (\mathbf{v}_k^\circ)^2}{2k_B T^2} + \frac{m_l T_l^\alpha (\mathbf{v}_l^\circ)^2}{2k_B T^2} - \frac{3}{2T} (T_k^\alpha + T_l^\alpha) \Bigg) - \alpha M_i^\alpha M_j^\alpha \left(\frac{m_i (\mathbf{u}_i^\alpha \cdot \mathbf{v}_i)}{k_B T} + \frac{m_j (\mathbf{u}_j^\alpha \cdot \mathbf{v}_j)}{k_B T} \right. \\ &+ \frac{m_i T_i^\alpha (\mathbf{v}_i)^2}{2k_B T^2} + \frac{m_j T_j^\alpha (\mathbf{v}_j)^2}{2k_B T^2} - \frac{3}{2T} (T_i^\alpha + T_j^\alpha) \Bigg) + O(\alpha^2). \end{aligned}$$

Thus part (b) is proven and the proof is complete. $\square$

5.4 Momentum balance equations

In this section, the momentum balance equations for the species in the reactive mixture will be derived from the scaled kinetic equations given in equation (5.3.1). This result is presented in the following lemma.

Lemma 5.4.1. *The momentum balance equation for each species in the reactive mixture is given by*

$$\alpha^2 m_i \frac{\partial}{\partial t} (c_i^\alpha \mathbf{u}_i^\alpha) + k_B \frac{\partial}{\partial \mathbf{x}} (c_i^\alpha (T + \alpha T_i^\alpha)) + \alpha^2 m_i \frac{\partial}{\partial \mathbf{x}} (c_i^\alpha (\mathbf{u}_i^\alpha \otimes \mathbf{u}_i^\alpha)) = \tilde{\mathcal{O}}_i - \tilde{\mathcal{P}}_i + \tilde{\mathcal{Q}}_i, \quad (5.4.1)$$

where

$$\tilde{\mathcal{O}}_i = m_i \mathcal{O}_i + O(\alpha) \quad (5.4.2)$$

$$\tilde{\mathcal{P}}_i = \frac{m_i \beta_{ij}}{\alpha^2} \mathcal{P}_i + O(\alpha), \quad (5.4.3)$$

$$\tilde{\mathcal{Q}}_i = \frac{m_i \beta_{ij}}{\alpha^2} (\mathcal{R}_1 + \mathcal{R}_2) + \frac{m_i \beta_{ij}}{\alpha^2} (\mathcal{R}_3 + \mathcal{R}_4) + O(\alpha) \quad (5.4.4)$$

with $\mathcal{O}_i$, $\mathcal{P}_i$, $\mathcal{R}_1$, $\mathcal{R}_2$, $\mathcal{R}_3$ and $\mathcal{R}_4$ defined as given in, equations (4.4.2), (4.4.3) and (4.4.44), respectively.

Proof. Setting $\varphi_i = m_i \mathbf{v}_i$ in equation (5.3.2), we obtain the momentum balance equation for each species, in the form given below:

$$\begin{aligned} & \alpha \int_{\mathbb{R}^3} m_i \mathbf{v}_i \frac{\partial f_i^\alpha}{\partial t} d\mathbf{v}_i + \int_{\mathbb{R}^3} m_i (\mathbf{v}_i \otimes \mathbf{v}_i) \frac{\partial f_i^\alpha}{\partial \mathbf{x}} d\mathbf{v}_i \\ &= \frac{1}{\alpha} \int_{\mathbb{R}^3} m_i \mathbf{v}_i J_i^{\alpha mE} d\mathbf{v}_i + \frac{1}{\alpha} \int_{\mathbb{R}^3} m_i \mathbf{v}_i J_i^{\alpha bE} d\mathbf{v}_i - \frac{1}{\alpha} \int_{\mathbb{R}^3} m_i \mathbf{v}_i J_{ij}^{\alpha b*E} d\mathbf{v}_i + \frac{1}{\alpha} \int_{\mathbb{R}^3} m_i \mathbf{v}_i J_i^{\alpha R} d\mathbf{v}_i. \end{aligned}$$

Using the Leibniz rule for differentiation under the integral sign for the two terms on the left-hand side of the previous equation, we obtain:

$$\begin{aligned}
\alpha \frac{\partial}{\partial t} \left(\int_{\mathbb{R}^3} m_i \mathbf{v}_i f_i^\alpha d\mathbf{v}_i \right) + \frac{\partial}{\partial \mathbf{x}} \left(\int_{\mathbb{R}^3} m_i (\mathbf{v}_i \otimes \mathbf{v}_i) f_i^\alpha d\mathbf{v}_i \right) \\
= \frac{1}{\alpha} \underbrace{\int_{\mathbb{R}^3} m_i \mathbf{v}_i J_i^{\alpha m E} d\mathbf{v}_i}_{\tilde{N}_i} + \frac{1}{\alpha} \underbrace{\int_{\mathbb{R}^3} m_i \mathbf{v}_i J_i^{\alpha b E} d\mathbf{v}_i}_{\tilde{O}_i} \\
- \frac{1}{\alpha} \underbrace{\int_{\mathbb{R}^3} m_i \mathbf{v}_i J_{ij}^{\alpha b * E} d\mathbf{v}_i}_{\tilde{P}_i} + \frac{1}{\alpha} \underbrace{\int_{\mathbb{R}^3} m_i \mathbf{v}_i J_i^{\alpha R} d\mathbf{v}_i}_{\tilde{Q}_i}. \quad (5.4.5)
\end{aligned}$$

Using the definition of the distribution function given in equation (5.3.3), we can write the first integral on the left-hand side of equation (5.4.5) as given below:

$$\int_{\mathbb{R}^3} m_i \mathbf{v}_i f_i^\alpha d\mathbf{v}_i = c_i^\alpha \left(\frac{m_i}{2\pi k_B (T + \alpha T_i^\alpha)} \right)^{\frac{3}{2}} \int_{\mathbb{R}^3} m_i \mathbf{v}_i \exp \left(- \frac{m_i (\mathbf{v}_i - \alpha \mathbf{u}_i^\alpha)^2}{2k_B (T + \alpha T_i^\alpha)} \right) d\mathbf{v}_i,$$

We can rewrite the previous integral using equation (4.3.7) as given below:

$$\begin{aligned}
\int_{\mathbb{R}^3} m_i \mathbf{v}_i f_i^\alpha d\mathbf{v}_i &= c_i^\alpha \left(\frac{m_i}{2\pi k_B (T + \alpha T_i^\alpha)} \right)^{\frac{3}{2}} \int_{\mathbb{R}^3} m_i (\boldsymbol{\xi}_i + \alpha \mathbf{u}_i^\alpha) \exp \left(- \frac{m_i (\boldsymbol{\xi}_i)^2}{2k_B (T + \alpha T_i^\alpha)} \right) d\boldsymbol{\xi}_i \\
&= c_i^\alpha \left(\frac{m_i}{2\pi k_B (T + \alpha T_i^\alpha)} \right)^{\frac{3}{2}} \left[m_i \int_{\mathbb{R}^3} \boldsymbol{\xi}_i \exp \left(- \frac{m_i (\boldsymbol{\xi}_i)^2}{2k_B (T + \alpha T_i^\alpha)} \right) d\boldsymbol{\xi}_i \right. \\
&\quad \left. + \alpha m_i \mathbf{u}_i^\alpha \int_{\mathbb{R}^3} \exp \left(- \frac{m_i (\boldsymbol{\xi}_i)^2}{2k_B (T + \alpha T_i^\alpha)} \right) d\boldsymbol{\xi}_i \right].
\end{aligned}$$

Using the fact that any vector can be written in terms of a unit vector, we have that $\boldsymbol{\xi}_i$ can be written as $\boldsymbol{\xi}_i = \xi_i \vec{v}$, where $\xi_i = \|\boldsymbol{\xi}_i\| = |\boldsymbol{\xi}_i|$ and $\vec{v}$ is a unit vector. Thus the first integral in the last equality of the previous equation can be written as given below:

$$\int_{\mathbb{R}^3} \boldsymbol{\xi}_i \exp \left(- \frac{m_i (\boldsymbol{\xi}_i)^2}{2k_B (T + \alpha T_i^\alpha)} \right) d\boldsymbol{\xi}_i = \int_{\mathbb{R}^3} \xi_i \vec{v} \exp \left(- \frac{m_i (\boldsymbol{\xi}_i)^2}{2k_B (T + \alpha T_i^\alpha)} \right) d\boldsymbol{\xi}_i.$$

Writing the integral on the right-hand side of the previous equation in spherical coordinates and integrating gives:

$$\begin{aligned}
&\int_{\mathbb{R}^3} \xi_i \vec{v} \exp \left(- \frac{m_i (\boldsymbol{\xi}_i)^2}{2k_B (T + \alpha T_i^\alpha)} \right) d\boldsymbol{\xi}_i \\
&= \int_0^\infty \int_0^\pi \int_0^{2\pi} \xi_i (\hat{x} \sin \theta \cos \phi + \hat{y} \sin \theta \sin \phi + \hat{z} \cos \theta) \\
&\quad \times \exp \left(- \frac{m_i (\boldsymbol{\xi}_i)^2}{2k_B (T + \alpha T_i^\alpha)} \right) \xi_i^2 \sin \theta d\phi d\theta d\xi_i
\end{aligned}$$

$$= \int_0^\infty \xi_i^3 \exp \left(- \frac{m_i(\boldsymbol{\xi}_i)^2}{2k_B(T + \alpha T_i^\alpha)} \right) d\xi_i \left(\underbrace{\hat{\mathbf{x}} \int_0^\pi \sin^2 \theta d\theta}_{\frac{\pi}{2}} \underbrace{\int_0^{2\pi} \cos \phi d\phi}_0 \right. \\ \left. + \hat{\mathbf{y}} \underbrace{\int_0^\pi \sin^2 \theta d\theta}_{\frac{\pi}{2}} \underbrace{\int_0^{2\pi} \sin \phi d\phi}_0 + \hat{\mathbf{z}} \underbrace{\int_0^\pi \cos \theta \sin \theta d\theta}_0 \underbrace{\int_0^{2\pi} d\phi}_{2\pi} \right),$$

where $\hat{\mathbf{x}}, \hat{\mathbf{y}}, \hat{\mathbf{z}}$ are the Cartesian unit vectors in $\mathbb{R}^3$. The integral in ξ_i can be evaluated using the integral representation of gamma given in equation (4.3.8) as given below:

$$\int_0^\infty \xi_i^3 \exp \left(- \frac{m_i(\boldsymbol{\xi}_i)^2}{2k_B(T + \alpha T_i^\alpha)} \right) d\xi_i = \frac{1}{2} \Gamma(2) \left(\frac{2k_B(T + \alpha T_i^\alpha)}{m_i} \right)^2 = \frac{1}{2} 1! \left(\frac{2k_B(T + \alpha T_i^\alpha)}{m_i} \right)^2.$$

Therefore,

$$\begin{aligned} \int_{\mathbb{R}^3} \boldsymbol{\xi}_i \exp \left(- \frac{m_i(\boldsymbol{\xi}_i)^2}{2k_B(T + \alpha T_i^\alpha)} \right) d\boldsymbol{\xi}_i &= \frac{1}{2} \left(\frac{2k_B(T + \alpha T_i^\alpha)}{m_i} \right)^2 [\hat{\mathbf{x}}(0) + \hat{\mathbf{y}}(0) + \hat{\mathbf{z}}(0)] \\ &= \frac{1}{2} \left(\frac{2k_B(T + \alpha T_i^\alpha)}{m_i} \right)^2 \times \mathbf{0} \\ &= \mathbf{0}. \end{aligned} \tag{5.4.6}$$

Hence

$$\int_{\mathbb{R}^3} m_i \mathbf{v}_i f_i^\alpha d\mathbf{v}_i = c_i^\alpha \left(\frac{m_i}{2\pi k_B(T + \alpha T_i^\alpha)} \right)^{\frac{3}{2}} \left[\mathbf{0} + \alpha m_i \mathbf{u}_i^\alpha \int_{\mathbb{R}^3} \exp \left(- \frac{m_i(\boldsymbol{\xi}_i)^2}{2k_B(T + \alpha T_i^\alpha)} \right) d\boldsymbol{\xi}_i \right].$$

Writing the integral on the right-hand side of the previous equation in spherical coordinates and integrating gives:

$$\begin{aligned} \int_{\mathbb{R}^3} \exp \left(- \frac{m_i(\boldsymbol{\xi}_i)^2}{2k_B(T + \alpha T_i^\alpha)} \right) d\boldsymbol{\xi}_i &= \int_0^\infty \int_0^\pi \int_0^{2\pi} \exp \left(- \frac{m_i(\boldsymbol{\xi}_i)^2}{2k_B(T + \alpha T_i^\alpha)} \right) \xi_i^2 \sin \theta d\phi d\theta d\xi_i \\ &= \int_0^\infty \xi_i^2 \exp \left(- \frac{m_i(\boldsymbol{\xi}_i)^2}{2k_B(T + \alpha T_i^\alpha)} \right) d\xi_i \underbrace{\int_0^\pi \sin \theta d\theta}_2 \underbrace{\int_0^{2\pi} d\phi}_{2\pi} \\ &= 4\pi \int_0^\infty \xi_i^2 \exp \left(- \frac{m_i(\boldsymbol{\xi}_i)^2}{2k_B(T + \alpha T_i^\alpha)} \right) d\xi_i. \end{aligned}$$

Using the integral representation of gamma function given in equation (4.3.8), we obtain:

$$\begin{aligned} \int_0^\infty \xi_i^2 \exp \left(- \frac{m_i(\boldsymbol{\xi}_i)^2}{2k_B(T + \alpha T_i^\alpha)} \right) d\xi_i &= \frac{1}{2} \Gamma \left(\frac{3}{2} \right) \left(\frac{2k_B(T + \alpha T_i^\alpha)}{m_i} \right)^{\frac{3}{2}} \\ &= \frac{1}{2} \frac{\sqrt{\pi}}{2} \left(\frac{2k_B(T + \alpha T_i^\alpha)}{m_i} \right)^{\frac{3}{2}}. \end{aligned}$$

Therefore,

$$\begin{aligned} \int_{\mathbb{R}^3} \exp\left(-\frac{m_i(\boldsymbol{\xi}_i)^2}{2k_B(T + \alpha T_i^\alpha)}\right) d\boldsymbol{\xi}_i &= 4\pi \frac{\sqrt{\pi}}{4} \left(\frac{2k_B(T + \alpha T_i^\alpha)}{m_i}\right)^{\frac{3}{2}} \\ &= \left(\frac{2\pi k_B(T + \alpha T_i^\alpha)}{m_i}\right)^{\frac{3}{2}}. \end{aligned} \quad (5.4.7)$$

Hence

$$\begin{aligned} \int_{\mathbb{R}^3} m_i \mathbf{v}_i f_i^\alpha d\mathbf{v}_i &= c_i^\alpha \left(\frac{m_i}{2\pi k_B(T + \alpha T_i^\alpha)}\right)^{\frac{3}{2}} \left[\mathbf{0} + \alpha m_i \mathbf{u}_i^\alpha \left(\frac{2\pi k_B(T + \alpha T_i^\alpha)}{m_i}\right)^{\frac{3}{2}}\right] \\ &= \alpha m_i c_i^\alpha \mathbf{u}_i^\alpha. \end{aligned} \quad (5.4.8)$$

Using the definition of the distribution function given in equation (5.3.3), we can write the second integral on the left-hand side of equation (5.4.5) as given below:

$$\int_{\mathbb{R}^3} m_i(\mathbf{v}_i \otimes \mathbf{v}_i) f_i^\alpha d\mathbf{v}_i = c_i^\alpha \left(\frac{m_i}{2\pi k_B(T + \alpha T_i^\alpha)}\right)^{\frac{3}{2}} \int_{\mathbb{R}^3} m_i(\mathbf{v}_i \otimes \mathbf{v}_i) \exp\left(-\frac{m_i(\mathbf{v}_i - \alpha \mathbf{u}_i^\alpha)^2}{2k_B(T + \alpha T_i^\alpha)}\right) d\mathbf{v}_i.$$

Using equation (4.3.7) gives:

$$\begin{aligned} \int_{\mathbb{R}^3} m_i(\mathbf{v}_i \otimes \mathbf{v}_i) f_i^\alpha d\mathbf{v}_i &= c_i^\alpha \left(\frac{m_i}{2\pi k_B(T + \alpha T_i^\alpha)}\right)^{\frac{3}{2}} \int_{\mathbb{R}^3} m_i((\boldsymbol{\xi}_i + \alpha \mathbf{u}_i^\alpha) \otimes (\boldsymbol{\xi}_i + \alpha \mathbf{u}_i^\alpha)) \\ &\quad \times \exp\left(-\frac{m_i(\boldsymbol{\xi}_i)^2}{2k_B(T + \alpha T_i^\alpha)}\right) d\boldsymbol{\xi}_i. \end{aligned}$$

Using equation (4.4.6), we can rewrite the previous equation as

$$\begin{aligned} \int_{\mathbb{R}^3} m_i(\mathbf{v}_i \otimes \mathbf{v}_i) f_i^\alpha d\mathbf{v}_i &= c_i^\alpha \left(\frac{m_i}{2\pi k_B(T + \alpha T_i^\alpha)}\right)^{\frac{3}{2}} \int_{\mathbb{R}^3} m_i(\boldsymbol{\xi}_i \otimes \boldsymbol{\xi}_i + 2\alpha(\boldsymbol{\xi}_i \otimes \mathbf{u}_i^\alpha) + \alpha^2(\mathbf{u}_i^\alpha \otimes \mathbf{u}_i^\alpha)) \\ &\quad \times \exp\left(-\frac{m_i(\boldsymbol{\xi}_i)^2}{2k_B(T + \alpha T_i^\alpha)}\right) d\boldsymbol{\xi}_i. \end{aligned}$$

Expanding, we obtain:

$$\begin{aligned} \int_{\mathbb{R}^3} m_i(\mathbf{v}_i \otimes \mathbf{v}_i) f_i^\alpha d\mathbf{v}_i &= c_i^\alpha \left(\frac{m_i}{2\pi k_B(T + \alpha T_i^\alpha)}\right)^{\frac{3}{2}} m_i \int_{\mathbb{R}^3} (\boldsymbol{\xi}_i \otimes \boldsymbol{\xi}_i) \exp\left(-\frac{m_i(\boldsymbol{\xi}_i)^2}{2k_B(T + \alpha T_i^\alpha)}\right) d\boldsymbol{\xi}_i \\ &\quad + c_i^\alpha \left(\frac{m_i}{2\pi k_B(T + \alpha T_i^\alpha)}\right)^{\frac{3}{2}} 2m_i \alpha \mathbf{u}_i^\alpha \otimes \int_{\mathbb{R}^3} \boldsymbol{\xi}_i \exp\left(-\frac{m_i(\boldsymbol{\xi}_i)^2}{2k_B(T + \alpha T_i^\alpha)}\right) d\boldsymbol{\xi}_i \\ &\quad + c_i^\alpha \left(\frac{m_i}{2\pi k_B(T + \alpha T_i^\alpha)}\right)^{\frac{3}{2}} m_i \alpha^2 (\mathbf{u}_i^\alpha \otimes \mathbf{u}_i^\alpha) \int_{\mathbb{R}^3} \exp\left(-\frac{m_i(\boldsymbol{\xi}_i)^2}{2k_B(T + \alpha T_i^\alpha)}\right) d\boldsymbol{\xi}_i. \end{aligned}$$

The second and third integrals on the right-hand side of the previous equation are the same as those

whose values are given in equations (5.4.6) and (5.4.7), respectively. Therefore,

$$\begin{aligned}
\int_{\mathbb{R}^3} m_i(\mathbf{v}_i \otimes \mathbf{v}_i) f_i^\alpha &= c_i^\alpha \left(\frac{m_i}{2\pi k_B(T + \alpha T_i^\alpha)} \right)^{\frac{3}{2}} m_i \int_{\mathbb{R}^3} (\boldsymbol{\xi}_i \otimes \boldsymbol{\xi}_i) \exp \left(-\frac{m_i(\boldsymbol{\xi}_i)^2}{2k_B(T + \alpha T_i^\alpha)} \right) d\boldsymbol{\xi}_i \\
&+ c_i^\alpha \left(\frac{m_i}{2\pi k_B(T + \alpha T_i^\alpha)} \right)^{\frac{3}{2}} 2m_i \alpha \mathbf{u}_i^\alpha \otimes \mathbf{0} + m_i \alpha^2 c_i^\alpha (\mathbf{u}_i^\alpha \otimes \mathbf{u}_i^\alpha) \\
&= c_i^\alpha \left(\frac{m_i}{2\pi k_B(T + \alpha T_i^\alpha)} \right)^{\frac{3}{2}} m_i \int_{\mathbb{R}^3} (\boldsymbol{\xi}_i \otimes \boldsymbol{\xi}_i) \exp \left(-\frac{m_i(\boldsymbol{\xi}_i)^2}{2k_B(T + \alpha T_i^\alpha)} \right) d\boldsymbol{\xi}_i \\
&+ m_i \alpha^2 c_i^\alpha (\mathbf{u}_i^\alpha \otimes \mathbf{u}_i^\alpha).
\end{aligned}$$

Now let us evaluate the integral on the right-hand side of the last equality of the previous equation. To do this, observe that

$$\int_{\mathbb{R}^3} (\boldsymbol{\xi}_i \otimes \boldsymbol{\xi}_i) \exp \left(-\frac{m_i(\boldsymbol{\xi}_i)^2}{2k_B(T + \alpha T_i^\alpha)} \right) d\boldsymbol{\xi}_i = \frac{1}{3} \mathbf{I} \int_{\mathbb{R}^3} (\boldsymbol{\xi}_i)^2 \exp \left(-\frac{m_i(\boldsymbol{\xi}_i)^2}{2k_B(T + \alpha T_i^\alpha)} \right) d\boldsymbol{\xi}_i,$$

where $\mathbf{I}$ is an identity tensor. Writing the previous equation in spherical coordinates and integrating, we obtain:

$$\begin{aligned}
&\int_{\mathbb{R}^3} (\boldsymbol{\xi}_i \otimes \boldsymbol{\xi}_i) \exp \left(-\frac{m_i(\boldsymbol{\xi}_i)^2}{2k_B(T + \alpha T_i^\alpha)} \right) d\boldsymbol{\xi}_i \\
&= \frac{1}{3} \mathbf{I} \int_0^\infty \int_0^\pi \int_0^{2\pi} (\boldsymbol{\xi}_i)^2 \exp \left(-\frac{m_i(\boldsymbol{\xi}_i)^2}{2k_B(T + \alpha T_i^\alpha)} \right) \xi_i^2 \sin \theta d\phi d\theta d\xi_i \\
&= \frac{1}{3} \mathbf{I} \int_0^\infty \xi_i^4 \exp \left(-\frac{m_i(\boldsymbol{\xi}_i)^2}{2k_B(T + \alpha T_i^\alpha)} \right) d\xi_i \underbrace{\int_0^\pi \sin \theta d\theta}_2 \underbrace{\int_0^{2\pi} d\phi}_{2\pi} \\
&= \frac{4\pi}{3} \mathbf{I} \int_0^\infty \xi_i^4 \exp \left(-\frac{m_i(\boldsymbol{\xi}_i)^2}{2k_B(T + \alpha T_i^\alpha)} \right) d\xi_i.
\end{aligned}$$

Using the integral representation of gamma function given in equation (4.3.8), we obtain:

$$\begin{aligned}
\int_{\mathbb{R}^3} (\boldsymbol{\xi}_i \otimes \boldsymbol{\xi}_i) \exp \left(-\frac{m_i(\boldsymbol{\xi}_i)^2}{2k_B(T + \alpha T_i^\alpha)} \right) d\boldsymbol{\xi}_i &= \frac{4\pi}{3} \mathbf{I} \frac{1}{2} \Gamma \left(\frac{5}{2} \right) \left(\frac{2k_B(T + \alpha T_i^\alpha)}{m_i} \right)^{\frac{5}{2}} \\
&= \frac{4\pi}{3} \mathbf{I} \frac{1}{2} \frac{3\sqrt{\pi}}{4} \left(\frac{2k_B(T + \alpha T_i^\alpha)}{m_i} \right)^{\frac{5}{2}} \\
&= \mathbf{I} \frac{1}{2} \left(\frac{2\pi k_B(T + \alpha T_i^\alpha)}{m_i} \right)^{\frac{3}{2}} \frac{2k_B(T + \alpha T_i^\alpha)}{m_i} \\
&= \mathbf{I} \left(\frac{2\pi k_B(T + \alpha T_i^\alpha)}{m_i} \right)^{\frac{3}{2}} \frac{k_B(T + \alpha T_i^\alpha)}{m_i}. \quad (5.4.9)
\end{aligned}$$

Thus,

$$\begin{aligned}
\int_{\mathbb{R}^3} m_i(\mathbf{v}_i \otimes \mathbf{v}_i) f_i^\alpha &= c_i^\alpha \left(\frac{m_i}{2\pi k_B(T + \alpha T_i^\alpha)} \right)^{\frac{3}{2}} m_i \mathbf{I} \left(\frac{2\pi k_B(T + \alpha T_i^\alpha)}{m_i} \right)^{\frac{3}{2}} \frac{k_B(T + \alpha T_i^\alpha)}{m_i} \\
&\quad + m_i \alpha^2 c_i^\alpha (\mathbf{u}_i^\alpha \otimes \mathbf{u}_i^\alpha) \\
&= c_i^\alpha k_B(T + \alpha T_i^\alpha) + m_i \alpha^2 c_i^\alpha (\mathbf{u}_i^\alpha \otimes \mathbf{u}_i^\alpha).
\end{aligned} \tag{5.4.10}$$

Substituting equations (5.4.8) and (5.4.10) into equation (5.4.5), we obtain:

$$\begin{aligned}
\alpha m_i \frac{\partial}{\partial t} (c_i^\alpha \mathbf{u}_i^\alpha) + \frac{\partial}{\partial \mathbf{x}} (c_i^\alpha k_B(T + \alpha T_i^\alpha) + m_i \alpha^2 c_i^\alpha (\mathbf{u}_i^\alpha \otimes \mathbf{u}_i^\alpha)) \\
= \frac{1}{\alpha} \underbrace{\int_{\mathbb{R}^3} m_i \mathbf{v}_i J_i^{\alpha m E} d\mathbf{v}_i}_{\tilde{N}_i} + \frac{1}{\alpha} \underbrace{\int_{\mathbb{R}^3} m_i \mathbf{v}_i J_i^{\alpha b E} d\mathbf{v}_i}_{\tilde{O}_i} \\
\quad - \frac{1}{\alpha} \underbrace{\int_{\mathbb{R}^3} m_i \mathbf{v}_i J_{ij}^{\alpha b * E} d\mathbf{v}_i}_{\tilde{P}_i} + \frac{1}{\alpha} \underbrace{\int_{\mathbb{R}^3} m_i \mathbf{v}_i J_i^{\alpha R} d\mathbf{v}_i}_{\tilde{Q}_i}.
\end{aligned} \tag{5.4.11}$$

Since the properties of the scaled collision operators are similar to their un-scaled version, the first integral on the right-hand side of equation (5.4.11) above vanishes. To see this, we use the weak form of the mono-species collision operator given in equation (2.3.37), but with $\varphi(\mathbf{v}_i) = m_i \mathbf{v}_i$. Then applying the conservation of linear momentum for single species (mono-species) collisions given in equation (2.2.2) to the resulting equation gives the desired result. Thus equation (5.4.11) reduces to:

$$\begin{aligned}
\alpha m_i \frac{\partial}{\partial t} (c_i^\alpha \mathbf{u}_i^\alpha) + \frac{\partial}{\partial \mathbf{x}} (c_i^\alpha k_B(T + \alpha T_i^\alpha) + m_i \alpha^2 c_i^\alpha (\mathbf{u}_i^\alpha \otimes \mathbf{u}_i^\alpha)) \\
= \frac{1}{\alpha} \underbrace{\int_{\mathbb{R}^3} m_i \mathbf{v}_i J_i^{\alpha b E} d\mathbf{v}_i}_{\tilde{O}_i} - \frac{1}{\alpha} \underbrace{\int_{\mathbb{R}^3} m_i \mathbf{v}_i J_{ij}^{\alpha b * E} d\mathbf{v}_i}_{\tilde{P}_i} + \frac{1}{\alpha} \underbrace{\int_{\mathbb{R}^3} m_i \mathbf{v}_i J_i^{\alpha R} d\mathbf{v}_i}_{\tilde{Q}_i}.
\end{aligned} \tag{5.4.12}$$

Substituting equation (5.3.4) with the subscript j replaced by s into the definition of the bi-species collision operator $J_i^{\alpha b E}$ given in equation (3.3.14) and expanding, we obtain that the integral $\tilde{O}_i$ can be written as:

$$\begin{aligned}
\tilde{O}_i &= \underbrace{\alpha \sum_{\substack{s=1 \\ s \neq i}}^4 \sigma_{is}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} m_i \mathbf{v}_i M_i^\alpha M_s^\alpha (\mathbf{a}_{is} \cdot (\mathbf{v}'_i - \mathbf{v}_i)) \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_s \rangle d\boldsymbol{\epsilon} d\mathbf{v}_s d\mathbf{v}_i}_{\tilde{O}_i^{(1)}} \\
&\quad + \underbrace{\frac{\alpha}{k_B T^2} \sum_{\substack{s=1 \\ s \neq i}}^4 \sigma_{is}^2 (T_i^\alpha - T_s^\alpha) \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} m_i \mathbf{v}_i M_i^\alpha M_s^\alpha \frac{m_i}{2} ((\mathbf{v}'_i)^2 - (\mathbf{v}_i)^2) \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_s \rangle d\boldsymbol{\epsilon} d\mathbf{v}_s d\mathbf{v}_i}_{\tilde{O}_i^{(2)}} \\
&\quad + O(\alpha^2).
\end{aligned} \tag{5.4.13}$$

First let us evaluate the integral $\tilde{O}_i^{(1)}$. To do this, we substitute equation (4.4.10) into it to obtain:

$$\begin{aligned}
\tilde{\mathcal{O}}_i^{(1)} &= \alpha \sum_{\substack{s=1 \\ s \neq i}}^4 \sigma_{is}^2 2\mu_{is} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} \mathbf{v}_i M_i^\alpha M_s^\alpha (\mathbf{a}_{is} \cdot (\mathbf{v}_s - \mathbf{v}_i) \cos \theta) \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_s \rangle d\boldsymbol{\epsilon} d\mathbf{v}_s d\mathbf{v}_i \\
&= \alpha \sum_{\substack{s=1 \\ s \neq i}}^4 \sigma_{is}^2 2\mu_{is} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} \mathbf{v}_i M_i^\alpha M_s^\alpha (\mathbf{a}_{is} \cdot (\mathbf{v}_s - \mathbf{v}_i)) \cos \theta \|\mathbf{v}_i - \mathbf{v}_s\| \cos \theta d\boldsymbol{\epsilon} d\mathbf{v}_s d\mathbf{v}_i \\
&= \alpha \sum_{\substack{s=1 \\ s \neq i}}^4 \sigma_{is}^2 2\mu_{is} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \mathbf{v}_i M_i^\alpha M_s^\alpha (\mathbf{a}_{is} \cdot (\mathbf{v}_s - \mathbf{v}_i)) \|\mathbf{v}_i - \mathbf{v}_s\| d\mathbf{v}_s d\mathbf{v}_i \underbrace{\int_0^{\frac{\pi}{2}} \cos^2 \theta \sin \theta d\theta}_{\frac{1}{3}} \underbrace{\int_0^{2\pi} d\phi}_{2\pi} \\
&= \alpha \sum_{\substack{s=1 \\ s \neq i}}^4 \sigma_{is}^2 \frac{4\pi\mu_{is}}{3} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \mathbf{v}_i M_i^\alpha M_s^\alpha (\mathbf{a}_{is} \cdot (\mathbf{v}_s - \mathbf{v}_i)) \|\mathbf{v}_i - \mathbf{v}_s\| d\mathbf{v}_s d\mathbf{v}_i \\
&= \alpha \sum_{\substack{s=1 \\ s \neq i}}^4 \sigma_{is}^2 \frac{4\pi\mu_{is}}{3} \frac{(m_i m_s)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_s^\alpha \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \mathbf{v}_i \exp\left(-\frac{m_i(\mathbf{v}_i)^2 + m_s(\mathbf{v}_s)^2}{2k_B T}\right) \\
&\quad \times (\mathbf{a}_{is} \cdot (\mathbf{v}_s - \mathbf{v}_i)) \|\mathbf{v}_i - \mathbf{v}_s\| d\mathbf{v}_s d\mathbf{v}_i.
\end{aligned}$$

It will be convenient to transform the above six fold integral from $\mathbf{v}_i$ and $\mathbf{v}_s$ to the centre of mass velocity $\mathbf{X}_*$ and relative velocity $\mathbf{V}_*$ given in equations (4.4.11) and (4.4.12), respectively. Therefore, using equations (4.4.13), (4.4.14), (4.4.15) with $m_i + m_s = M_{is}$ and (4.4.16), we can rewrite $\tilde{\mathcal{O}}_i^{(1)}$ as follows:

$$\begin{aligned}
\tilde{\mathcal{O}}_i^{(1)} &= \alpha \sum_{\substack{s=1 \\ s \neq i}}^4 \sigma_{is}^2 \frac{4\pi\mu_{is}}{3} \frac{(m_i m_s)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_s^\alpha \\
&\quad \times \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \left(\mathbf{X}_* - \frac{m_s \mathbf{V}_*}{M_{is}} \right) \exp\left(-\frac{M_{is} X_*^2 + \mu_{is} V_*^2}{2k_B T}\right) (\mathbf{a}_{is} \cdot \mathbf{V}_*) \|\mathbf{V}_*\| d\mathbf{X}_* d\mathbf{V}_* \\
&= \alpha \sum_{\substack{s=1 \\ s \neq i}}^4 \sigma_{is}^2 \frac{4\pi\mu_{is}}{3} \frac{(m_i m_s)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_s^\alpha \\
&\quad \times \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \left(\mathbf{X}_* - \frac{m_s \mathbf{V}_*}{M_{is}} \right) \exp\left(-\frac{M_{is} X_*^2 + \mu_{is} V_*^2}{2k_B T}\right) (\mathbf{a}_{is} \cdot \mathbf{V}_*) V_* d\mathbf{X}_* d\mathbf{V}_* \\
&= \alpha \sum_{\substack{s=1 \\ s \neq i}}^4 \sigma_{is}^2 \frac{4\pi\mu_{is}}{3} \frac{(m_i m_s)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_s^\alpha \\
&\quad \times \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \mathbf{X}_* \exp\left(-\frac{M_{is} X_*^2 + \mu_{is} V_*^2}{2k_B T}\right) (\mathbf{a}_{is} \cdot \mathbf{V}_*) V_* d\mathbf{X}_* d\mathbf{V}_* \\
&\quad - \alpha \sum_{\substack{s=1 \\ s \neq i}}^4 \sigma_{is}^2 \frac{4\pi\mu_{is}}{3} \frac{(m_i m_s)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_s^\alpha \frac{m_s}{M_{is}} \\
&\quad \times \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \mathbf{V}_* \exp\left(-\frac{M_{is} X_*^2 + \mu_{is} V_*^2}{2k_B T}\right) (\mathbf{a}_{is} \cdot \mathbf{V}_*) V_* d\mathbf{X}_* d\mathbf{V}_*
\end{aligned}$$

$$\begin{aligned}
&= \alpha \sum_{\substack{s=1 \\ s \neq i}}^4 \sigma_{is}^2 \frac{4\pi\mu_{is}}{3} \frac{(m_i m_s)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_s^\alpha \\
&\quad \times \int_{\mathbb{R}^3} \mathbf{X}_* \exp\left(-\frac{M_{is} X_*^2}{2k_B T}\right) d\mathbf{X}_* \underbrace{\int_{\mathbb{R}^3} \exp\left(-\frac{\mu_{is} V_*^2}{2k_B T}\right) V_* (\mathbf{a}_{is} \cdot \mathbf{V}_*) d\mathbf{V}_*}_{\mathcal{C}} \\
&- \alpha \sum_{\substack{s=1 \\ s \neq i}}^4 \sigma_{is}^2 \frac{4\pi\mu_{is}}{3} \frac{(m_i m_s)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_s^\alpha \frac{m_s}{M_{is}} \\
&\quad \times \int_{\mathbb{R}^3} \exp\left(-\frac{M_{is} X_*^2}{2k_B T}\right) d\mathbf{X}_* \underbrace{\int_{\mathbb{R}^3} \mathbf{V}_* \exp\left(-\frac{\mu_{is} V_*^2}{2k_B T}\right) V_* (\mathbf{a}_{is} \cdot \mathbf{V}_*) d\mathbf{V}_*}_{\mathcal{D}},
\end{aligned}$$

where the fact that $\mathbf{V}_* = \mathbf{v}_s - \mathbf{v}_i$ which implies that $\mathbf{v}_i - \mathbf{v}_s = -\mathbf{V}_*$ and $\|-\mathbf{V}_*\| = \|-1\| \|\mathbf{V}_*\| = 1 \|\mathbf{V}_*\| = V_*$ have been used.

The values of the first and second integrals in $\mathbf{X}_*$ on the right-hand side of the last equality of the previous equation are given in equations (4.4.20) and (4.4.17), respectively. The integral $\mathcal{C}$ can be written in spherical coordinates and evaluated as given below:

$$\begin{aligned}
\mathcal{C} &= \int_0^\infty \int_0^\pi \int_0^{2\pi} \exp\left(-\frac{\mu_{is} V_*^2}{2k_B T}\right) V_* (a_{is} V_* \cos \theta) V_*^2 \sin \theta d\phi d\theta dV_* \\
&= a_{is} \int_0^\infty V_*^4 \exp\left(-\frac{\mu_{is} V_*^2}{2k_B T}\right) dV_* \underbrace{\int_0^\pi \cos \theta \sin \theta d\theta}_0 \underbrace{\int_0^{2\pi} d\phi}_{2\pi},
\end{aligned}$$

where $a_{is} = \|\mathbf{a}_{is}\|$. The value of the integral in V_* above is given in Eq. (4.4.18) therefore,

$$\mathcal{C} = \frac{3\sqrt{\pi}}{8} \left(\frac{2k_B T}{\mu_{is}}\right)^{\frac{5}{2}} \times 0 \times 2\pi = 0. \quad (5.4.14)$$

The integral $\mathcal{D}$ is similar to the integral given in equation (4.4.23) with $\mathbf{a}_i$ replaced by $\mathbf{a}_{is}$. Therefore,

$$\int_{\mathbb{R}^3} \mathbf{V}_* (\mathbf{a}_{is} \cdot \mathbf{V}_*) \exp\left(-\frac{\mu_{is} V_*^2}{2k_B T}\right) V_* d\mathbf{V}_* = \mathbf{a}_{is} \frac{4\pi}{3} \left(\frac{2k_B T}{\mu_{is}}\right)^3. \quad (5.4.15)$$

Substituting equations (4.4.17), (4.4.20), (5.4.14) and (5.4.15) into $\tilde{\mathcal{O}}_i^{(1)}$, we obtain:

$$\begin{aligned}
\tilde{\mathcal{O}}_i^{(1)} &= \alpha \sum_{\substack{s=1 \\ s \neq i}}^4 \sigma_{is}^2 \frac{4\pi\mu_{is}}{3} \frac{(m_i m_s)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_s^\alpha (\mathbf{0} \times \mathbf{0}) \\
&- \alpha \sum_{\substack{s=1 \\ s \neq i}}^4 \sigma_{is}^2 \frac{4\pi\mu_{is}}{3} \frac{(m_i m_s)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_s^\alpha \frac{m_s}{M_{is}} \left(\frac{2\pi k_B T}{M_{is}}\right)^{\frac{3}{2}} \mathbf{a}_{is} \frac{4\pi}{3} \left(\frac{2k_B T}{\mu_{is}}\right)^3
\end{aligned}$$

$$\begin{aligned}
&= -\alpha \sum_{\substack{s=1 \\ s \neq i}}^4 \sigma_{is}^2 \frac{4\pi\mu_{is}}{3} \frac{(m_i m_s)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_s^\alpha \frac{m_s}{M_{is}} \left(\frac{2\pi k_B T}{M_{is}} \right)^{\frac{3}{2}} \frac{4\pi m_i}{3k_B T} \left(\frac{2k_B T}{\mu_{is}} \right)^3 (\mathbf{u}_i^\alpha - \mathbf{u}_s^\alpha) \\
&= -\alpha \sum_{\substack{s=1 \\ s \neq i}}^4 \sigma_{is}^2 \frac{16\pi^2 \mu_{is} m_i}{9k_B T} \left(\frac{\mu_{is}}{2\pi k_B T} \right)^{\frac{3}{2}} c_i^\alpha c_s^\alpha \frac{m_s}{M_{is}} \left(\frac{2k_B T}{\mu_{is}} \right)^3 (\mathbf{u}_i^\alpha - \mathbf{u}_s^\alpha) \\
&= -\alpha \sum_{\substack{s=1 \\ s \neq i}}^4 \sigma_{is}^2 \frac{16\mu_{is}^2}{9k_B T} \left(\frac{\mu_{is}}{2\pi k_B T} \right)^{\frac{3}{2}} c_i^\alpha c_s^\alpha \left(\frac{2\pi k_B T}{\mu_{is}} \right)^2 \left(\frac{2k_B T}{\mu_{is}} \right) (\mathbf{u}_i^\alpha - \mathbf{u}_s^\alpha) \\
&= -\alpha \frac{32}{9} \sum_{\substack{s=1 \\ s \neq i}}^4 \sigma_{is}^2 (2\pi\mu_{is}k_B T)^{\frac{1}{2}} c_i^\alpha c_s^\alpha (\mathbf{u}_i^\alpha - \mathbf{u}_s^\alpha), \tag{5.4.16}
\end{aligned}$$

where the definition of $\mathbf{a}_{ij}$ given in equation (5.3.6) have been used with j replaced by s .

The integral $\tilde{\mathcal{O}}_i^{(2)}$ given in equation (5.4.13) vanishes upon evaluation, that is,

$$\tilde{\mathcal{O}}_i^{(2)} = 0, \tag{5.4.17}$$

see Appendix B section B.1 for details of the computation. Therefore, substituting equations (5.4.16) and (5.4.17) into equation (5.4.13) we obtain:

$$\tilde{\mathcal{O}}_i = -\alpha \frac{32}{9} \sum_{\substack{s=1 \\ s \neq i}}^4 \sigma_{is}^2 (2\pi\mu_{is}k_B T)^{\frac{1}{2}} c_i^\alpha c_s^\alpha (\mathbf{u}_i^\alpha - \mathbf{u}_s^\alpha) + O(\alpha^2). \tag{5.4.18}$$

Next, let us evaluate the integral $\tilde{\mathcal{P}}_i$ given in equation (5.4.12). To do this, we substitute equation (5.3.4) into the definition of $J_i^{\alpha b * E}$ given in equation (3.3.15) and expand to obtain:

$$\begin{aligned}
\tilde{\mathcal{P}}_i &= \alpha \beta_{ij} \sigma_{ij}^2 \left. \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} m_i \mathbf{v}_i M_i^\alpha M_j^\alpha (\mathbf{a}_{ij} \cdot (\mathbf{v}'_i - \mathbf{v}_i)) \right. \\
&\quad \times \Theta(\langle \boldsymbol{\epsilon}, c_0 \mathbf{v}_i - c_0 \mathbf{v}_j \rangle - \Xi_{ij}) \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_j \rangle d\boldsymbol{\epsilon} d\mathbf{v}_j d\mathbf{v}_i \left. \right\} \tilde{\mathcal{P}}_i^{(1)} \\
&+ \alpha \beta_{ij} \sigma_{ij}^2 \frac{T_i^\alpha - T_j^\alpha}{k_B T^2} \left. \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} m_i \mathbf{v}_i M_i^\alpha M_j^\alpha \frac{m_i}{2} \left((\mathbf{v}'_i)^2 - (\mathbf{v}_i)^2 \right) \right. \\
&\quad \times \Theta(\langle \boldsymbol{\epsilon}, c_0 \mathbf{v}_i - c_0 \mathbf{v}_j \rangle - \Xi_{ij}) \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_j \rangle d\boldsymbol{\epsilon} d\mathbf{v}_j d\mathbf{v}_i \left. \right\} \tilde{\mathcal{P}}_i^{(2)} \\
&+ O(\alpha^2). \tag{5.4.19}
\end{aligned}$$

To evaluate the integral $\tilde{\mathcal{P}}_i^{(1)}$, we substitute equation (4.4.10) with s replaced by j into $\tilde{\mathcal{P}}_i^{(1)}$ and obtain:

$$\begin{aligned}
\tilde{\mathcal{P}}_i^{(1)} &= \alpha \beta_{ij} \sigma_{ij}^2 2\mu_{ij} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} \mathbf{v}_i M_i^\alpha M_j^\alpha (\mathbf{a}_{ij} \cdot (\mathbf{v}_j - \mathbf{v}_i) \cos \theta) \\
&\quad \times \Theta(\langle \boldsymbol{\epsilon}, c_0 \mathbf{v}_i - c_0 \mathbf{v}_j \rangle - \Xi_{ij}) \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_j \rangle d\boldsymbol{\epsilon} d\mathbf{v}_j d\mathbf{v}_i.
\end{aligned}$$

Using equation (4.4.26), we obtain:

$$\begin{aligned}
\tilde{\mathcal{P}}_i^{(1)} &= \alpha \beta_{ij} \sigma_{ij}^2 \frac{4\pi\mu_{ij}}{3} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \mathbf{v}_i M_i^\alpha M_j^\alpha (\mathbf{a}_{ij} \cdot (\mathbf{v}_j - \mathbf{v}_i)) \Theta \left(\|\mathbf{v}_i - \mathbf{v}_j\| - \frac{\Xi_{ij}}{c_0} \right) \\
&\quad \times \|\mathbf{v}_i - \mathbf{v}_j\| \left[1 - \left(\frac{\Xi_{ij}}{c_0 \|\mathbf{v}_i - \mathbf{v}_j\|} \right)^3 \right] d\mathbf{v}_j d\mathbf{v}_i \\
&= \alpha \beta_{ij} \sigma_{ij}^2 \frac{4\pi\mu_{ij}}{3} \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_j^\alpha \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \mathbf{v}_i \exp \left(-\frac{m_i(\mathbf{v}_i)^2 + m_j(\mathbf{v}_j)^2}{2k_B T} \right) (\mathbf{a}_{ij} \cdot (\mathbf{v}_j - \mathbf{v}_i)) \\
&\quad \times \Theta \left(\|\mathbf{v}_i - \mathbf{v}_j\| - \frac{\Xi_{ij}}{c_0} \right) \|\mathbf{v}_i - \mathbf{v}_j\| \left[1 - \left(\frac{\Xi_{ij}}{c_0 \|\mathbf{v}_i - \mathbf{v}_j\|} \right)^3 \right] d\mathbf{v}_j d\mathbf{v}_i.
\end{aligned}$$

It will be convenient to transform the above six fold integral from $\mathbf{v}_i$ and $\mathbf{v}_j$ to the centre of mass velocity $\mathbf{X}^*$ and relative velocity $\mathbf{V}^*$, given by equations (2.4.6) and (2.4.7), respectively. Therefore, using equations (2.4.10), (2.4.11) and (2.4.12) together with the fact that the Jacobian of the transformation has absolute value of unity, which implies equation (4.3.21), as well as $\|\mathbf{v}_i - \mathbf{v}_j\| = \|-\mathbf{V}^*\| = |-1| \|\mathbf{V}^*\| = \|\mathbf{V}^*\| = V^*$, we obtain:

$$\begin{aligned}
\tilde{\mathcal{P}}_i^{(1)} &= \alpha \beta_{ij} \sigma_{ij}^2 \frac{4\pi\mu_{ij}}{3} \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_j^\alpha \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \left(\mathbf{X}^* - \frac{m_j \mathbf{V}^*}{M} \right) \exp \left(-\frac{M X^{*2} + \mu_{ij} V^{*2}}{2k_B T} \right) \\
&\quad \times (\mathbf{a}_{ij} \cdot \mathbf{V}^*) \Theta \left(V^* - \frac{\Xi_{ij}}{c_0} \right) V^* \left[1 - \left(\frac{\Xi_{ij}}{c_0 V^*} \right)^3 \right] d\mathbf{X}^* d\mathbf{V}^* \\
&= \alpha \beta_{ij} \sigma_{ij}^2 \frac{4\pi\mu_{ij}}{3} \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_j^\alpha \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \left(\mathbf{X}^* - \frac{m_j \mathbf{V}^*}{M} \right) \exp \left(-\frac{M X^{*2} + \mu_{ij} V^{*2}}{2k_B T} \right) \\
&\quad \times (\mathbf{a}_{ij} \cdot \mathbf{V}^*) \Theta \left(V^* - \frac{\Xi_{ij}}{c_0} \right) V^* d\mathbf{X}^* d\mathbf{V}^* \\
&\quad - \alpha \beta_{ij} \sigma_{ij}^2 \frac{4\pi\mu_{ij}}{3} \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_j^\alpha \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \left(\mathbf{X}^* - \frac{m_j \mathbf{V}^*}{M} \right) \exp \left(-\frac{M X^{*2} + \mu_{ij} V^{*2}}{2k_B T} \right) \\
&\quad \times (\mathbf{a}_{ij} \cdot \mathbf{V}^*) \Theta \left(V^* - \frac{\Xi_{ij}}{c_0} \right) V^* \left(\frac{\Xi_{ij}}{c_0 V^*} \right)^3 d\mathbf{X}^* d\mathbf{V}^* \\
&= \alpha \beta_{ij} \sigma_{ij}^2 \frac{4\pi\mu_{ij}}{3} \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_j^\alpha \\
&\quad \times \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \mathbf{X}^* \exp \left(-\frac{M X^{*2} + \mu_{ij} V^{*2}}{2k_B T} \right) (\mathbf{a}_{ij} \cdot \mathbf{V}^*) \Theta \left(V^* - \frac{\Xi_{ij}}{c_0} \right) V^* d\mathbf{X}^* d\mathbf{V}^* \\
&\quad - \alpha \beta_{ij} \sigma_{ij}^2 \frac{4\pi\mu_{ij}}{3} \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_j^\alpha \frac{m_j}{M} \\
&\quad \times \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \mathbf{V}^* \exp \left(-\frac{M X^{*2} + \mu_{ij} V^{*2}}{2k_B T} \right) (\mathbf{a}_{ij} \cdot \mathbf{V}^*) \Theta \left(V^* - \frac{\Xi_{ij}}{c_0} \right) V^* d\mathbf{X}^* d\mathbf{V}^* \\
&\quad - \alpha \beta_{ij} \sigma_{ij}^2 \frac{4\pi\mu_{ij}}{3} \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_j^\alpha \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \mathbf{X}^* \exp \left(-\frac{M X^{*2} + \mu_{ij} V^{*2}}{2k_B T} \right) (\mathbf{a}_{ij} \cdot \mathbf{V}^*)
\end{aligned}$$

$$\begin{aligned}
& \times \Theta \left(V^* - \frac{\Xi_{ij}}{c_0} \right) V^* \left(\frac{\Xi_{ij}}{c_0 V^*} \right)^3 d\mathbf{X}^* dV^* \\
& + \alpha \beta_{ij} \sigma_{ij}^2 \frac{4\pi \mu_{ij}}{3} \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_j^\alpha \frac{m_j}{M} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \mathbf{V}^* \exp \left(- \frac{MX^{*2} + \mu_{ij} V^{*2}}{2k_B T} \right) (\mathbf{a}_{ij} \cdot \mathbf{V}^*) \\
& \quad \times \Theta \left(V^* - \frac{\Xi_{ij}}{c_0} \right) V^* \left(\frac{\Xi_{ij}}{c_0 V^*} \right)^3 d\mathbf{X}^* dV^* \\
& = \alpha \beta_{ij} \sigma_{ij}^2 \frac{4\pi \mu_{ij}}{3} \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_j^\alpha \int_{\mathbb{R}^3} \mathbf{X}^* \exp \left(- \frac{MX^{*2}}{2k_B T} \right) d\mathbf{X}^* \\
& \quad \times \underbrace{\int_{\mathbb{R}^3} \exp \left(- \frac{\mu_{ij} V^{*2}}{2k_B T} \right) (\mathbf{a}_{ij} \cdot \mathbf{V}^*) \Theta \left(V^* - \frac{\Xi_{ij}}{c_0} \right) V^* dV^*}_{\mathcal{X}_1} \\
& - \alpha \beta_{ij} \sigma_{ij}^2 \frac{4\pi \mu_{ij}}{3} \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_j^\alpha \frac{m_j}{M} \int_{\mathbb{R}^3} \exp \left(- \frac{MX^{*2}}{2k_B T} \right) d\mathbf{X}^* \\
& \quad \times \underbrace{\int_{\mathbb{R}^3} \mathbf{V}^* \exp \left(- \frac{\mu_{ij} V^{*2}}{2k_B T} \right) (\mathbf{a}_{ij} \cdot \mathbf{V}^*) \Theta \left(V^* - \frac{\Xi_{ij}}{c_0} \right) V^* dV^*}_{\mathcal{X}_2} \\
& - \alpha \beta_{ij} \sigma_{ij}^2 \frac{4\pi \mu_{ij}}{3} \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_j^\alpha \int_{\mathbb{R}^3} \mathbf{X}^* \exp \left(- \frac{MX^{*2}}{2k_B T} \right) d\mathbf{X}^* \\
& \quad \times \underbrace{\int_{\mathbb{R}^3} \exp \left(- \frac{\mu_{ij} V^{*2}}{2k_B T} \right) (\mathbf{a}_{ij} \cdot \mathbf{V}^*) \Theta \left(V^* - \frac{\Xi_{ij}}{c_0} \right) V^* \left(\frac{\Xi_{ij}}{c_0 V^*} \right)^3 dV^*}_{\mathcal{X}_3} \\
& + \alpha \beta_{ij} \sigma_{ij}^2 \frac{4\pi \mu_{ij}}{3} \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_j^\alpha \frac{m_j}{M} \int_{\mathbb{R}^3} \exp \left(- \frac{MX^{*2}}{2k_B T} \right) d\mathbf{X}^* \\
& \quad \times \underbrace{\int_{\mathbb{R}^3} \mathbf{V}^* \exp \left(- \frac{\mu_{ij} V^{*2}}{2k_B T} \right) (\mathbf{a}_{ij} \cdot \mathbf{V}^*) \Theta \left(V^* - \frac{\Xi_{ij}}{c_0} \right) V^* \left(\frac{\Xi_{ij}}{c_0 V^*} \right)^3 dV^*}_{\mathcal{X}_4}.
\end{aligned}$$

The values of the integrals in $\mathbf{X}^*$ on the right-hand side of the last equality of the previous equation are given in Eq. (4.4.28). Now let us evaluate the integrals $\mathcal{X}_1$, $\mathcal{X}_2$, $\mathcal{X}_3$ and $\mathcal{X}_4$.

Writing the integral $\mathcal{X}_1$ in spherical coordinates and integrating gives:

$$\begin{aligned}
\mathcal{X}_1 &= \int_0^\infty \int_0^\pi \int_0^{2\pi} \exp \left(- \frac{\mu_{ij} V^{*2}}{2k_B T} \right) (a_{ij} V^* \cos \theta) \Theta \left(V^* - \frac{\Xi_{ij}}{c_0} \right) V^* V^{*2} \sin \theta d\phi d\theta dV^* \\
&= a_{ij} \int_{V^* \geq \frac{\Xi_{ij}}{c_0}}^\infty \int_0^\pi \int_0^{2\pi} V^{*4} \exp \left(- \frac{\mu_{ij} V^{*2}}{2k_B T} \right) \cos \theta \sin \theta d\phi d\theta dV^* \\
&= a_{ij} \int_{V^* \geq \frac{\Xi_{ij}}{c_0}}^\infty V^{*4} \exp \left(- \frac{\mu_{ij} V^{*2}}{2k_B T} \right) dV^* \underbrace{\int_0^\pi \sin \theta \cos \theta d\theta}_0 \underbrace{\int_0^{2\pi} d\phi}_{2\pi}, \tag{5.4.20}
\end{aligned}$$

where $a_{ij} = \|\mathbf{a}_{ij}\|$. The value of the integral in V^* is given in equation (4.4.29). Therefore,

$$\begin{aligned} \int_{\mathbb{R}^3} (\mathbf{a}_{ij} \cdot \mathbf{V}^*) \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) V^* d\mathbf{V}^* &= a_{ij} \frac{1}{2} \left(\frac{2k_B T}{\mu_{ij}}\right)^{\frac{5}{2}} \Gamma\left(\frac{5}{2}, z_i^*\right) \times 0 \times 2\pi \\ &= 0. \end{aligned} \quad (5.4.21)$$

Next we evaluate the integral $\mathcal{X}_2$. Observe that it can be rewritten as follows:

$$\begin{aligned} \mathcal{X}_2 &= \int_{\mathbb{R}^3} V^* \vec{v} \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) (\mathbf{a}_{ij} \cdot \mathbf{V}^*) \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) V^* d\mathbf{V}^* \\ &= \int_{\mathbb{R}^3} V^* \vec{v} \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) (a_{ij} V^* \cos \theta) \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) V^* d\mathbf{V}^*, \end{aligned}$$

where the fact that any vector $\mathbf{V}^*$ can be written in terms of a unit vector as $\mathbf{V}^* = V^* \vec{v}$, with $V^* = \|\mathbf{V}^*\|$ and $\vec{v}$ a unit vector have been used. Writing the integral in the last equality of the previous equation in spherical coordinates and integrating gives

$$\begin{aligned} \mathcal{X}_2 &= \int_0^\infty \int_0^\pi \int_0^{2\pi} V^* (\hat{x} \sin \theta \cos \phi + \hat{y} \sin \theta \sin \phi + \hat{z} \cos \theta) \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) \\ &\quad \times (a_{ij} V^* \cos \theta) \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) V^* V^{*2} \sin \theta d\phi d\theta dV^* \\ &= a_{ij} \int_{V^* \geq \frac{\Xi_{ij}}{c_0}}^\infty V^{*5} \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) dV^* \left(\hat{x} \underbrace{\int_0^\pi \sin^2 \theta \cos \theta d\theta}_0 \underbrace{\int_0^{2\pi} \cos \phi d\phi}_0 \right. \\ &\quad \left. + \hat{y} \underbrace{\int_0^\pi \sin^2 \theta \cos \theta d\theta}_0 \underbrace{\int_0^{2\pi} \sin \phi d\phi}_0 + \hat{z} \underbrace{\int_0^\pi \sin \theta \cos^2 \theta d\theta}_{\frac{2}{3}} \underbrace{\int_0^{2\pi} d\phi}_{2\pi} \right), \end{aligned}$$

where $\hat{x}, \hat{y}, \hat{z}$ are the Cartesian unit vectors in $\mathbb{R}^3$. The value of the integral in V^* above is given in equation (4.4.33). Therefore,

$$\begin{aligned} \int_{\mathbb{R}^3} \mathbf{V}^* \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) (\mathbf{a}_{ij} \cdot \mathbf{V}^*) \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) V^* d\mathbf{V}^* \\ &= a_{ij} \left(\frac{2k_B T}{\mu_{ij}}\right)^3 \frac{1}{2} \Gamma(3, z_i^*) \left[\hat{x}(0 \times 0) + \hat{y}(0 \times 0) + \hat{z}\left(\frac{2}{3} \times 2\pi\right) \right] \\ &= a_{ij} \left(\frac{2k_B T}{\mu_{ij}}\right)^3 \frac{1}{2} \Gamma(3, z_i^*) \hat{z} \left(\frac{4\pi}{3}\right) \\ &= a_{ij} \frac{2\pi}{3} \left(\frac{2k_B T}{\mu_{ij}}\right)^3 \Gamma(3, z_i^*). \end{aligned} \quad (5.4.22)$$

Now let us evaluate the integral $\mathcal{X}_3$. To do this, we write it in spherical coordinates and integrate as given below:

$$\begin{aligned}
\mathcal{X}_3 &= \int_0^\infty \int_0^\pi \int_0^{2\pi} \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) (a_{ij} V^* \cos \theta) \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) V^* \left(\frac{\Xi_{ij}}{c_0 V^*}\right)^3 V^{*2} \sin \theta d\phi d\theta dV^* \\
&= \left(\frac{\Xi_{ij}}{c_0}\right)^3 a_{ij} \int_{V^* \geq \frac{\Xi_{ij}}{c_0}}^\infty V^* \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) dV^* \underbrace{\int_0^\pi \sin \theta \cos \theta d\theta}_0 \underbrace{\int_0^{2\pi} d\phi}_{2\pi}.
\end{aligned}$$

The value of the integral in V^* above is given in equation (4.4.31). Therefore,

$$\begin{aligned}
&\int_{\mathbb{R}^3} \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) (\mathbf{a}_{ij} \cdot \mathbf{V}^*) \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) V^* \left(\frac{\Xi_{ij}}{c_0 V^*}\right)^3 d\mathbf{V}^* \\
&= \left(\frac{\Xi_{ij}}{c_0 V}\right)^3 a_{ij} \frac{1}{2} \left(\frac{2k_B T}{\mu_{ij}}\right) \Gamma(1, z_i^*) \times 0 \times 2\pi \\
&= 0.
\end{aligned} \tag{5.4.23}$$

Finally, the integral $\mathcal{X}_4$ can be rewritten as given below:

$$\begin{aligned}
\mathcal{X}_4 &= \int_{\mathbb{R}^3} V^* \vec{\mathbf{v}} \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) (\mathbf{a}_{ij} \cdot \mathbf{V}^*) \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) V^* \left(\frac{\Xi_{ij}}{c_0 V^*}\right)^3 d\mathbf{V}^* \\
&= \int_{\mathbb{R}^3} V^* \vec{\mathbf{v}} \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) (a_{ij} V^* \cos \theta) \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) V^* \left(\frac{\Xi_{ij}}{c_0 V^*}\right)^3 d\mathbf{V}^*,
\end{aligned}$$

where the fact that any vector $\mathbf{V}^*$ can be written in terms of a unit vector as $\mathbf{V}^* = V^* \vec{\mathbf{v}}$, with $V^* = \|\mathbf{V}^*\|$ and $\vec{\mathbf{v}}$ a unit vector have been used. Writing the integral $\mathcal{X}_4$ in spherical coordinates and integrating, we obtain:

$$\begin{aligned}
\mathcal{X}_4 &= \int_0^\infty \int_0^\pi \int_0^{2\pi} V^* (\hat{\mathbf{x}} \sin \theta \cos \phi + \hat{\mathbf{y}} \sin \theta \sin \phi + \hat{\mathbf{z}} \cos \theta) \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) \\
&\quad \times (a_{ij} V^* \cos \theta) \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) V^* \left(\frac{\Xi_{ij}}{c_0 V^*}\right)^3 V^{*2} \sin \theta d\phi d\theta dV^* \\
&= \left(\frac{\Xi_{ij}}{c_0}\right)^3 a_{ij} \int_{V^* \geq \frac{\Xi_{ij}}{c_0}}^\infty V^{*2} \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) dV^* \left(\hat{\mathbf{x}} \underbrace{\int_0^\pi \sin^2 \theta \cos \theta d\theta}_0 \underbrace{\int_0^{2\pi} \cos \phi d\phi}_0 \right. \\
&\quad \left. + \hat{\mathbf{y}} \underbrace{\int_0^\pi \sin^2 \theta \cos \theta d\theta}_0 \underbrace{\int_0^{2\pi} \sin \phi d\phi}_0 + \hat{\mathbf{z}} \underbrace{\int_0^\pi \sin \theta \cos^2 \theta d\theta}_{\frac{2}{3}} \underbrace{\int_0^{2\pi} d\phi}_{2\pi} \right),
\end{aligned}$$

where $\hat{\mathbf{x}}, \hat{\mathbf{y}}, \hat{\mathbf{z}}$ are the Cartesian unit vectors in $\mathbb{R}^3$. The value of the integral in V^* above is given in equation (4.4.35). Therefore,

$$\int_{\mathbb{R}^3} \mathbf{V}^* \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) (\mathbf{a}_{ij} \cdot \mathbf{V}^*) \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) V^* \left(\frac{\Xi_{ij}}{c_0 V^*}\right)^3 d\mathbf{V}^*$$

$$\begin{aligned}
&= \left(\frac{\Xi_{ij}}{c_0}\right)^3 a_{ij} \frac{1}{2} \left(\frac{2k_B T}{\mu_{ij}}\right)^{\frac{3}{2}} \Gamma\left(\frac{3}{2}, z_i^*\right) \left[\hat{\mathbf{x}}(0 \times 0) + \hat{\mathbf{y}}(0 \times 0) + \hat{\mathbf{z}}\left(\frac{2}{3} \times 2\pi\right)\right] \\
&= \left(\frac{\Xi_{ij}}{c_0}\right)^3 a_{ij} \frac{1}{2} \left(\frac{2k_B T}{\mu_{ij}}\right)^{\frac{3}{2}} \Gamma\left(\frac{3}{2}, z_i^*\right) \hat{\mathbf{z}}\left(\frac{4\pi}{3}\right) \\
&= \left(\frac{\Xi_{ij}}{c_0}\right)^3 \mathbf{a}_{ij} \frac{2\pi}{3} \left(\frac{2k_B T}{\mu_{ij}}\right)^{\frac{3}{2}} \Gamma\left(\frac{3}{2}, z_i^*\right). \tag{5.4.24}
\end{aligned}$$

Substituting equations (4.4.28), (5.4.21), (5.4.22), (5.4.23) and (5.4.24) into $\tilde{\mathcal{P}}_i^{(1)}$ gives:

$$\begin{aligned}
\tilde{\mathcal{P}}_i^{(1)} &= -\alpha\beta_{ij}\sigma_{ij}^2 \frac{4\pi\mu_{ij}}{3} \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_j^\alpha \frac{m_j}{M} \left(\frac{2\pi k_B T}{M}\right)^{\frac{3}{2}} \mathbf{a}_{ij} \frac{2\pi}{3} \left(\frac{2k_B T}{\mu_{ij}}\right)^3 \Gamma(3, z_i^*) \\
&\quad + \alpha\beta_{ij}\sigma_{ij}^2 \frac{4\pi\mu_{ij}}{3} \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_j^\alpha \frac{m_j}{M} \left(\frac{2\pi k_B T}{M}\right)^{\frac{3}{2}} \left(\frac{\Xi_{ij}}{c_0}\right)^3 \mathbf{a}_{ij} \frac{2\pi}{3} \left(\frac{2k_B T}{\mu_{ij}}\right)^{\frac{3}{2}} \Gamma\left(\frac{3}{2}, z_i^*\right) \\
&= -\alpha\beta_{ij}\sigma_{ij}^2 \frac{4\pi\mu_{ij}}{3} \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_j^\alpha \frac{m_j}{M} \left(\frac{2\pi k_B T}{M}\right)^{\frac{3}{2}} \mathbf{a}_{ij} \frac{2\pi}{3} \left(\frac{2k_B T}{\mu_{ij}}\right)^{\frac{3}{2}} \\
&\quad \times \left[\left(\frac{2k_B T}{\mu_{ij}}\right)^{\frac{3}{2}} \Gamma(3, z_i^*) - \left(\frac{\Xi_{ij}}{c_0}\right)^3 \Gamma\left(\frac{3}{2}, z_i^*\right) \right] \\
&= -\alpha\beta_{ij}\sigma_{ij}^2 \frac{8\pi^2\mu_{ij}}{9} \left(\frac{\mu_{ij}}{2\pi k_B T}\right)^{\frac{3}{2}} c_i^\alpha c_j^\alpha \frac{m_j}{M} \mathbf{a}_{ij} \left(\frac{2k_B T}{\mu_{ij}}\right)^{\frac{3}{2}} \\
&\quad \times \left[\left(\frac{2k_B T}{\mu_{ij}}\right)^{\frac{3}{2}} \Gamma(3, z_i^*) - \left(\frac{\Xi_{ij}}{c_0}\right)^3 \Gamma\left(\frac{3}{2}, z_i^*\right) \right] \\
&= -\alpha\beta_{ij}\sigma_{ij}^2 \frac{8\sqrt{\pi}\mu_{ij}}{9} c_i^\alpha c_j^\alpha \frac{m_j}{M} \frac{m_i(\mathbf{u}_i^\alpha - \mathbf{u}_j^\alpha)}{k_B T} \left[\left(\frac{2k_B T}{\mu_{ij}}\right)^{\frac{3}{2}} \Gamma(3, z_i^*) - \left(\frac{\Xi_{ij}}{c_0}\right)^3 \Gamma\left(\frac{3}{2}, z_i^*\right) \right] \\
&= -\alpha\beta_{ij}\sigma_{ij}^2 \frac{8\sqrt{\pi}}{9} \frac{\mu_{ij}^2}{k_B T} c_i^\alpha c_j^\alpha \left[\left(\frac{2k_B T}{\mu_{ij}}\right)^{\frac{3}{2}} \Gamma(3, z_i^*) - \left(\frac{\Xi_{ij}}{c_0}\right)^3 \Gamma\left(\frac{3}{2}, z_i^*\right) \right] (\mathbf{u}_i^\alpha - \mathbf{u}_j^\alpha). \tag{5.4.25}
\end{aligned}$$

The integral $\tilde{\mathcal{P}}_i^{(2)}$ given in equation (5.4.19) vanishes upon evaluation, that is

$$\tilde{\mathcal{P}}_i^{(2)} = 0, \tag{5.4.26}$$

see Appendix B section B.2 for details of the computation. Therefore, substituting equations (5.4.25) and (5.4.26) into equation (5.4.19), we obtain:

$$\begin{aligned}
\tilde{\mathcal{P}}_i &= -\alpha\beta_{ij}\sigma_{ij}^2 \frac{8\sqrt{\pi}}{9} \frac{\mu_{ij}^2}{k_B T} c_i^\alpha c_j^\alpha \\
&\quad \times \left[\left(\frac{2k_B T}{\mu_{ij}}\right)^{\frac{3}{2}} \Gamma(3, z_i^*) - \left(\frac{\Xi_{ij}}{c_0}\right)^3 \Gamma\left(\frac{3}{2}, z_i^*\right) \right] (\mathbf{u}_i^\alpha - \mathbf{u}_j^\alpha) + O(\alpha^2). \tag{5.4.27}
\end{aligned}$$

Finally, let us evaluate the integral $\tilde{\mathcal{Q}}_i$ given in equation (5.4.12). To do this, we substitute equation (5.3.5) into the definition of the reactive collision operator $J_i^{\alpha R}$ given in equation (3.3.16) and expand to obtain:

$$\begin{aligned}
\tilde{\mathcal{Q}}_i = & \left. \beta_{ij} \sigma_{ij}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} m_i \mathbf{v}_i \left[\left(\frac{\mu_{ij}}{\mu_{kl}} \right)^2 M_k^{\alpha\circ} M_l^{\alpha\circ} - M_i^\alpha M_j^\alpha \right] \right. \\
& \times \Theta(\langle \boldsymbol{\epsilon}, c_0 \mathbf{v}_i - c_0 \mathbf{v}_j \rangle - \Xi_{ij}) \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_j \rangle d\boldsymbol{\epsilon} d\mathbf{v}_j d\mathbf{v}_i \left. \right\} \tilde{\mathcal{Q}}_i^{(1)} \\
& + \alpha \beta_{ij} \sigma_{ij}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} m_i \mathbf{v}_i \left[\left(\frac{\mu_{ij}}{\mu_{kl}} \right)^2 M_k^{\alpha\circ} M_l^{\alpha\circ} (\mathbf{a}_k \cdot \mathbf{v}_k^\circ + \mathbf{a}_l \cdot \mathbf{v}_l^\circ) - M_i^\alpha M_j^\alpha (\mathbf{a}_i \cdot \mathbf{v}_i + \mathbf{a}_j \cdot \mathbf{v}_j) \right] \\
& \times \Theta(\langle \boldsymbol{\epsilon}, c_0 \mathbf{v}_i - c_0 \mathbf{v}_j \rangle - \Xi_{ij}) \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_j \rangle d\boldsymbol{\epsilon} d\mathbf{v}_j d\mathbf{v}_i \left. \right\} \tilde{\mathcal{Q}}_i^{(2)} \\
& + \alpha \beta_{ij} \sigma_{ij}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} m_i \mathbf{v}_i \left[\left(\frac{\mu_{ij}}{\mu_{kl}} \right)^2 M_k^{\alpha\circ} M_l^{\alpha\circ} (b_k + b_l) - M_i^\alpha M_j^\alpha (b_i + b_j) \right] \\
& \times \Theta(\langle \boldsymbol{\epsilon}, c_0 \mathbf{v}_i - c_0 \mathbf{v}_j \rangle - \Xi_{ij}) \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_j \rangle d\boldsymbol{\epsilon} d\mathbf{v}_j d\mathbf{v}_i \left. \right\} \tilde{\mathcal{Q}}_i^{(3)} \\
& + \alpha \beta_{ij} \sigma_{ij}^2 \frac{3}{2T} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} m_i \mathbf{v}_i \left[- \left(\frac{\mu_{ij}}{\mu_{kl}} \right)^2 M_k^{\alpha\circ} M_l^{\alpha\circ} (T_k^\alpha + T_l^\alpha) + M_i^\alpha M_j^\alpha (T_i^\alpha + T_j^\alpha) \right] \\
& \times \Theta(\langle \boldsymbol{\epsilon}, c_0 \mathbf{v}_i - c_0 \mathbf{v}_j \rangle - \Xi_{ij}) \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_j \rangle d\boldsymbol{\epsilon} d\mathbf{v}_j d\mathbf{v}_i \left. \right\} \tilde{\mathcal{Q}}_i^{(4)} \\
& + O(\alpha^2). \tag{5.4.28}
\end{aligned}$$

The integrals $\tilde{\mathcal{Q}}_i^{(1)}$, $\tilde{\mathcal{Q}}_i^{(3)}$ and $\tilde{\mathcal{Q}}_i^{(4)}$ all vanish upon evaluation. That is,

$$\tilde{\mathcal{Q}}_i^{(1)} = 0, \quad \tilde{\mathcal{Q}}_i^{(3)} = 0, \quad \tilde{\mathcal{Q}}_i^{(4)} = 0, \tag{5.4.29}$$

see Appendix B sections B.3, B.4 and B.5, respectively for the details of the computations. Let us now compute the integral $\tilde{\mathcal{Q}}_i^{(2)}$. Expanding it, we obtain:

$$\begin{aligned}
\tilde{\mathcal{Q}}_i^{(2)} = & \left. \alpha \beta_{ij} \sigma_{ij}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} m_i \mathbf{v}_i \left(\frac{\mu_{ij}}{\mu_{kl}} \right)^2 M_k^{\alpha\circ} M_l^{\alpha\circ} (\mathbf{a}_k \cdot \mathbf{v}_k^\circ) \right. \\
& \times \Theta(\langle \boldsymbol{\epsilon}, c_0 \mathbf{v}_i - c_0 \mathbf{v}_j \rangle - \Xi_{ij}) \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_j \rangle d\boldsymbol{\epsilon} d\mathbf{v}_j d\mathbf{v}_i \left. \right\} \tilde{\mathcal{R}}_1 \\
& + \alpha \beta_{ij} \sigma_{ij}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} m_i \mathbf{v}_i \left(\frac{\mu_{ij}}{\mu_{kl}} \right)^2 M_k^{\alpha\circ} M_l^{\alpha\circ} (\mathbf{a}_l \cdot \mathbf{v}_l^\circ) \\
& \times \Theta(\langle \boldsymbol{\epsilon}, c_0 \mathbf{v}_i - c_0 \mathbf{v}_j \rangle - \Xi_{ij}) \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_j \rangle d\boldsymbol{\epsilon} d\mathbf{v}_j d\mathbf{v}_i \left. \right\} \tilde{\mathcal{R}}_2 \\
& - \underbrace{\alpha \beta_{ij} \sigma_{ij}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} m_i \mathbf{v}_i M_i^\alpha M_j^\alpha (\mathbf{a}_i \cdot \mathbf{v}_i) \Theta(\langle \boldsymbol{\epsilon}, c_0 \mathbf{v}_i - c_0 \mathbf{v}_j \rangle - \Xi_{ij}) \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_j \rangle d\boldsymbol{\epsilon} d\mathbf{v}_j d\mathbf{v}_i}_{\tilde{\mathcal{R}}_3} \\
& - \underbrace{\alpha \beta_{ij} \sigma_{ij}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} m_i \mathbf{v}_i M_i^\alpha M_j^\alpha (\mathbf{a}_j \cdot \mathbf{v}_j) \Theta(\langle \boldsymbol{\epsilon}, c_0 \mathbf{v}_i - c_0 \mathbf{v}_j \rangle - \Xi_{ij}) \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_j \rangle d\boldsymbol{\epsilon} d\mathbf{v}_j d\mathbf{v}_i}_{\tilde{\mathcal{R}}_4}.
\end{aligned}$$

It will be convenient to transform the integrals $\tilde{\mathcal{R}}_1$ and $\tilde{\mathcal{R}}_2$ from $(\mathbf{v}_i, \mathbf{v}_j)$ to $(\mathbf{v}_k^\circ, \mathbf{v}_l^\circ)$. To do this, we use equation (4.4.43) together with equation (2.3.20) and obtain:

$$\begin{aligned}
\tilde{\mathcal{R}}_1 &= \alpha \sigma_{ij}^2 \beta_{ij} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} m_k \mathbf{v}_k^\circ \left(\frac{\mu_{ij}}{\mu_{kl}} \right)^2 M_k^{\alpha\circ} M_l^{\alpha\circ} (\mathbf{a}_k \cdot \mathbf{v}_k^\circ) \Theta(\langle \boldsymbol{\epsilon}, c_0 \mathbf{v}_k^\circ - c_0 \mathbf{v}_l^\circ \rangle - \Xi_{kl}) \\
&\quad \times \left(\frac{\mu_{kl}}{\mu_{ij}} \right)^{\frac{1}{2}} \omega^+ \left(\frac{\mu_{kl}}{\mu_{ij}} \right)^{\frac{3}{2}} \frac{\langle \boldsymbol{\epsilon}, \mathbf{v}_k^\circ - \mathbf{v}_l^\circ \rangle}{\omega^+} d\boldsymbol{\epsilon} d\mathbf{v}_k^\circ d\mathbf{v}_l^\circ \\
&= \alpha \sigma_{ij}^2 \beta_{ij} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} m_k \mathbf{v}_k^\circ M_k^{\alpha\circ} M_l^{\alpha\circ} (\mathbf{a}_k \cdot \mathbf{v}_k^\circ) \Theta(\langle \boldsymbol{\epsilon}, c_0 \mathbf{v}_k^\circ - c_0 \mathbf{v}_l^\circ \rangle - \Xi_{kl}) \langle \boldsymbol{\epsilon}, \mathbf{v}_k^\circ - \mathbf{v}_l^\circ \rangle d\boldsymbol{\epsilon} d\mathbf{v}_k^\circ d\mathbf{v}_l^\circ, \\
\tilde{\mathcal{R}}_2 &= \alpha \sigma_{ij}^2 \beta_{ij} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} m_k \mathbf{v}_k^\circ \left(\frac{\mu_{ij}}{\mu_{kl}} \right)^2 M_k^{\alpha\circ} M_l^{\alpha\circ} (\mathbf{a}_l \cdot \mathbf{v}_l^\circ) \Theta(\langle \boldsymbol{\epsilon}, c_0 \mathbf{v}_k^\circ - c_0 \mathbf{v}_l^\circ \rangle - \Xi_{kl}) \\
&\quad \times \left(\frac{\mu_{kl}}{\mu_{ij}} \right)^{\frac{1}{2}} \omega^+ \left(\frac{\mu_{kl}}{\mu_{ij}} \right)^{\frac{3}{2}} \frac{\langle \boldsymbol{\epsilon}, \mathbf{v}_k^\circ - \mathbf{v}_l^\circ \rangle}{\omega^+} d\boldsymbol{\epsilon} d\mathbf{v}_k^\circ d\mathbf{v}_l^\circ \\
&= \alpha \sigma_{ij}^2 \beta_{ij} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} m_k \mathbf{v}_k^\circ M_k^{\alpha\circ} M_l^{\alpha\circ} (\mathbf{a}_l \cdot \mathbf{v}_l^\circ) \Theta(\langle \boldsymbol{\epsilon}, c_0 \mathbf{v}_k^\circ - c_0 \mathbf{v}_l^\circ \rangle - \Xi_{kl}) \langle \boldsymbol{\epsilon}, \mathbf{v}_k^\circ - \mathbf{v}_l^\circ \rangle d\boldsymbol{\epsilon} d\mathbf{v}_k^\circ d\mathbf{v}_l^\circ.
\end{aligned}$$

Thus the integral $\tilde{\mathcal{Q}}_i^{(2)}$ can be rewritten as given below:

$$\begin{aligned}
\tilde{\mathcal{Q}}_i^{(2)} &= \underbrace{\alpha \sigma_{ij}^2 \beta_{ij} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} m_k \mathbf{v}_k^\circ M_k^{\alpha\circ} M_l^{\alpha\circ} (\mathbf{a}_k \cdot \mathbf{v}_k^\circ) \Theta(\langle \boldsymbol{\epsilon}, c_0 \mathbf{v}_k^\circ - c_0 \mathbf{v}_l^\circ \rangle - \Xi_{kl}) \langle \boldsymbol{\epsilon}, \mathbf{v}_k^\circ - \mathbf{v}_l^\circ \rangle d\boldsymbol{\epsilon} d\mathbf{v}_k^\circ d\mathbf{v}_l^\circ}_{\tilde{\mathcal{R}}_1} \\
&\quad + \underbrace{\alpha \sigma_{ij}^2 \beta_{ij} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} m_k \mathbf{v}_k^\circ M_k^{\alpha\circ} M_l^{\alpha\circ} (\mathbf{a}_l \cdot \mathbf{v}_l^\circ) \Theta(\langle \boldsymbol{\epsilon}, c_0 \mathbf{v}_k^\circ - c_0 \mathbf{v}_l^\circ \rangle - \Xi_{kl}) \langle \boldsymbol{\epsilon}, \mathbf{v}_k^\circ - \mathbf{v}_l^\circ \rangle d\boldsymbol{\epsilon} d\mathbf{v}_k^\circ d\mathbf{v}_l^\circ}_{\tilde{\mathcal{R}}_2} \\
&\quad - \underbrace{\alpha \beta_{ij} \sigma_{ij}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} m_i \mathbf{v}_i M_i^\alpha M_j^\alpha (\mathbf{a}_i \cdot \mathbf{v}_i) \Theta(\langle \boldsymbol{\epsilon}, c_0 \mathbf{v}_i - c_0 \mathbf{v}_j \rangle - \Xi_{ij}) \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_j \rangle d\boldsymbol{\epsilon} d\mathbf{v}_j d\mathbf{v}_i}_{\tilde{\mathcal{R}}_3} \\
&\quad - \underbrace{\alpha \beta_{ij} \sigma_{ij}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} m_i \mathbf{v}_i M_i^\alpha M_j^\alpha (\mathbf{a}_j \cdot \mathbf{v}_j) \Theta(\langle \boldsymbol{\epsilon}, c_0 \mathbf{v}_i - c_0 \mathbf{v}_j \rangle - \Xi_{ij}) \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_j \rangle d\boldsymbol{\epsilon} d\mathbf{v}_j d\mathbf{v}_i}_{\tilde{\mathcal{R}}_4}.
\end{aligned}$$

The integrals $\tilde{\mathcal{R}}_1$, $\tilde{\mathcal{R}}_2$, $\tilde{\mathcal{R}}_3$ and $\tilde{\mathcal{R}}_4$ above are similar to $\bar{\mathcal{P}}_i^{(1)}$ given in equation (5.4.19). Therefore, using similar steps as those used in the computation of $\tilde{\mathcal{P}}_i^{(1)}$, we obtain:

$$\begin{aligned}
\tilde{\mathcal{Q}}_i^{(2)} &= \left. \begin{aligned} &\alpha \sigma_{ij}^2 \beta_{ij} \frac{m_k}{M} c_k^\alpha c_l^\alpha \mathbf{u}_k^\alpha \left(\frac{2\pi k_B T}{\mu_{kl}} \right)^{\frac{1}{2}} \left[m_k \Gamma(2, z_{i*}) + \frac{2m_l}{3} \Gamma(3, z_{i*}) \right] \\ &- \alpha \sigma_{ij}^2 \beta_{ij} \frac{m_k}{M} c_k^\alpha c_l^\alpha \mathbf{u}_k^\alpha \left(\frac{2\pi \mu_{kl}}{k_B T} \right)^{\frac{1}{2}} \left(\frac{\Xi_{kl}}{c_0} \right)^2 \left[m_k \Gamma(1, z_{i*}) + \frac{2m_l}{3} \Gamma(2, z_{i*}) \right] \end{aligned} \right\} \tilde{\mathcal{R}}_1 \\
&\quad + \left. \begin{aligned} &+ 2\alpha \sigma_{ij}^2 \beta_{ij} \frac{m_k}{M} c_k^\alpha c_l^\alpha m_l \mathbf{u}_l^\alpha \left(\frac{2\pi k_B T}{\mu_{kl}} \right)^{\frac{1}{2}} \left[\Gamma(2, z_{i*}) - \frac{2}{3} \Gamma(3, z_{i*}) \right] \\ &- \alpha \sigma_{ij}^2 \beta_{ij} \frac{m_k}{M} c_k^\alpha c_l^\alpha m_l \mathbf{u}_l^\alpha \left(\frac{\Xi_{kl}}{c_0} \right)^2 \left(\frac{2\pi \mu_{kl}}{k_B T} \right)^{\frac{1}{2}} \left[\Gamma(1, z_{i*}) - \frac{2}{3} \Gamma(2, z_{i*}) \right] \end{aligned} \right\} \tilde{\mathcal{R}}_2
\end{aligned}$$

$$\begin{aligned}
& \left. \begin{aligned}
& -2\alpha\beta_{ij}\sigma_{ij}^2 c_i^\alpha c_j^\alpha \frac{m_i}{M} \mathbf{u}_i^\alpha \left(\frac{2\pi k_B T}{\mu_{ij}} \right)^{\frac{1}{2}} \left[m_i \Gamma(2, z_i^*) + \frac{2}{3} m_j \Gamma(3, z_i^*) \right] \\
& + \alpha\beta_{ij}\sigma_{ij}^2 c_i^\alpha c_j^\alpha \frac{m_i}{M} \mathbf{u}_i^\alpha \left(\frac{\Xi_{ij}}{c_0} \right)^2 \left(\frac{2\pi\mu_{ij}}{k_B T} \right)^{\frac{1}{2}} \left[m_i \Gamma(1, z_i^*) + \frac{2}{3} m_j \Gamma(2, z_i^*) \right]
\end{aligned} \right\} \tilde{\mathcal{R}}_3 \\
& \left. \begin{aligned}
& -2\alpha\beta_{ij}\sigma_{ij}^2 c_i^\alpha c_j^\alpha m_i \mathbf{u}_j^\alpha \left(\frac{2\pi k_B T}{\mu_{ij}} \right)^{\frac{1}{2}} \frac{m_j}{M} \left[\Gamma(2, z_i^*) - \frac{2}{3} \Gamma(3, z_i^*) \right] \\
& + \alpha\beta_{ij}\sigma_{ij}^2 c_i^\alpha c_j^\alpha m_i \mathbf{u}_j^\alpha \left(\frac{\Xi_{ij}}{c_0} \right)^2 \left(\frac{2\pi\mu_{ij}}{k_B T} \right)^{\frac{1}{2}} \frac{m_j}{M} \left[\Gamma(1, z_i^*) - \frac{2}{3} \Gamma(2, z_i^*) \right],
\end{aligned} \right\} \tilde{\mathcal{R}}_4 \quad (5.4.30)
\end{aligned}$$

where $\Gamma(., .)$ the incomplete Euler gamma function defined as given in equation (4.3.3), z_{i*} , z_i^* and M are as defined in equations (4.3.4), (4.4.45) and (2.4.3), respectively.

Substituting equations (5.4.29) and (5.4.30) into equation (5.4.28), we obtain:

$$\begin{aligned}
\tilde{\mathcal{Q}}_i &= 0 + \tilde{\mathcal{Q}}_i^{(2)} + 0 + 0 + O(\alpha^2) \\
&= \tilde{\mathcal{Q}}_i^{(2)} + O(\alpha^2) \quad (5.4.31)
\end{aligned}$$

where $\tilde{\mathcal{Q}}_i^{(2)}$ is as given in equation (5.4.30).

Now substituting equations (5.4.18), (5.4.27) and (5.4.31) into equation (5.4.12) gives the desired result. Therefore, the proof is complete. $\square$

5.5 Formal Asymptotic Analysis

In this section, the formal asymptotic analysis of the momentum balance equations given by equation (5.4.1) to obtain the reactive Maxwell-Stefan equations will be carried out. More precisely, the proof of Theorem 5.2.1 will be given.

5.5.1 Proof of the Main Result

The result given in Theorem 5.2.1 is a consequence of Lemma 5.4.1. To prove Theorem 5.2.1, we substitute equation (4.5.4) into equation (5.4.12) and divide both sides of the resulting equation by k_B :

$$\alpha^2 \frac{m_i}{k_B} \frac{\partial}{\partial t} (\mathbf{J}_i^\alpha + c_i^\alpha \mathbf{u}^\alpha) + \frac{\partial}{\partial \mathbf{x}} \left(c_i^\alpha (T + \alpha T_i^\alpha) \right) + \alpha^2 \frac{m_i}{k_B} \frac{\partial}{\partial \mathbf{x}} \left(c_i^\alpha (\mathbf{u}_i^\alpha \otimes \mathbf{u}_i^\alpha) \right) = \frac{1}{\alpha k_B} (\tilde{\mathcal{O}}_i + \tilde{\mathcal{P}}_i + \tilde{\mathcal{Q}}_i),$$

where $\mathbf{u}^\alpha$, $\tilde{\mathcal{O}}_i$, $\tilde{\mathcal{P}}_i$ and $\tilde{\mathcal{Q}}_i$ are as given in equations (4.5.5), (5.4.18), (5.4.27) and (5.4.31), respectively. Furthermore, observe that similar to equation (4.5.4), one has that

$$c_k^\alpha \mathbf{u}_k^\alpha = \mathbf{J}_k^\alpha + c_k^\alpha \mathbf{u}^\alpha, \quad c_l^\alpha \mathbf{u}_l^\alpha = \mathbf{J}_l^\alpha + c_l^\alpha \mathbf{u}^\alpha, \quad c_s^\alpha \mathbf{u}_s^\alpha = \mathbf{J}_s^\alpha + c_s^\alpha \mathbf{u}^\alpha, \quad c_j^\alpha \mathbf{u}_j^\alpha = \mathbf{J}_j^\alpha + c_j^\alpha \mathbf{u}^\alpha. \quad (5.5.1)$$

Therefore, substituting (4.5.4) and (5.5.1) into equations (5.4.18), (5.4.27) and (5.4.31), one obtains that the term $c_i^\alpha c_s^\alpha (\mathbf{u}_i^\alpha - \mathbf{u}_s^\alpha)$ given in equation (5.4.18) becomes:

$$\begin{aligned}
c_i^\alpha c_s^\alpha (\mathbf{u}_i^\alpha - \mathbf{u}_s^\alpha) &= c_s^\alpha (\mathbf{J}_i^\alpha + c_i^\alpha \mathbf{u}^\alpha) - c_i^\alpha (\mathbf{J}_s^\alpha + c_s^\alpha \mathbf{u}^\alpha) \\
&= c_s^\alpha \mathbf{J}_i^\alpha + c_i^\alpha c_s^\alpha \mathbf{u}^\alpha - c_i^\alpha \mathbf{J}_s^\alpha - c_i^\alpha c_s^\alpha \mathbf{u}^\alpha \\
&= c_s^\alpha \mathbf{J}_i^\alpha - c_i^\alpha \mathbf{J}_s^\alpha.
\end{aligned}$$

Similarly, the term $c_i^\alpha c_j^\alpha (\mathbf{u}_i^\alpha - \mathbf{u}_j^\alpha)$ given in (5.4.27) becomes:

$$c_i^\alpha c_j^\alpha (\mathbf{u}_i^\alpha - \mathbf{u}_j^\alpha) = c_j^\alpha \mathbf{J}_i^\alpha - c_i^\alpha \mathbf{J}_j^\alpha.$$

Now taking the limit as $\alpha \rightarrow 0$, we obtain:

$$\frac{\partial}{\partial \mathbf{x}}(c_i T) = \frac{1}{k_B} (\tilde{\mathcal{O}}_i^* + \tilde{\mathcal{P}}_i^* + \tilde{\mathcal{Q}}_i^*), \quad (5.5.2)$$

where

$$\begin{aligned}
c_i &= \lim_{\alpha \rightarrow 0} c_i^\alpha, & \mathbf{J}_i &= \lim_{\alpha \rightarrow 0} \mathbf{J}_i^\alpha & \mathbf{u} &= \lim_{\alpha \rightarrow 0} \mathbf{u}^\alpha = 0 \\
\tilde{\mathcal{O}}_i^* &= \lim_{\alpha \rightarrow 0} \tilde{\mathcal{O}}_i^\alpha, & \tilde{\mathcal{P}}_i^* &= \lim_{\alpha \rightarrow 0} \tilde{\mathcal{P}}_i^\alpha, & \text{and} & \tilde{\mathcal{Q}}_i^* &= \lim_{\alpha \rightarrow 0} \tilde{\mathcal{Q}}_i^\alpha.
\end{aligned}$$

That $\mathbf{u}$ vanishes follows from assumption (a) given in subsection 5.3.2. Finally, performing a little algebra on the terms on the right-hand side of equation (5.5.2) gives the desired result.

5.6 Conclusion and discussion

In this chapter, the non-isothermal and isothermal reactive MS equations given in equations (5.2.1) and (5.2.2), respectively, were derived from the SRS kinetic model that describe a quaternary mixture of monatomic ideal gases undergoing a reversible chemical reaction of bi-molecular type. These derivations are the main results of this chapter. They were obtained thanks to the scaling of the kinetic equations, for which both mechanical collisions and chemical reactions have comparable relaxation times. The diffusion coefficients of the non-isothermal and isothermal reactive MS equations have been derived explicitly. With the exception of the first term on the right-hand side of the reactive MS equations, all other terms are new and they describe diffusion of the reactive species with enough energy to produce a chemical reaction.

In the general case of non-isothermal evolution, the reactive MS equations given in equation (5.2.1) should be coupled with the evolution equations for the concentration of the constituents and the energy conservation equation for the mixture. These equations are obtained by setting $\varphi_i = 1$ and $\varphi_i = \frac{1}{2}m_i \mathbf{v}_i + E_i$, respectively in equation (5.3.2) and integrating. The resulting system of equations will describe the evolution of $(c_i, \mathbf{J}_i, T)$. On the other hand, in the particular case of isothermal evolution, the reactive MS equations given in equation (5.2.2) should be coupled with the evolution equations for the concentration of the constituents. The resulting system of equations will describe the evolution of $(c_i, \mathbf{J}_i)$.

Finally, the analysis developed in this chapter can be extended to a reactive mixture of polyatomic gases and the resulting equations will certainly describe in a more complete way the involved chemical kinetics.

Chapter 6

On the Maxwell-Stefan diffusion limit for a reactive mixture of polyatomic gases in non-isothermal setting

This chapter contains the results published in Kinet. Relat. Models 2020, in collaboration with Mazia Bisi, Francesco Salvarani and Ana Jacinta Soares.

6.1 Introduction

Realistic models of multicomponent diffusion phenomena are crucial for many applications in fluid mechanics and chemistry. In the case of isothermal non-reactive gaseous mixtures, composed of at least three different constituents, the diffusive behaviour of the species is well described by the equations introduced by Maxwell and Stefan in [83, 105], which provide a more general and appropriate framework than the standard Fickian approach [52, 53].

Despite the popularity of Maxwell-Stefan (MS) model and its irreplaceability for many applications in chemical engineering [76, 77], the mathematical properties of the MS diffusion equations have only recently been investigated. In particular, the first studies have been devoted to the matrix formulation of the gradient-flux relationships (see [55] and the references therein). Subsequently, the well-posedness and the long-time behaviour of the solutions of the MS system (or some variants) have been studied in [23, 26, 41, 63, 70, 71]. Furthermore, the numerical simulation of the MS system has been the subject of [21, 26, 54, 87] and the relationships between Fickian diffusion and the MS model have been analysed in [29, 102]. By following the research line initiated by Bardos, Golse and Levermore in the Nineties – whose goal was the derivation of the equations of fluid mechanics starting from the Maxwell-Boltzmann equation [10, 11] – several articles have been published on the formal derivation of isothermal multicomponent MS type diffusion equations starting from the Maxwell-Boltzmann system for monatomic non-reactive gaseous mixtures [29, 27, 28, 68]. The case of a reactive mixture described by the SRS kinetic model, which retains the main features of the reaction mechanism without taking into account the internal degrees of

freedom of the particles, has been investigated in [5].

However, if one considers gaseous mixtures composed of polyatomic gases, with vibrational and rotational degrees of freedom, the standard monatomic models are no longer valid and the presence of possible chemical reactions in the mixture can considerably modify the behaviour of the system, making the model non-isothermal and non-conservative (at the level of the single species). The derivation of the precise structure of the equations describing the diffusive regime in this situation is – of course – crucial, and this is precisely the goal of this chapter.

The approach consists in obtaining the macroscopic equations starting from a kinetic system of equations defined in the phase-space, under a diffusive scaling. The effects of binary interactions between particles are treated as a simple scattering event involving, at the microscopic scale, only some fundamental laws (in particular, the conservation of momentum and total energy), without needing supplementary phenomenological hypotheses. Because of the solidity of the kinetic structure, the main macroscopic collective features of the system can subsequently be rigorously deduced by means of an appropriate limiting procedure of the kinetic model, rather than heuristically introduced in the macroscopic model. The result of this approach is a hierarchy of simpler models, which are validated by a precise asymptotic study considering the order of magnitude of the relevant parameters, and are suitable to be applied in some particular regime.

In the literature, there is a variety of kinetic models which have been proposed to go beyond the monatomic and non-reactive setting. Polyatomic non-reactive mixtures have been studied at the kinetic level, for example, in [17, 18, 31, 44], whereas various kinetic models for polyatomic reactive mixtures have been derived and studied in [12, 16, 45, 62].

The polyatomic structure of particles may be modelled by means of a set of discrete internal energy levels, or through a proper continuous internal energy variable. The basic features of the discrete levels description may be found in [55], while the state of art of Kinetic and Extended Thermodynamics approaches with a continuous energy have been summarised in [100].

In this chapter, the kinetic system proposed in [45] and described in section 2.4 will be considered. This kinetic model is based on the Borgnakke-Larsen procedure [22]. The kinetic model considered in this chapter have been chosen because of its main features and advantages detailed in [45]. This kinetic model describe a mixture of reactive polyatomic gases by adding to the usual independent variables of the phase-space of the system (that is, time t , position $\mathbf{x}$ and velocity $\mathbf{v}$) a continuous internal energy variable $I \in \mathbb{R}^+$, which governs, together with the kinetic energy, the binary encounters – both of reactive and of non-reactive type. By carefully choosing a set of measures $\varphi_i(I)dI$, the model is moreover consistent, at the macroscopic level, with the energy law of any type of polyatomic gas, and it does not need to take into account a large number of discrete energy levels.

In this chapter, for the sake of clarity, the study is limited to a quaternary mixture of polyatomic gases in the presence of a reversible chemical reaction of bimolecular type. This framework allows one to work in the general non-isothermal setting. Furthermore, some assumptions will be made at the kinetic level to enable the derivation a non-isothermal reaction-diffusion system where the diffusion process is modelled

by the MS equations as limit equations of the considered kinetic model. More specifically, we will assume that the bulk velocity of the mixture is small and vanishes in the limit, and also that the distribution functions are initially local Maxwellians centred at the average velocity of the species and remain with this structure during the evolution up to an error which vanishes in the limit. The set of equations obtained in this way include the evolution equations for the chemical species, the MS equations for the diffusive fluxes and the evolution equation for the temperature of the mixture. Of course, generalisations to more complicated mixtures with different types of chemical reactions are possible by considering an appropriate kinetic models and by introducing suitable modifications in the computations of chemical production rates. With respect to the standard isothermal non-reactive MS system, the equations obtained in this chapter show some crucial differences. First of all, the continuity equations for the various species, which would assure the conservation of the molar densities of the species, are replaced by balance equations, whose right-hand side takes into account the effects of the chemical reactions on the densities of the reactants. The balance terms, once the equilibrium is reached, guarantee the validity of the law of mass action, which depends on the internal energy structure of the species, on the temperature of the mixture and on the reaction heat Q_R . Moreover, one needs to also take into account the energy balance due to the effects of the chemical reactions.

In addition, worthy of mention is the fact that the target equations derived here are, up to the best of my knowledge, the only ones which take into account both the polyatomic structure of the constituents of the mixtures and the effect of chemical reactions in the non-isothermal setting.

The structure of this chapter is the following. In section 6.2, the scaling of the kinetic equations to be considered together with the assumptions needed for the derivation of the target equations will be introduced. In section 6.3, the moments of order zero and one of the scaled kinetic equations together with the energy balance equation for the mixture are deduced. The limiting diffusive equations for the reactive mixture are deduced in section 6.4. Finally, the conclusion which summarises the results presented in this chapter is given in section 6.5.

6.2 Scaled Equations and Assumptions

In this section, the scaling regime of the kinetic equations given in section 2.4, which describes the evolution of the polyatomic reactive mixture to be studied, is introduced. This will be followed by the assumptions to be considered at the kinetic level, to derive the non-isothermal reaction-diffusion system of MS type as the hydrodynamic limit equations of the considered kinetic model.

The evolution domain of the mixture is here represented by an open bounded domain $\Omega \subset \mathbb{R}^3$, with regular boundary.

6.2.1 Scaling regime

In this chapter, a diffusive scaling regime of the kinetic equations given in equation (2.4.56) for which elastic collisions are dominant with respect to reactive collisions, is considered. This regime is achieved

by setting $p = 1$ and $q = -1$ in the scaled kinetic equation given in equation (3.3.19). Accordingly, the starting point of the analysis presented in this chapter is the following scaled Cauchy problem for the distribution functions f_i^ε ,

$$\varepsilon \frac{\partial f_i^\varepsilon}{\partial t} + \mathbf{v} \cdot \nabla_{\mathbf{x}} f_i^\varepsilon = \frac{1}{\varepsilon} \sum_{j=1}^4 Q_{ij}^e(f_i^\varepsilon, f_j^\varepsilon) + \varepsilon Q_i^{react}, \quad i = 1, \dots, 4, \quad (6.2.1)$$

$$\text{for } (t, \mathbf{x}, \mathbf{v}, I) \in]0, +\infty[\times \mathbb{R}^3 \times \mathbb{R}^3 \times [0, +\infty[,$$

$$f_i^\varepsilon(0, \mathbf{x}, \mathbf{v}, I) = (f_i^{\text{in}})^\varepsilon(\mathbf{x}, \mathbf{v}, I), \quad \text{for } (\mathbf{x}, \mathbf{v}, I) \in \mathbb{R}^3 \times \mathbb{R}^3 \times [0, +\infty[, \quad (6.2.2)$$

where the elastic and reactive collision operators $Q_{ij}^e(f_i^\varepsilon, f_j^\varepsilon)$ and Q_i^{react} are as defined in equations (3.3.20) and (3.3.21), respectively.

Remark 6.2.1. *Note that the properties of the collision operators stated in subsection 2.4.2, with the obvious adjustments, are still valid for the scaled collision operators.* $\square$

6.2.2 Assumptions

In view of the reaction-diffusion limit to be investigated in this chapter, the following assumptions will be considered:

- (a) The reactive mixture is a non-isothermal system, meaning that the temperature of the mixture is, in general, not constant in time and non-uniform in space.
- (b) The bulk (mean or average) velocity of the mixture is small and goes to zero as the parameter ε tends to zero.
- (c) The initial conditions $(f_i^{\text{in}})^\varepsilon$ are Maxwellian functions centred at the species mean velocity $\varepsilon \mathbf{u}_i^{(\text{in})}(\mathbf{x})$ with species temperature $T^{(\text{in})}(\mathbf{x}) + \varepsilon T_i^{\varepsilon(\text{in})}(\mathbf{x})$ such that for $i = 1, 2, 3, 4$:

$$\begin{aligned} (f_i^{\text{in}})^\varepsilon(\mathbf{x}, \mathbf{v}, I) &= (M_i^{\text{in}})^\varepsilon \\ &= \frac{n_i^{\varepsilon(\text{in})}(\mathbf{x})}{q_i(T^{(\text{in})}(\mathbf{x}) + \varepsilon T_i^{\varepsilon(\text{in})}(\mathbf{x}))} \left(\frac{m_i}{2\pi k_B(T^{(\text{in})}(\mathbf{x}) + \varepsilon T_i^{\varepsilon(\text{in})}(\mathbf{x}))} \right)^{3/2} \\ &\quad \times \exp \left[-\frac{m_i(\mathbf{v} - \varepsilon \mathbf{u}_i^{\varepsilon(\text{in})}(\mathbf{x}))^2}{2k_B(T^{(\text{in})}(\mathbf{x}) + \varepsilon T_i^{\varepsilon(\text{in})}(\mathbf{x}))} \right] \\ &\quad \times \exp \left[-\frac{I}{k_B(T^{(\text{in})}(\mathbf{x}) + \varepsilon T_i^{\varepsilon(\text{in})}(\mathbf{x}))} \right] \end{aligned} \quad (6.2.3)$$

for some $n_i^{\varepsilon(\text{in})}$, $T^{(\text{in})}$, $T_i^{\varepsilon(\text{in})}$: $\Omega \rightarrow \mathbb{R}^+$ and $\mathbf{u}_i^{\varepsilon(\text{in})}$: $\Omega \rightarrow \mathbb{R}^3$.

- (d) The time evolution of f_i^ε established by the equations given in equation (6.2.1) preserves for any time $t > 0$ the initial Maxwellian structure of species distributions; more precisely, the distribution

functions f_i^ε , at time $t > 0$, are Maxwellians of the following form:

$$f_i^\varepsilon(\mathbf{v}, I) = \frac{n_i^\varepsilon(t, \mathbf{x})}{q_i(T(t, \mathbf{x}) + \varepsilon T_i^\varepsilon(t, \mathbf{x}))} \left(\frac{m_i}{2\pi k_B(T(t, \mathbf{x}) + \varepsilon T_i^\varepsilon(t, \mathbf{x}))} \right)^{3/2} \times \exp \left[-\frac{m_i(\mathbf{v} - \varepsilon \mathbf{u}_i^\varepsilon(t, \mathbf{x}))^2}{2k_B(T(t, \mathbf{x}) + \varepsilon T_i^\varepsilon(t, \mathbf{x}))} \right] \exp \left[-\frac{I}{k_B(T(t, \mathbf{x}) + \varepsilon T_i^\varepsilon(t, \mathbf{x}))} \right] \quad (6.2.4)$$

for some functions $n_i^\varepsilon, T_i^\varepsilon, T : \mathbb{R}^+ \times \Omega \rightarrow \mathbb{R}^+$ and $\mathbf{u}_i^\varepsilon : \mathbb{R}^+ \times \Omega \rightarrow \mathbb{R}^3$, with $i = 1, 2, 3, 4$.

Assumptions (c) and (d) are consistent with the fact that the scaled kinetic equations given in equation (6.2.1) provide, as $\varepsilon \rightarrow 0$,

$$\sum_{j=1}^4 Q_{ij}^e(f_i^\varepsilon, f_j^\varepsilon) = O(\varepsilon).$$

Hence the distributions f_i^ε should be, as $\varepsilon \rightarrow 0$, $O(\varepsilon)$ perturbations of collision equilibria of global elastic scattering operator, which are provided by local Maxwellians sharing the common zero mean velocity and a common temperature. Therefore, for any time $t > 0$, the species distributions may be considered to have the form:

$$f_i^\varepsilon(\mathbf{v}, I) = M_i^\varepsilon(n_i^\varepsilon(t, \mathbf{x}), \mathbf{0}, T(t, \mathbf{x})) (1 + O(\varepsilon)), \quad (6.2.5)$$

where M_i^ε is an elastic Maxwellian equilibrium state similar to the one defined in equation (2.4.75). Hence, up to the order $O(\varepsilon)$, one can suppose that

$$f_i^\varepsilon(\mathbf{v}, I) = M_i^\varepsilon(n_i^\varepsilon(t, \mathbf{x}), \varepsilon \mathbf{u}_i^\varepsilon(t, \mathbf{x}), T(t, \mathbf{x}) + \varepsilon T_i^\varepsilon(t, \mathbf{x}))$$

with

$$\lim_{\varepsilon \rightarrow 0} (n_i^\varepsilon(t, \mathbf{x}), \varepsilon \mathbf{u}_i^\varepsilon(t, \mathbf{x}), T(t, \mathbf{x}) + \varepsilon T_i^\varepsilon(t, \mathbf{x})) = (n_i(t, \mathbf{x}), \mathbf{0}, T(t, \mathbf{x})), \quad (6.2.6)$$

and

$$\mathbf{u}_i^\varepsilon(t, \mathbf{x}) = O(1), \quad T_i^\varepsilon(t, \mathbf{x}) = O(1).$$

The assumption given in equation (6.2.4) is one of the simplest options to fulfil the property given in equation (6.2.5), and it will be sufficient to obtain a system of MS type in the asymptotic limit $\varepsilon \rightarrow 0$.

6.3 Macroscopic Equations for the Reactive Mixture

In this section, the macroscopic equations that will be used to obtain the target system of equations, is derived. In particular, we will derive the balance equations for the number density of the species, the momentum balance equations for the species and the energy balance equation for the mixture, from the scaled kinetic equations given in equation (6.2.1). As usual in kinetic theory [10, 11, 13, 29, 68, 70], these equations are obtained by taking appropriate moments of the scaled kinetic equations with respect

to the velocity $\mathbf{v}$ and here also with respect to the internal energy parameter I . The macroscopic equations obtained in this section will be used in section 6.4 to obtain the non-isothermal reaction-diffusion system where the diffusion process is modelled by the MS equations. Furthermore, assumptions (d) given in subsection 6.2.2 play a crucial role in the computations presented in this section.

6.3.1 Preliminaries

In what follows, instead of the unit vector $\boldsymbol{\omega} \in \mathbb{S}^2$ parametrization used to obtain equations (2.4.23) and (2.4.44) for the elastic and reactive post-collision velocities, we will use the following unit vector $\boldsymbol{\sigma} \in \mathbb{S}^2$ parametrization and show how to pass from one to the other.

Proposition 6.3.1. *Let*

$$\boldsymbol{\sigma} = \mathbf{y} - 2(\boldsymbol{\omega} \cdot \mathbf{y})\boldsymbol{\omega}, \quad \mathbf{y} = \frac{\mathbf{v} - \mathbf{v}_*}{|\mathbf{v} - \mathbf{v}_*|}, \quad (6.3.1)$$

where $\boldsymbol{\sigma}$ and $\boldsymbol{\omega}$ are unit vectors in the sphere $\mathbb{S}^2$ and $\mathbf{v}$, $\mathbf{v}_*$ denote the velocities of the colliding pair of particles. The Jacobian of the transformation from $\boldsymbol{\omega}$ to $\boldsymbol{\sigma}$ is given by

$$J_{\boldsymbol{\omega} \rightarrow \boldsymbol{\sigma}} = 4|\boldsymbol{\omega} \cdot \mathbf{y}|, \quad \forall \mathbf{y} \in \mathbb{R}^3. \quad (6.3.2)$$

Proof. See [90], page 41. □

Remark 6.3.2.

- (i) Using the $\boldsymbol{\sigma}$ -parametrization given in equation (6.3.1), the post-collision velocities given in equation (2.4.29) for a bi-species elastic collision between a particle of species i with in-going parameters $(\mathbf{v}, I)$ and a particle of species j with parameters $(\mathbf{v}_j, I_j)$ can be rewritten as

$$\begin{aligned} \mathbf{v}'_i &= \frac{m_i \mathbf{v} + m_j \mathbf{v}_j}{m_i + m_j} + \frac{m_j}{m_i + m_j} \sqrt{\frac{2R\mathcal{E}}{\mu_{ij}}} \boldsymbol{\sigma}, \\ \mathbf{v}'_j &= \frac{m_i \mathbf{v} + m_j \mathbf{v}_j}{m_i + m_j} - \frac{m_i}{m_i + m_j} \sqrt{\frac{2R\mathcal{E}}{\mu_{ij}}} \boldsymbol{\sigma}. \end{aligned} \quad (6.3.3)$$

Therefore,

$$\mathbf{v}'_i - \mathbf{v} = \frac{m_j}{m_i + m_j} \widehat{\mathbf{V}}^* + \frac{m_j}{m_i + m_j} \sqrt{\frac{2R\mathcal{E}}{\mu_{ij}}} \boldsymbol{\sigma}, \quad (6.3.4)$$

where

$$\widehat{\mathbf{V}}^* = \mathbf{v}_j - \mathbf{v} \quad (6.3.5)$$

is the relative velocity.

(ii) As a consequence of Proposition 6.3.1, the bi-species elastic and the reactive collision kernels can be written as follows (see [108]):

$$B_{ij}(\mathbf{v}, \mathbf{v}_j, I, I_j, R, r, \boldsymbol{\omega}) d\boldsymbol{\omega} = 2 |\boldsymbol{\omega} \cdot \mathbf{y}| B_{ij}(\mathbf{v}, \mathbf{v}_j, I, I_j, R, r, \boldsymbol{\sigma}) d\boldsymbol{\sigma}, \quad (6.3.6)$$

$$B^{react}(\mathbf{v}, \mathbf{v}_j, I, I_j, R, r, \boldsymbol{\omega}) d\boldsymbol{\omega} = 2 |\boldsymbol{\omega} \cdot \mathbf{y}| B^{react}(\mathbf{v}, \mathbf{v}_j, I, I_j, R, r, \boldsymbol{\sigma}) d\boldsymbol{\sigma}, \quad (6.3.7)$$

$$\text{where } \mathbf{y} = -\frac{\widehat{\mathbf{V}}^*}{|\widehat{\mathbf{V}}^*|}.$$

□

From now on, for brevity the dependencies of distribution functions on velocity and internal energy, will be skipped, that is, the following notations will be used:

$$f_i^\varepsilon = f_i^\varepsilon(\mathbf{v}, I), f_j^\varepsilon = f_j^\varepsilon(\mathbf{v}_j, I_j), f_i^{\varepsilon'} = f_i^\varepsilon(\mathbf{v}'_i, I'_i), f_j^{\varepsilon'} = f_j^\varepsilon(\mathbf{v}'_j, I'_j).$$

Analogously for Maxwellian distributions, its dependence on $n_i^\varepsilon, \mathbf{0}, T$ will be omitted and the following notation $M_i^\varepsilon = M_i^\varepsilon(n_i^\varepsilon(t, \mathbf{x}), \mathbf{0}, T(t, \mathbf{x}))$, will be used.

Proposition 6.3.3. Using the Taylor expansion with respect to ε of the distribution functions given in equation (6.2.4), one can write

$$(a) f_i^{\varepsilon'} f_j^{\varepsilon'} - f_i^\varepsilon f_j^\varepsilon = M_i^\varepsilon M_j^\varepsilon \left[\varepsilon \left(\mathbf{a}_{ij} \cdot (\mathbf{v}'_i - \mathbf{v}) \right) + \varepsilon \left(\frac{T_i^\varepsilon}{k_B T^2} - \frac{T_j^\varepsilon}{k_B T^2} \right) \right. \\ \left. \times \left(\frac{m_i(\mathbf{v}'_i)^2}{2} - \frac{m_i(\mathbf{v})^2}{2} + I'_i - I \right) + O(\varepsilon^2) \right], \quad (6.3.8)$$

$$(b) \left(\frac{m_i m_j}{m_k m_l} \right)^3 f_k^{\varepsilon'} f_l^{\varepsilon'} - f_i^\varepsilon f_j^\varepsilon = \left(\frac{m_i m_j}{m_k m_l} \right)^3 M_k^{\varepsilon'} M_l^{\varepsilon'} - M_i^\varepsilon M_j^\varepsilon + \varepsilon \left[\left(\frac{m_i m_j}{m_k m_l} \right)^3 \right. \\ \times M_k^{\varepsilon'} M_l^{\varepsilon'} \left(\mathbf{a}_k \cdot \mathbf{v}'_k + \frac{m_k T_k^\varepsilon (\mathbf{v}'_k)^2}{2 k_B T^2} + \frac{T_k^\varepsilon I'_k}{k_B T^2} - \frac{T_k^\varepsilon}{T} \frac{q_k^*(T)}{k_B T q_k(T)} \right. \\ \left. - \frac{3 T_k^\varepsilon}{2 T} + \mathbf{a}_l \cdot \mathbf{v}'_l + \frac{m_l T_l^\varepsilon (\mathbf{v}'_l)^2}{2 k_B T^2} + \frac{T_l^\varepsilon I'_l}{k_B T^2} - \frac{T_l^\varepsilon}{T} \frac{q_l^*(T)}{k_B T q_l(T)} - \frac{3 T_l^\varepsilon}{2 T} \right) \\ \left. - M_i^\varepsilon M_j^\varepsilon \left(\mathbf{a}_i \cdot \mathbf{v} + \frac{m_i T_i^\varepsilon (\mathbf{v})^2}{2 k_B T^2} + \frac{T_i^\varepsilon I}{k_B T^2} - \frac{T_i^\varepsilon}{T} \frac{q_i^*(T)}{k_B T q_i(T)} - \frac{3 T_i^\varepsilon}{2 T} \right. \right. \\ \left. \left. + \mathbf{a}_j \cdot \mathbf{v}_j + \frac{m_j T_j^\varepsilon (\mathbf{v}_j)^2}{2 k_B T^2} + \frac{T_j^\varepsilon I_j}{k_B T^2} - \frac{T_j^\varepsilon}{T} \frac{q_j^*(T)}{k_B T q_j(T)} - \frac{3 T_j^\varepsilon}{2 T} \right) \right] + O(\varepsilon^2), \quad (6.3.9)$$

where

$$\mathbf{a}_{ij} = \frac{m_i(\mathbf{u}_i^\varepsilon - \mathbf{u}_j^\varepsilon)}{k_B T}, \quad \mathbf{a}_i = \frac{m_i \mathbf{u}_i^\varepsilon}{k_B T}, \quad \mathbf{a}_j = \frac{m_j \mathbf{u}_j^\varepsilon}{k_B T}, \quad \mathbf{a}_k = \frac{m_k \mathbf{u}_k^\varepsilon}{k_B T}, \quad \mathbf{a}_l = \frac{m_l \mathbf{u}_l^\varepsilon}{k_B T}, \quad (6.3.10)$$

$$q_i^*(T) = \int_0^{+\infty} I \varphi_i(I) \exp\left(-\frac{I}{k_B T}\right) dI, \quad (6.3.11)$$

$$M_i^\varepsilon := \frac{n_i^\varepsilon}{q_i(T)} \left(\frac{m_i}{2\pi k_B T} \right)^{\frac{3}{2}} \exp \left(-\frac{m_i(\mathbf{v})^2}{2k_B T} - \frac{I}{k_B T} \right), \quad (6.3.12)$$

and M_j^ε , $M_k^{\varepsilon'}$, $M_l^{\varepsilon'}$ are similarly defined.

Proof. Observe that following the same procedures as those used to obtain equations (5.3.7) and (5.3.8), we obtain:

$$\exp \left(-\frac{m_i(\mathbf{v} - \varepsilon \mathbf{u}_i^\varepsilon)^2}{2k_B(T + \varepsilon T_i^\varepsilon)} \right) = \exp \left(-\frac{m_i(\mathbf{v})^2}{2k_B T} \right) \left(1 + \varepsilon \frac{m_i \mathbf{u}_i^\varepsilon \cdot \mathbf{v}}{k_B T} + \varepsilon \frac{m_i T_i^\varepsilon (\mathbf{v})^2}{2k_B T^2} + O(\varepsilon^2) \right) \quad (6.3.13)$$

and

$$\left(\frac{m_i}{2\pi k_B(T + \varepsilon T_i^\varepsilon)} \right)^{\frac{3}{2}} = \left(\frac{m_i}{2\pi k_B T} \right)^{\frac{3}{2}} \left(1 - \varepsilon \frac{3T_i}{2T} + O(\varepsilon^2) \right), \quad (6.3.14)$$

respectively. Taylor expanding the second exponential in equation (6.2.4) with respect to ε gives:

$$\begin{aligned} \exp \left(-\frac{I}{k_B(T + \varepsilon T_i^\varepsilon)} \right) &= \exp \left(-\frac{I}{k_B T} \right) + \varepsilon \frac{T_i^\varepsilon I}{k_B T^2} \exp \left(-\frac{I}{k_B T} \right) + O(\varepsilon^2) \\ &= \exp \left(-\frac{I}{k_B T} \right) \left(1 + \varepsilon \frac{T_i^\varepsilon I}{k_B T^2} + O(\varepsilon^2) \right). \end{aligned} \quad (6.3.15)$$

Taylor expanding the first term on the right-hand side of equation (6.2.4) with respect to ε gives:

$$\begin{aligned} \frac{n_i^\varepsilon}{q_i(T + \varepsilon T_i^\varepsilon)} &= \frac{n_i^\varepsilon}{q_i(T)} - \varepsilon \frac{q_i^*(T)}{k_B T q_i(T)} \frac{T_i^\varepsilon}{T} \frac{n_i^\varepsilon}{q_i(T)} + O(\varepsilon^2) \\ &= \frac{n_i^\varepsilon}{q_i(T)} \left(1 - \varepsilon \frac{q_i^*(T)}{k_B T q_i(T)} \frac{T_i^\varepsilon}{T} + O(\varepsilon^2) \right), \end{aligned} \quad (6.3.16)$$

where $q_i^*(T)$ is as defined in equation (6.3.11).

Taking the product of equations (6.3.13), (6.3.14), (6.3.15) and (6.3.16) gives the following expanded form of the distribution function:

$$\begin{aligned} f_i^\varepsilon &= \frac{n_i^\varepsilon}{q_i(T)} \left(\frac{m_i}{2\pi k_B T} \right)^{\frac{3}{2}} \exp \left(-\frac{m_i(\mathbf{v})^2}{2k_B T} - \frac{I}{k_B T} \right) \\ &\times \left[1 + \varepsilon \frac{m_i \mathbf{v} \cdot \mathbf{u}_i^\varepsilon}{k_B T} + \varepsilon \frac{m_i(\mathbf{v})^2 T_i^\varepsilon}{2k_B T^2} + \varepsilon \frac{I T_i^\varepsilon}{k_B T^2} - \varepsilon \frac{q_i^*(T)}{k_B T q_i(T)} \frac{T_i^\varepsilon}{T} - \varepsilon \frac{3 T_i^\varepsilon}{2 T} + O(\varepsilon^2) \right] \\ &= M_i^\varepsilon \left[1 + \varepsilon \frac{m_i \mathbf{v} \cdot \mathbf{u}_i^\varepsilon}{k_B T} + \varepsilon \frac{m_i(\mathbf{v})^2 T_i^\varepsilon}{2k_B T^2} + \varepsilon \frac{I T_i^\varepsilon}{k_B T^2} - \varepsilon \frac{q_i^*(T)}{k_B T q_i(T)} \frac{T_i^\varepsilon}{T} - \varepsilon \frac{3 T_i^\varepsilon}{2 T} + O(\varepsilon^2) \right]. \end{aligned} \quad (6.3.17)$$

Similarly, expansion like equation (6.3.17) can be obtained for f_j^ε , $f_i^{\varepsilon'}$, $f_j^{\varepsilon'}$, $f_k^{\varepsilon'}$ and $f_l^{\varepsilon'}$.

To prove part (a), observe that using the expanded form of the distribution functions, we obtain:

$$f_i^\varepsilon f_j^\varepsilon = M_i^\varepsilon M_j^\varepsilon \left[1 + \varepsilon \frac{m_i \mathbf{v} \cdot \mathbf{u}_i^\varepsilon}{k_B T} + \varepsilon \frac{m_i(\mathbf{v})^2 T_i^\varepsilon}{2k_B T^2} + \varepsilon \frac{I T_i^\varepsilon}{k_B T^2} + \varepsilon \frac{m_j \mathbf{v}_j \cdot \mathbf{u}_j^\varepsilon}{k_B T} + \varepsilon \frac{m_j(\mathbf{v}_j)^2 T_j^\varepsilon}{2k_B T^2} \right]$$

$$+ \varepsilon \frac{I_j T_j^\varepsilon}{k_B T^2} - \varepsilon \frac{q_i^*(T)}{k_B T q_i(T)} \frac{T_i^\varepsilon}{T} - \varepsilon \frac{3 T_i^\varepsilon}{2 T} - \varepsilon \frac{q_j^*(T)}{k_B T q_j(T)} \frac{T_j^\varepsilon}{T} - \varepsilon \frac{3 T_j^\varepsilon}{2 T} + O(\varepsilon^2) \Big] \quad (6.3.18)$$

and

$$\begin{aligned} f_i^{\varepsilon'} f_j^{\varepsilon'} = & M_i^{\varepsilon'} M_j^{\varepsilon'} \left[1 + \varepsilon \frac{m_i \mathbf{v}_i' \cdot \mathbf{u}_i^\varepsilon}{k_B T} + \varepsilon \frac{m_i (\mathbf{v}_i')^2 T_i^\varepsilon}{2 k_B T^2} + \varepsilon \frac{I_i' T_i^\varepsilon}{k_B T^2} + \varepsilon \frac{m_j \mathbf{v}_j' \cdot \mathbf{u}_j^\varepsilon}{k_B T} + \varepsilon \frac{m_j (\mathbf{v}_j')^2 T_j^\varepsilon}{2 k_B T^2} \right. \\ & \left. + \varepsilon \frac{I_j' T_j^\varepsilon}{k_B T^2} - \varepsilon \frac{q_i^*(T)}{k_B T q_i(T)} \frac{T_i^\varepsilon}{T} - \varepsilon \frac{3 T_i^\varepsilon}{2 T} - \varepsilon \frac{q_j^*(T)}{k_B T q_j(T)} \frac{T_j^\varepsilon}{T} - \varepsilon \frac{3 T_j^\varepsilon}{2 T} + O(\varepsilon^2) \right]. \quad (6.3.19) \end{aligned}$$

Furthermore, observe that

$$M_i^{\varepsilon'} M_j^{\varepsilon'} = \frac{n_i^\varepsilon}{q_i(T)} \left(\frac{m_i}{2\pi k_B T} \right)^{\frac{3}{2}} \frac{n_j^\varepsilon}{q_j(T)} \left(\frac{m_j}{2\pi k_B T} \right)^{\frac{3}{2}} \exp \left(-\frac{m_i (\mathbf{v}_i')^2 + m_j (\mathbf{v}_j')^2}{2 k_B T} - \frac{I_i' + I_j'}{k_B T} \right).$$

Using the conservation of energy for elastic collisions given in equation (2.4.2), we obtain:

$$\begin{aligned} M_i^{\varepsilon'} M_j^{\varepsilon'} &= \frac{n_i^\varepsilon}{q_i(T)} \left(\frac{m_i}{2\pi k_B T} \right)^{\frac{3}{2}} \frac{n_j^\varepsilon}{q_j(T)} \left(\frac{m_j}{2\pi k_B T} \right)^{\frac{3}{2}} \exp \left(-\frac{m_i (\mathbf{v})^2 + m_j (\mathbf{v}_j)^2}{2 k_B T} - \frac{I + I_j}{k_B T} \right) \\ &= M_i^\varepsilon M_j^\varepsilon. \end{aligned}$$

Therefore,

$$\begin{aligned} f_i^{\varepsilon'} f_j^{\varepsilon'} - f_i^\varepsilon f_j^\varepsilon &= M_i^\varepsilon M_j^\varepsilon \left[1 + \varepsilon \frac{m_i \mathbf{v}_i' \cdot \mathbf{u}_i^\varepsilon}{k_B T} + \varepsilon \frac{m_i (\mathbf{v}_i')^2 T_i^\varepsilon}{2 k_B T^2} + \varepsilon \frac{I_i' T_i^\varepsilon}{k_B T^2} + \varepsilon \frac{m_j \mathbf{v}_j' \cdot \mathbf{u}_j^\varepsilon}{k_B T} + \varepsilon \frac{m_j (\mathbf{v}_j')^2 T_j^\varepsilon}{2 k_B T^2} \right. \\ &+ \varepsilon \frac{I_j' T_j^\varepsilon}{k_B T^2} - \varepsilon \frac{q_i^*(T)}{k_B T q_i(T)} \frac{T_i^\varepsilon}{T} - \varepsilon \frac{3 T_i^\varepsilon}{2 T} - \varepsilon \frac{q_j^*(T)}{k_B T q_j(T)} \frac{T_j^\varepsilon}{T} - \varepsilon \frac{3 T_j^\varepsilon}{2 T} + O(\varepsilon^2) \Big] \\ &- M_i^\varepsilon M_j^\varepsilon \left[1 + \varepsilon \frac{m_i \mathbf{v} \cdot \mathbf{u}_i^\varepsilon}{k_B T} + \varepsilon \frac{m_i (\mathbf{v})^2 T_i^\varepsilon}{2 k_B T^2} + \varepsilon \frac{I T_i^\varepsilon}{k_B T^2} + \varepsilon \frac{m_j \mathbf{v}_j \cdot \mathbf{u}_j^\varepsilon}{k_B T} + \varepsilon \frac{m_j (\mathbf{v}_j)^2 T_j^\varepsilon}{2 k_B T^2} \right. \\ &+ \varepsilon \frac{I_j T_j^\varepsilon}{k_B T^2} - \varepsilon \frac{q_i^*(T)}{k_B T q_i(T)} \frac{T_i^\varepsilon}{T} - \varepsilon \frac{3 T_i^\varepsilon}{2 T} - \varepsilon \frac{q_j^*(T)}{k_B T q_j(T)} \frac{T_j^\varepsilon}{T} - \varepsilon \frac{3 T_j^\varepsilon}{2 T} + O(\varepsilon^2) \Big]. \end{aligned}$$

Putting together terms of the same order in ε gives:

$$\begin{aligned} f_i^{\varepsilon'} f_j^{\varepsilon'} - f_i^\varepsilon f_j^\varepsilon &= \left[M_i^\varepsilon M_j^\varepsilon - M_i^\varepsilon M_j^\varepsilon \right] + \varepsilon M_i^\varepsilon M_j^\varepsilon \left[\frac{m_i (\mathbf{u}_i^\varepsilon \cdot \mathbf{v}_i')}{k_B T} - \frac{m_i (\mathbf{u}_i^\varepsilon \cdot \mathbf{v})}{k_B T} + \frac{m_i T_i^\varepsilon (\mathbf{v}_i')^2}{2 k_B T^2} \right. \\ &- \frac{m_i T_i^\varepsilon (\mathbf{v})^2}{2 k_B T^2} + \frac{I_i' T_i^\varepsilon}{k_B T^2} - \frac{I T_i^\varepsilon}{k_B T^2} + \frac{m_j (\mathbf{u}_j^\varepsilon \cdot \mathbf{v}_j')}{k_B T} - \frac{m_j (\mathbf{u}_j^\varepsilon \cdot \mathbf{v}_j)}{k_B T} + \frac{m_j T_j^\varepsilon (\mathbf{v}_j')^2}{2 k_B T^2} \\ &- \frac{m_j T_j^\varepsilon (\mathbf{v}_j)^2}{2 k_B T^2} + \frac{I_j' T_j^\varepsilon}{k_B T^2} - \frac{I_j T_j^\varepsilon}{k_B T^2} - \frac{q_i^*(T)}{k_B T q_i(T)} \frac{T_i^\varepsilon}{T} + \frac{q_i^*(T)}{k_B T q_i(T)} \frac{T_i^\varepsilon}{T} \\ &- \frac{q_j^*(T)}{k_B T q_j(T)} \frac{T_j^\varepsilon}{T} + \frac{q_j^*(T)}{k_B T q_j(T)} \frac{T_j^\varepsilon}{T} - \frac{3 T_i^\varepsilon}{2 T} + \frac{3 T_i^\varepsilon}{2 T} - \frac{3 T_j^\varepsilon}{2 T} + \frac{3 T_j^\varepsilon}{2 T} \Big] + O(\varepsilon^2) \end{aligned}$$

$$\begin{aligned}
&= \varepsilon M_i^\varepsilon M_j^\varepsilon \left[\frac{m_i(\mathbf{u}_i^\varepsilon \cdot \mathbf{v}_i')}{k_B T} - \frac{m_i(\mathbf{u}_i^\varepsilon \cdot \mathbf{v})}{k_B T} + \frac{m_i T_i^\varepsilon (\mathbf{v}_i')^2}{2k_B T^2} - \frac{m_i T_i^\varepsilon (\mathbf{v})^2}{2k_B T^2} + \frac{I_i' T_i^\varepsilon}{k_B T^2} \right. \\
&\quad - \frac{I T_i^\varepsilon}{k_B T^2} + \frac{m_j(\mathbf{u}_j^\varepsilon \cdot \mathbf{v}_j')}{k_B T} - \frac{m_j(\mathbf{u}_j^\varepsilon \cdot \mathbf{v}_j)}{k_B T} + \frac{m_j T_j^\varepsilon (\mathbf{v}_j')^2}{2k_B T^2} - \frac{m_j T_j^\varepsilon (\mathbf{v}_j)^2}{2k_B T^2} + \frac{I_j' T_j^\varepsilon}{k_B T^2} \\
&\quad \left. - \frac{I_j T_j^\varepsilon}{k_B T^2} \right] + O(\varepsilon^2) \\
&= \varepsilon M_i^\varepsilon M_j^\varepsilon \left[\frac{\mathbf{u}_i^\varepsilon \cdot m_i(\mathbf{v}_i' - \mathbf{v})}{k_B T} + \frac{\mathbf{u}_j^\varepsilon \cdot m_j(\mathbf{v}_j' - \mathbf{v}_j)}{k_B T} + \frac{T_i^\varepsilon}{k_B T^2} \left(\frac{m_i(\mathbf{v}_i')^2}{2} - \frac{m_i(\mathbf{v})^2}{2} + I_i' - I \right) \right. \\
&\quad \left. + \frac{T_j^\varepsilon}{k_B T^2} \left(\frac{m_j(\mathbf{v}_j')^2}{2} - \frac{m_j(\mathbf{v}_j)^2}{2} + I_j' - I_j \right) \right] + O(\varepsilon^2).
\end{aligned}$$

Using the conservation laws of linear momentum given in equation (2.4.1) and kinetic energy given in equation (2.4.2), for elastic collisions, but rewritten as given below

$$\begin{aligned}
m_i(\mathbf{v}_i' - \mathbf{v}) &= -m_j(\mathbf{v}_j' - \mathbf{v}_j), \\
\frac{1}{2}m_i(\mathbf{v}_i')^2 - \frac{1}{2}m_i(\mathbf{v})^2 + I_i' - I &= \frac{1}{2}m_j(\mathbf{v}_j')^2 - \frac{1}{2}m_j(\mathbf{v}_j)^2 + I_j' - I_j,
\end{aligned}$$

we obtain:

$$\begin{aligned}
&f_i^{\varepsilon'} f_j^{\varepsilon'} - f_i^\varepsilon f_j^\varepsilon \\
&= \varepsilon M_i^\varepsilon M_j^\varepsilon \left[\frac{\mathbf{u}_i^\varepsilon \cdot m_i(\mathbf{v}_i' - \mathbf{v})}{k_B T} - \frac{\mathbf{u}_j^\varepsilon \cdot m_i(\mathbf{v}_i' - \mathbf{v})}{k_B T} + \frac{T_i^\varepsilon}{k_B T^2} \left(\frac{m_i(\mathbf{v}_i')^2}{2} - \frac{m_i(\mathbf{v})^2}{2} + I_i' - I \right) \right. \\
&\quad \left. - \frac{T_j^\varepsilon}{k_B T^2} \left(\frac{m_i(\mathbf{v}_i')^2}{2} - \frac{m_i(\mathbf{v})^2}{2} + I_i' - I \right) \right] + O(\varepsilon^2). \\
&= \varepsilon M_i^\varepsilon M_j^\varepsilon \left[\frac{m_i(\mathbf{u}_i^\varepsilon - \mathbf{u}_j^\varepsilon)}{k_B T} \cdot (\mathbf{v}_i' - \mathbf{v}) + \left(\frac{T_i^\varepsilon}{k_B T^2} - \frac{T_j^\varepsilon}{k_B T^2} \right) \left(\frac{m_i(\mathbf{v}_i')^2}{2} - \frac{m_i(\mathbf{v})^2}{2} + I_i' - I \right) \right] \\
&\quad + O(\varepsilon^2)
\end{aligned}$$

and part (a) is proven.

To prove part (b), we again use the expanded form of the distribution functions to obtain:

$$\begin{aligned}
\left(\frac{m_i m_j}{m_k m_l} \right)^3 f_k^{\varepsilon'} f_l^{\varepsilon'} &= \left(\frac{m_i m_j}{m_k m_l} \right)^3 M_k^{\varepsilon'} M_l^{\varepsilon'} \left[1 + \varepsilon \frac{m_k \mathbf{v}_k' \cdot \mathbf{u}_k^\varepsilon}{k_B T} + \varepsilon \frac{m_k (\mathbf{v}_k')^2 T_k^\varepsilon}{2k_B T^2} + \varepsilon \frac{I_k' T_k^\varepsilon}{k_B T^2} \right. \\
&\quad + \varepsilon \frac{m_l \mathbf{v}_l' \cdot \mathbf{u}_l^\varepsilon}{k_B T} + \varepsilon \frac{m_l (\mathbf{v}_l')^2 T_l^\varepsilon}{2k_B T^2} + \varepsilon \frac{I_l' T_l^\varepsilon}{k_B T^2} - \varepsilon \frac{q_k^*(T)}{k_B T q_k(T)} \frac{T_k^\varepsilon}{T} - \varepsilon \frac{3}{2} \frac{T_k^\varepsilon}{T} \\
&\quad \left. - \varepsilon \frac{q_l^*(T)}{k_B T q_l(T)} \frac{T_l^\varepsilon}{T} - \varepsilon \frac{3}{2} \frac{T_l^\varepsilon}{T} + O(\varepsilon^2) \right]. \quad (6.3.20)
\end{aligned}$$

Using equations (6.3.18) and (6.3.20), we obtain:

$$\left(\frac{m_i m_j}{m_k m_l} \right)^3 f_k^{\varepsilon'} f_l^{\varepsilon'} - f_i^\varepsilon f_j^\varepsilon = \left(\frac{m_i m_j}{m_k m_l} \right)^3 M_k^{\varepsilon'} M_l^{\varepsilon'} \left[1 + \varepsilon \frac{m_k \mathbf{v}_k' \cdot \mathbf{u}_k^\varepsilon}{k_B T} + \varepsilon \frac{m_k (\mathbf{v}_k')^2 T_k^\varepsilon}{2k_B T^2} + \varepsilon \frac{I_k' T_k^\varepsilon}{k_B T^2} \right.$$

$$\begin{aligned}
& + \varepsilon \frac{m_l \mathbf{v}_l' \cdot \mathbf{u}_l^\varepsilon}{k_B T} + \varepsilon \frac{m_l (\mathbf{v}_l')^2 T_l^\varepsilon}{2k_B T^2} + \varepsilon \frac{I_l' T_l^\varepsilon}{k_B T^2} - \varepsilon \frac{q_k^*(T)}{k_B T q_k(T)} \frac{T_k^\varepsilon}{T} - \varepsilon \frac{3 T_k^\varepsilon}{2 T} \\
& - \varepsilon \frac{q_l^*(T)}{k_B T q_l(T)} \frac{T_l^\varepsilon}{T} - \varepsilon \frac{3 T_l^\varepsilon}{2 T} + O(\varepsilon^2) \Big] - M_i^\varepsilon M_j^\varepsilon \left[1 + \varepsilon \frac{m_i \mathbf{v} \cdot \mathbf{u}_i^\varepsilon}{k_B T} \right. \\
& + \varepsilon \frac{m_i (\mathbf{v})^2 T_i^\varepsilon}{2k_B T^2} + \varepsilon \frac{I T_i^\varepsilon}{k_B T^2} + \varepsilon \frac{m_j \mathbf{v}_j \cdot \mathbf{u}_j^\varepsilon}{k_B T} + \varepsilon \frac{m_j (\mathbf{v}_j)^2 T_j^\varepsilon}{2k_B T^2} + \varepsilon \frac{I_j T_j^\varepsilon}{k_B T^2} \\
& \left. - \varepsilon \frac{q_i^*(T)}{k_B T q_i(T)} \frac{T_i^\varepsilon}{T} - \varepsilon \frac{3 T_i^\varepsilon}{2 T} - \varepsilon \frac{q_j^*(T)}{k_B T q_j(T)} \frac{T_j^\varepsilon}{T} - \varepsilon \frac{3 T_j^\varepsilon}{2 T} + O(\varepsilon^2) \right].
\end{aligned}$$

Putting together terms of the same order in ε , we obtain:

$$\begin{aligned}
\left(\frac{m_i m_j}{m_k m_l} \right)^3 f_k^{\varepsilon'} f_l^{\varepsilon'} - f_i^\varepsilon f_j^\varepsilon &= \left(\frac{m_i m_j}{m_k m_l} \right)^3 M_k^{\varepsilon'} M_l^{\varepsilon'} - M_i^\varepsilon M_j^\varepsilon + \varepsilon \left(\frac{m_i m_j}{m_k m_l} \right)^3 M_k^{\varepsilon'} M_l^{\varepsilon'} \left[\frac{m_k \mathbf{v}_k' \cdot \mathbf{u}_k^\varepsilon}{k_B T} \right. \\
& + \frac{m_k (\mathbf{v}_k')^2 T_k^\varepsilon}{2k_B T^2} + \frac{I_k' T_k^\varepsilon}{k_B T^2} + \frac{m_l \mathbf{v}_l' \cdot \mathbf{u}_l^\varepsilon}{k_B T} + \frac{m_l (\mathbf{v}_l')^2 T_l^\varepsilon}{2k_B T^2} + \frac{I_l' T_l^\varepsilon}{k_B T^2} \\
& - \frac{q_k^*(T)}{k_B T q_k(T)} \frac{T_k^\varepsilon}{T} - \frac{3 T_k^\varepsilon}{2 T} - \frac{q_l^*(T)}{k_B T q_l(T)} \frac{T_l^\varepsilon}{T} - \frac{3 T_l^\varepsilon}{2 T} \Big] - \varepsilon M_i^\varepsilon M_j^\varepsilon \left[\frac{m_i \mathbf{v} \cdot \mathbf{u}_i^\varepsilon}{k_B T} \right. \\
& + \frac{m_i (\mathbf{v})^2 T_i^\varepsilon}{2k_B T^2} + \frac{I T_i^\varepsilon}{k_B T^2} + \frac{m_j \mathbf{v}_j \cdot \mathbf{u}_j^\varepsilon}{k_B T} + \frac{m_j (\mathbf{v}_j)^2 T_j^\varepsilon}{2k_B T^2} + \frac{I_j T_j^\varepsilon}{k_B T^2} \\
& \left. - \frac{q_i^*(T)}{k_B T q_i(T)} \frac{T_i^\varepsilon}{T} - \frac{3 T_i^\varepsilon}{2 T} - \frac{q_j^*(T)}{k_B T q_j(T)} \frac{T_j^\varepsilon}{T} - \frac{3 T_j^\varepsilon}{2 T} \right] + O(\varepsilon^2)
\end{aligned}$$

and part (b) is proven. Therefore, the proof is complete. $\square$

Using equation (6.3.8) of Proposition 5.3.1 together with equations (6.3.4) and (6.3.6), we can write the bi-species elastic collision operator given in (3.3.20) as follows:

$$\begin{aligned}
Q_{ij}^e(f_i^\varepsilon, f_j^\varepsilon) &= \varepsilon \frac{m_j}{m_i + m_j} \int_{\mathbb{R}^3} \int_0^{+\infty} \int_0^1 \int_0^1 \int_{\mathbb{S}^2} (\mathbf{a}_{ij} \cdot \widehat{\mathbf{V}}^*) M_i^\varepsilon M_j^\varepsilon \\
& \quad \times B_{ij}(\mathbf{v}, \mathbf{v}_j, I, I_j, R, r, \boldsymbol{\sigma}) \frac{2 \cos \theta (1 - R)}{\widehat{V}^* \varphi_i(I)} d\boldsymbol{\sigma} dr dR dI_j d\mathbf{v}_j \\
& + \varepsilon \frac{m_j}{m_i + m_j} \mathbf{a}_{ij} \cdot \int_{\mathbb{R}^3} \int_0^{+\infty} \int_0^1 \int_0^1 \int_{\mathbb{S}^2} \sqrt{\frac{2R\mathcal{E}}{\mu_{ij}}} \boldsymbol{\sigma} M_i^\varepsilon M_j^\varepsilon \\
& \quad \times B_{ij}(\mathbf{v}, \mathbf{v}_j, I, I_j, R, r, \boldsymbol{\sigma}) \frac{2 \cos \theta (1 - R)}{\widehat{V}^* \varphi_i(I)} d\boldsymbol{\sigma} dr dR dI_j d\mathbf{v}_j \\
& + \varepsilon \int_{\mathbb{R}^3} \int_0^{+\infty} \int_0^1 \int_0^1 \int_{\mathbb{S}^2} \left(\frac{T_i^\varepsilon}{k_B T^2} - \frac{T_j^\varepsilon}{k_B T^2} \right) \left(\frac{m_i (\mathbf{v}_i')^2}{2} - \frac{m_i (\mathbf{v})^2}{2} + I_i' - I \right) M_i^\varepsilon M_j^\varepsilon \\
& \quad \times B_{ij}(\mathbf{v}, \mathbf{v}_j, I, I_j, R, r, \boldsymbol{\sigma}) \frac{2 \cos \theta (1 - R)}{\widehat{V}^* \varphi_i(I)} d\boldsymbol{\sigma} dr dR dI_j d\mathbf{v}_j \\
& + O(\varepsilon^2),
\end{aligned} \tag{6.3.21}$$

where $|\boldsymbol{\omega} \cdot \mathbf{y}| = \cos \theta$, $\widehat{V}^* = |\mathbf{v} - \mathbf{v}_j| = \|\widehat{\mathbf{V}}^*\|$.

Similarly, using equation (6.3.9) of Proposition 5.3.1 together with equation (6.3.7), we can write the reactive collision operator given in equation (3.3.21) as follows:

$$Q_i^{react} = \int_{\mathbb{R}^3} \int_0^{+\infty} \int_0^1 \int_0^1 \int_{\mathbb{S}^2} \left[\left(\frac{m_i m_j}{m_k m_l} \right)^3 M_k^{\varepsilon'} M_l^{\varepsilon'} - M_i^{\varepsilon} M_j^{\varepsilon} \right] H_i 2 \cos \theta (1 - R) \widehat{V}^{*-1} \quad (6.3.22)$$

$$\times B^{react}(\mathbf{v}, \mathbf{v}_j, I, I_j, R, r, \boldsymbol{\sigma}) \varphi_i(I)^{-1} (m_i m_j)^{-2} d\boldsymbol{\sigma} dr dR dI_j d\mathbf{v}_j + O(\varepsilon),$$

where for the forward and backward reactive collision operators, the indices (i, j, k, l) are such that $(i, j, k, l) \in \{(1, 2, 3, 4), (2, 1, 4, 3)\}$ and $(i, j, k, l) \in \{(3, 4, 1, 2), (4, 3, 2, 1)\}$, respectively.

In this chapter, general collision kernels are considered. Consequently, in what follows, both the bi-species and reactive collision kernels will be split into the product of kinetic and angular collision kernels (see [108]) as given below:

$$B_{ij}(\mathbf{v}, \mathbf{v}_j, I, I_j, R, r, \boldsymbol{\sigma}) = \underbrace{|\mathbf{v} - \mathbf{v}_j|^\gamma \Phi_{ij}(I, I_j, R, r)}_{\text{kinetic}} \underbrace{b_{ij}(\cos \theta)}_{\text{angular}}, \quad (6.3.23)$$

$$B^{react}(\mathbf{v}, \mathbf{v}_j, I, I_j, R, r, \boldsymbol{\sigma}) = \underbrace{|\mathbf{v} - \mathbf{v}_j|^\gamma \Phi^{react}(I, I_j, R, r)}_{\text{kinetic}} \underbrace{b^{react}(\cos \theta)}_{\text{angular}}, \quad (6.3.24)$$

where γ is a parameter which is such that $\gamma \geq 1$. This decomposition of the collision kernels is enough to obtain appropriate expressions for the integral production terms.

6.3.2 Moment of order zero

From the scaled kinetic equations, let us derive the evolution equation for the number density of each constituent. The result is given in the following lemma.

Lemma 6.3.4. *The balance equation for the number density of each constituent in the reactive mixture can be written in the form*

$$\frac{\partial n_i}{\partial t} + \nabla_{\mathbf{x}} \cdot (n_i \mathbf{u}_i) = -\lambda_i A, \quad i = 1, 2, 3, 4, \quad (6.3.25)$$

where

$$n_i = \lim_{\varepsilon \rightarrow 0} n_i^\varepsilon, \quad \mathbf{u}_i = \lim_{\varepsilon \rightarrow 0} \mathbf{u}_i^\varepsilon,$$

and

$$\lambda_1 = \lambda_2 = 1, \quad \lambda_3 = \lambda_4 = -1 \quad (6.3.26)$$

are stoichiometric coefficients. Moreover, A is the production term defining the chemical rate of the reactants of the backward chemical reaction. More specifically, A is the formal limit for $\varepsilon \rightarrow 0$ of

$$A^\varepsilon = \left[\left(\frac{m_3 m_4}{m_1 m_2} \right)^{3/2} \frac{n_1^\varepsilon n_2^\varepsilon}{q_1(T) q_2(T)} \exp \left(-\frac{Q_R}{k_B T} \right) - \frac{n_3^\varepsilon n_4^\varepsilon}{q_3(T) q_4(T)} \right]$$

$$\times \frac{4}{\sqrt{\pi} (m_3 m_4)^2} \left(\frac{2k_B T}{\mu_{34}} \right)^{(\gamma-1)/2} \Gamma \left(\frac{\gamma+2}{2} \right) \int_0^{+\infty} \int_0^{+\infty} \int_0^1 \int_0^1 \int_{\mathbb{S}^2} \exp \left(-\frac{I+I_4}{k_B T} \right) \quad (6.3.27)$$

$$\times \Phi^{react}(I, I_4, R, r) b^{react}(\cos \theta) \cos \theta (1 - R) d\boldsymbol{\sigma} dr dR dI_4 dI + O(\varepsilon).$$

Proof. Multiplying the scaled kinetic equations given in equation (6.2.1) by $\varphi_i(I)$ and integrating the resulting equations with respect to $\mathbf{v} \in \mathbb{R}^3$ and $I \in \mathbb{R}_+$, we obtain:

$$\begin{aligned} \varepsilon \int_{\mathbb{R}^3} \int_0^{+\infty} \frac{\partial f_i^\varepsilon}{\partial t} \varphi_i(I) dI d\mathbf{v} + \int_{\mathbb{R}^3} \int_0^{+\infty} \mathbf{v} \cdot \nabla_{\mathbf{x}} f_i^\varepsilon \varphi_i(I) dI d\mathbf{v} \\ = \frac{1}{\varepsilon} \sum_{j=1}^4 \int_{\mathbb{R}^3} \int_0^{+\infty} Q_{ij}^e(f_i^\varepsilon, f_j^\varepsilon) \varphi_i(I) dI d\mathbf{v} + \varepsilon \int_{\mathbb{R}^3} \int_0^{+\infty} Q_i^{react} \varphi_i(I) dI d\mathbf{v}, \end{aligned}$$

for $i = 1, \dots, 4$. Applying the Leibniz integral rule to the two terms on the left-hand side of the previous equation and splitting the elastic collision operator into the mono-species and the bi-species collision operators, we obtain:

$$\begin{aligned} \varepsilon \frac{\partial}{\partial t} \left(\int_{\mathbb{R}^3} \int_0^{+\infty} f_i^\varepsilon \varphi_i(I) dI d\mathbf{v} \right) + \nabla_{\mathbf{x}} \cdot \left(\int_{\mathbb{R}^3} \int_0^{+\infty} \mathbf{v} f_i^\varepsilon \varphi_i(I) dI d\mathbf{v} \right) \\ = \frac{1}{\varepsilon} \int_{\mathbb{R}^3} \int_0^{+\infty} Q_{ii}^e(f_i^\varepsilon, f_i^\varepsilon) \varphi_i(I) dI d\mathbf{v} + \frac{1}{\varepsilon} \sum_{\substack{j=1 \\ j \neq i}}^4 \int_{\mathbb{R}^3} \int_0^{+\infty} Q_{ij}^e(f_i^\varepsilon, f_j^\varepsilon) \varphi_i(I) dI d\mathbf{v} \\ + \varepsilon \int_{\mathbb{R}^3} \int_0^{+\infty} Q_i^{react} \varphi_i(I) dI d\mathbf{v}. \quad (6.3.28) \end{aligned}$$

Using the definition of the distribution functions given in equation (6.2.4), we can write the first integral on the left-hand side of equation (6.3.28) above as given below:

$$\begin{aligned} \int_{\mathbb{R}^3} \int_0^{+\infty} f_i^\varepsilon \varphi_i(I) dI d\mathbf{v} &= \frac{n_i^\varepsilon}{q_i(T + \varepsilon T_i^\varepsilon)} \left(\frac{m_i}{2\pi k_B(T + \varepsilon T_i^\varepsilon)} \right)^{3/2} \\ &\times \int_{\mathbb{R}^3} \int_0^{+\infty} \exp\left(-\frac{m_i(\mathbf{v} - \varepsilon \mathbf{u}_i^\varepsilon)^2}{2k_B(T + \varepsilon T_i^\varepsilon)}\right) \exp\left(-\frac{I}{k_B(T + \varepsilon T_i^\varepsilon)}\right) \varphi_i(I) dI d\mathbf{v} \\ &= \frac{n_i^\varepsilon}{q_i(T + \varepsilon T_i^\varepsilon)} \left(\frac{m_i}{2\pi k_B(T + \varepsilon T_i^\varepsilon)} \right)^{3/2} \\ &\times \int_{\mathbb{R}^3} \exp\left(-\frac{m_i(\mathbf{v} - \varepsilon \mathbf{u}_i^\varepsilon)^2}{2k_B(T + \varepsilon T_i^\varepsilon)}\right) d\mathbf{v} \int_0^{+\infty} \varphi_i(I) \exp\left(-\frac{I}{k_B(T + \varepsilon T_i^\varepsilon)}\right) dI. \end{aligned}$$

The second integral in the last equality of the previous equation is given by

$$q_i(T + \varepsilon T_i^\varepsilon) = \int_0^{+\infty} \varphi_i(I) \exp\left(-\frac{I}{k_B(T + \varepsilon T_i^\varepsilon)}\right) dI. \quad (6.3.29)$$

Therefore,

$$\int_{\mathbb{R}^3} \int_0^{+\infty} f_i^\varepsilon \varphi_i(I) dI d\mathbf{v} = n_i^\varepsilon \left(\frac{m_i}{2\pi k_B(T + \varepsilon T_i^\varepsilon)} \right)^{3/2} \int_{\mathbb{R}^3} \exp\left(-\frac{m_i(\mathbf{v} - \varepsilon \mathbf{u}_i^\varepsilon)^2}{2k_B(T + \varepsilon T_i^\varepsilon)}\right) d\mathbf{v}.$$

Introducing the peculiar velocity

$$\boldsymbol{\xi} = \mathbf{v} - \varepsilon \mathbf{u}_i^\varepsilon \iff \mathbf{v} = \boldsymbol{\xi} + \varepsilon \mathbf{u}_i^\varepsilon \quad \text{and} \quad d\mathbf{v} = d\boldsymbol{\xi}, \quad (6.3.30)$$

we obtain that

$$\int_{\mathbb{R}^3} \int_0^{+\infty} f_i^\varepsilon \varphi_i(I) dI d\mathbf{v} = n_i^\varepsilon \left(\frac{m_i}{2\pi k_B(T + \varepsilon T_i^\varepsilon)} \right)^{3/2} \int_{\mathbb{R}^3} \exp \left(- \frac{m_i(\boldsymbol{\xi})^2}{2k_B(T + \varepsilon T_i^\varepsilon)} \right) d\boldsymbol{\xi}.$$

The integral on the right-hand side of the previous equation is similar to that whose value is given in equation (5.4.7). Therefore,

$$\int_{\mathbb{R}^3} \exp \left(- \frac{m_i(\boldsymbol{\xi})^2}{2k_B(T + \varepsilon T_i^\varepsilon)} \right) d\boldsymbol{\xi} = \left(\frac{2\pi k_B(T + \varepsilon T_i^\varepsilon)}{m_i} \right)^{\frac{3}{2}}. \quad (6.3.31)$$

Thus

$$\int_{\mathbb{R}^3} \int_0^{+\infty} f_i^\varepsilon \varphi_i(I) dI d\mathbf{v} = n_i^\varepsilon \left(\frac{m_i}{2\pi k_B(T + \varepsilon T_i^\varepsilon)} \right)^{3/2} \left(\frac{2\pi k_B(T + \varepsilon T_i^\varepsilon)}{m_i} \right)^{\frac{3}{2}} = n_i^\varepsilon. \quad (6.3.32)$$

The second integral on the left-hand side of equation (6.3.28) can be written as:

$$\begin{aligned} \int_{\mathbb{R}^3} \int_0^{+\infty} \mathbf{v} f_i^\varepsilon \varphi_i(I) dI d\mathbf{v} &= \frac{n_i^\varepsilon}{q_i(T + \varepsilon T_i^\varepsilon)} \left(\frac{m_i}{2\pi k_B(T + \varepsilon T_i^\varepsilon)} \right)^{3/2} \\ &\times \int_{\mathbb{R}^3} \int_0^{+\infty} \mathbf{v} \exp \left(- \frac{m_i(\mathbf{v} - \varepsilon \mathbf{u}_i^\varepsilon)^2}{2k_B(T + \varepsilon T_i^\varepsilon)} \right) \exp \left(- \frac{I}{k_B(T + \varepsilon T_i^\varepsilon)} \right) \varphi_i(I) dI d\mathbf{v} \\ &= \frac{n_i^\varepsilon}{q_i(T + \varepsilon T_i^\varepsilon)} \left(\frac{m_i}{2\pi k_B(T + \varepsilon T_i^\varepsilon)} \right)^{3/2} \\ &\times \int_{\mathbb{R}^3} \mathbf{v} \exp \left(- \frac{m_i(\mathbf{v} - \varepsilon \mathbf{u}_i^\varepsilon)^2}{2k_B(T + \varepsilon T_i^\varepsilon)} \right) d\mathbf{v} \int_0^{+\infty} \varphi_i(I) \exp \left(- \frac{I}{k_B(T + \varepsilon T_i^\varepsilon)} \right) dI. \end{aligned}$$

Using equation (6.3.29), we obtain:

$$\int_{\mathbb{R}^3} \int_0^{+\infty} \mathbf{v} f_i^\varepsilon \varphi_i(I) dI d\mathbf{v} = n_i^\varepsilon \left(\frac{m_i}{2\pi k_B(T + \varepsilon T_i^\varepsilon)} \right)^{3/2} \int_{\mathbb{R}^3} \mathbf{v} \exp \left(- \frac{m_i(\mathbf{v} - \varepsilon \mathbf{u}_i^\varepsilon)^2}{2k_B(T + \varepsilon T_i^\varepsilon)} \right) d\mathbf{v}. \quad (6.3.33)$$

Using equation (6.3.30), we can rewrite the integral on the right-hand side of the previous equation as given below:

$$\int_{\mathbb{R}^3} \mathbf{v} \exp \left(- \frac{m_i(\mathbf{v} - \varepsilon \mathbf{u}_i^\varepsilon)^2}{2k_B(T + \varepsilon T_i^\varepsilon)} \right) d\mathbf{v} = \int_{\mathbb{R}^3} (\boldsymbol{\xi} + \varepsilon \mathbf{u}_i^\varepsilon) \exp \left(- \frac{m_i(\boldsymbol{\xi})^2}{2k_B(T + \varepsilon T_i^\varepsilon)} \right) d\boldsymbol{\xi}$$

$$\begin{aligned}
&= \int_{\mathbb{R}^3} \boldsymbol{\xi} \exp \left(-\frac{m_i(\boldsymbol{\xi})^2}{2k_B(T + \varepsilon T_i^\varepsilon)} \right) d\boldsymbol{\xi} \\
&+ \varepsilon \mathbf{u}_i^\varepsilon \int_{\mathbb{R}^3} \exp \left(-\frac{m_i(\boldsymbol{\xi})^2}{2k_B(T + \varepsilon T_i^\varepsilon)} \right) d\boldsymbol{\xi}.
\end{aligned}$$

The first integral on the right-hand side of the last equality in the previous equation is similar to the one evaluated in equation (5.4.6). Therefore, upon evaluation, one obtains:

$$\int_{\mathbb{R}^3} \boldsymbol{\xi} \exp \left(-\frac{m_i(\boldsymbol{\xi})^2}{2k_B(T + \varepsilon T_i^\varepsilon)} \right) d\boldsymbol{\xi} = \mathbf{0} \quad (6.3.34)$$

Thus

$$\int_{\mathbb{R}^3} \mathbf{v} \exp \left(-\frac{m_i(\mathbf{v} - \varepsilon \mathbf{u}_i^\varepsilon)^2}{2k_B(T + \varepsilon T_i^\varepsilon)} \right) d\mathbf{v} = \mathbf{0} + \varepsilon \mathbf{u}_i^\varepsilon \int_{\mathbb{R}^3} \exp \left(-\frac{m_i(\boldsymbol{\xi})^2}{2k_B(T + \varepsilon T_i^\varepsilon)} \right) d\boldsymbol{\xi}.$$

The value of integral on the right-hand side of the previous equation is given in equation (6.3.31). Therefore,

$$\int_{\mathbb{R}^3} \mathbf{v} \exp \left(-\frac{m_i(\mathbf{v} - \varepsilon \mathbf{u}_i^\varepsilon)^2}{2k_B(T + \varepsilon T_i^\varepsilon)} \right) d\mathbf{v} = \varepsilon \mathbf{u}_i^\varepsilon \left(\frac{2\pi k_B(T + \varepsilon T_i^\varepsilon)}{m_i} \right)^{\frac{3}{2}}. \quad (6.3.35)$$

Substituting equation (6.3.35) into equation (6.3.33) gives:

$$\int_{\mathbb{R}^3} \int_0^{+\infty} \mathbf{v} f_i^\varepsilon \varphi_i(I) dI d\mathbf{v} = \varepsilon n_i^\varepsilon \mathbf{u}_i^\varepsilon. \quad (6.3.36)$$

Now substituting equations (6.3.32) and (6.3.36) into equation (6.3.28), we obtain:

$$\begin{aligned}
\varepsilon \frac{\partial n_i^\varepsilon}{\partial t} + \varepsilon \nabla_{\mathbf{x}} \cdot (n_i^\varepsilon \mathbf{u}_i^\varepsilon) &= \frac{1}{\varepsilon} \int_{\mathbb{R}^3} \int_0^{+\infty} Q_{ii}^e(f_i^\varepsilon, f_i^\varepsilon) \varphi_i(I) dI d\mathbf{v} + \frac{1}{\varepsilon} \sum_{\substack{j=1 \\ j \neq i}}^4 \int_{\mathbb{R}^3} \int_0^{+\infty} Q_{ij}^e(f_i^\varepsilon, f_j^\varepsilon) \varphi_i(I) dI d\mathbf{v} \\
&+ \varepsilon \int_{\mathbb{R}^3} \int_0^{+\infty} Q_i^{react} \varphi_i(I) dI d\mathbf{v}. \quad (6.3.37)
\end{aligned}$$

Since the properties of the scaled collision operators are similar to their un-scaled version, the first and second integrals on the right-hand side of equation (6.3.37) both vanish. To see this, set $\psi(\mathbf{v}, I) = 1$ in equations (2.4.67) and (2.4.68), respectively. Therefore, equation (6.3.37) reduces to:

$$\varepsilon \frac{\partial n_i^\varepsilon}{\partial t} + \nabla_{\mathbf{x}} \cdot (\varepsilon n_i^\varepsilon \mathbf{u}_i^\varepsilon) = \varepsilon \int_{\mathbb{R}^3} \int_0^{+\infty} Q_i^{react} \varphi_i(I) dI d\mathbf{v}. \quad (6.3.38)$$

To evaluate the integral on the right-hand side of equation (6.3.38), we use the more convenient form of the reactive collision operator Q_i^{react} given in equation (6.3.22), together with the decomposition of the reactive collision kernel given in equation (6.3.24) and the conservation of total energy for reactive collisions given in equation (2.4.5). More precisely, we will compute the production rate for $i = 3$. To do this, we set $i = 3$ in equation (6.3.22). Therefore, the integral on the right-hand side of equation (6.3.38)

becomes:

$$\begin{aligned}
& \int_{\mathbb{R}^3} \int_0^{+\infty} Q_3^{react}(\mathbf{v}, I) \varphi_3(I) dI d\mathbf{v} \\
&= \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_0^{+\infty} \int_0^{+\infty} \int_0^1 \int_0^1 \int_{\mathbb{S}^2} \left[\left(\frac{m_3 m_4}{m_1 m_2} \right)^3 M_1^{\varepsilon'} M_2^{\varepsilon'} - M_3^{\varepsilon} M_4^{\varepsilon} \right] \\
&\quad \times B^{react}(\mathbf{v}, \mathbf{v}_4, I, I_4, R, r, \boldsymbol{\sigma}) (m_3 m_4)^{-2} \tilde{V}^{-1} 2 \cos \theta (1-R) d\boldsymbol{\sigma} dr dR dI_4 dI d\mathbf{v}_4 d\mathbf{v} + O(\varepsilon),
\end{aligned}$$

where $H_3(I_4, r, R, \mathbf{v}_4) = 1$ and $\tilde{V} = |\mathbf{v} - \mathbf{v}_4|$ have been used. Using (6.3.24), we obtain:

$$\begin{aligned}
& \int_{\mathbb{R}^3} \int_0^{+\infty} Q_3^{react}(\mathbf{v}, I) \varphi_3(I) dI d\mathbf{v} \\
&= \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_0^{+\infty} \int_0^{+\infty} \int_0^1 \int_0^1 \int_{\mathbb{S}^2} \left[\left(\frac{m_3 m_4}{m_1 m_2} \right)^3 M_1^{\varepsilon'} M_2^{\varepsilon'} - M_3^{\varepsilon} M_4^{\varepsilon} \right] 2 \cos \theta \\
&\quad \times \tilde{V}^{\gamma-1} \Phi^{react}(I, I_j, R, r) b^{react}(\cos \theta) (m_3 m_4)^{-2} (1-R) d\boldsymbol{\sigma} dr dR dI_4 dI d\mathbf{v}_4 d\mathbf{v} + O(\varepsilon).
\end{aligned}$$

Now, using equation (6.3.12), observe that

$$\begin{aligned}
& \left(\frac{m_3 m_4}{m_1 m_2} \right)^3 M_1^{\varepsilon'} M_2^{\varepsilon'} - M_3^{\varepsilon} M_4^{\varepsilon} \\
&= \left(\frac{m_3 m_4}{m_1 m_2} \right)^3 \frac{n_1^{\varepsilon} n_2^{\varepsilon}}{q_1(T) q_2(T)} \frac{(m_1 m_2)^{\frac{3}{2}}}{(2\pi k_B T)^3} \exp \left(-\frac{m_1(\mathbf{v}'_1)^2 + (\mathbf{v}'_2)^2}{2k_B T} - \frac{I'_1 + I'_2}{k_B T} \right) \\
&\quad - \frac{n_3^{\varepsilon} n_4^{\varepsilon}}{q_3(T) q_4(T)} \frac{(m_3 m_4)^{\frac{3}{2}}}{(2\pi k_B T)^3} \exp \left(-\frac{m_3(\mathbf{v})^2 + m_4(\mathbf{v}_4)^2}{2k_B T} - \frac{I + I_4}{k_B T} \right) \\
&= \left[\left(\frac{m_3 m_4}{m_1 m_2} \right)^3 \exp \left(-\frac{m_1(\mathbf{v}'_1)^2 + m_2(\mathbf{v}'_2)^2 - m_3(\mathbf{v})^2 - m_4(\mathbf{v}_4)^2}{2k_B T} - \frac{I'_1 + I'_2 - I - I_4}{k_B T} \right) \right. \\
&\quad \times \frac{n_1^{\varepsilon} n_2^{\varepsilon}}{q_1(T) q_2(T)} \frac{(m_1 m_2)^{\frac{3}{2}}}{(2\pi k_B T)^3} - \frac{n_3^{\varepsilon} n_4^{\varepsilon}}{q_3(T) q_4(T)} \frac{(m_3 m_4)^{\frac{3}{2}}}{(2\pi k_B T)^3} \left. \right] \exp \left(-\frac{m_3(\mathbf{v})^2 + m_4(\mathbf{v}_4)^2}{2k_B T} - \frac{I + I_4}{k_B T} \right).
\end{aligned}$$

Using equation (2.4.5), we can rewrite the previous equation as

$$\begin{aligned}
& \left(\frac{m_3 m_4}{m_1 m_2} \right)^3 M_1^{\varepsilon'} M_2^{\varepsilon'} - M_3^{\varepsilon} M_4^{\varepsilon} \\
&= \left[\left(\frac{m_3 m_4}{m_1 m_2} \right)^3 \frac{n_1^{\varepsilon} n_2^{\varepsilon}}{q_1(T) q_2(T)} \frac{(m_1 m_2)^{\frac{3}{2}}}{(2\pi k_B T)^3} \exp \left(-\frac{Q_R}{k_B T} \right) - \frac{n_3^{\varepsilon} n_4^{\varepsilon}}{q_3(T) q_4(T)} \frac{(m_3 m_4)^{\frac{3}{2}}}{(2\pi k_B T)^3} \right] \\
&\quad \times \exp \left(-\frac{m_3(\mathbf{v})^2 + m_4(\mathbf{v}_4)^2}{2k_B T} - \frac{I + I_4}{k_B T} \right) \\
&= \frac{(m_3 m_4)^{\frac{3}{2}}}{(2\pi k_B T)^3} \left[\left(\frac{m_3 m_4}{m_1 m_2} \right)^{\frac{3}{2}} \frac{n_1^{\varepsilon} n_2^{\varepsilon}}{q_1(T) q_2(T)} \exp \left(-\frac{Q_R}{k_B T} \right) - \frac{n_3^{\varepsilon} n_4^{\varepsilon}}{q_3(T) q_4(T)} \right] \\
&\quad \times \exp \left(-\frac{m_3(\mathbf{v})^2 + m_4(\mathbf{v}_4)^2}{2k_B T} - \frac{I + I_4}{k_B T} \right),
\end{aligned}$$

where Q_R is as defined in (2.3.3). Therefore,

$$\begin{aligned}
& \int_{\mathbb{R}^3} \int_0^{+\infty} Q_3^{react}(\mathbf{v}, I) \varphi_3(I) dI d\mathbf{v} \\
&= \frac{(m_3 m_4)^{\frac{3}{2}}}{(2\pi k_B T)^3} \left[\left(\frac{m_3 m_4}{m_1 m_2} \right)^{\frac{3}{2}} \frac{n_1^\varepsilon n_2^\varepsilon}{q_1(T) q_2(T)} \exp\left(-\frac{Q_R}{k_B T}\right) - \frac{n_3^\varepsilon n_4^\varepsilon}{q_3(T) q_4(T)} \right] \\
&\times \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_0^{+\infty} \int_0^{+\infty} \int_0^1 \int_0^1 \int_{\mathbb{S}^2} \exp\left(-\frac{m_3(\mathbf{v})^2 + m_3(\mathbf{v}_4)^2}{2k_B T} - \frac{I_3 + I_4}{k_B T}\right) \\
&\times \frac{2 \cos \theta}{(m_3 m_4)^2} \tilde{V}^{\gamma-1} \Phi^{react}(I, I_j, R, r) b^{react}(\cos \theta) (1-R) d\boldsymbol{\sigma} dr dR dI_4 dI d\mathbf{v}_4 d\mathbf{v} + O(\varepsilon).
\end{aligned}$$

It will be convenient to transform the integrals in $\mathbf{v}, \mathbf{v}_4$ to the centre of mass velocity and relative velocity

$$\tilde{\mathbf{X}} = \frac{m_3 \mathbf{v} + m_4 \mathbf{v}_4}{M_{34}} \quad \text{and} \quad \tilde{\mathbf{V}} = \mathbf{v}_4 - \mathbf{v},$$

respectively. Consequently, following the steps used to obtain equations (2.4.10), (2.4.11) and (2.4.12), we obtain:

$$\mathbf{v} = \tilde{\mathbf{X}} - \frac{m_4 \tilde{\mathbf{V}}}{m_3 + m_4}, \quad (6.3.39)$$

$$\mathbf{v}_4 = \tilde{\mathbf{X}} + \frac{m_3 \tilde{\mathbf{V}}}{m_3 + m_4}, \quad (6.3.40)$$

$$m_3(\mathbf{v})^2 + m_4(\mathbf{v}_4)^2 = M_{34} \tilde{X}^2 + \mu_{34} \tilde{V}^2, \quad (6.3.41)$$

respectively, where $\tilde{X} = \|\tilde{\mathbf{X}}\|$, $\tilde{V} = \|\tilde{\mathbf{V}}\|$, $M_{34} = m_3 + m_4$ and $\mu_{34} = \frac{m_3 m_4}{m_3 + m_4}$. Also the Jacobian of this transformation is unity which implies that $d\mathbf{v} d\mathbf{v}_4 = d\tilde{\mathbf{X}} d\tilde{\mathbf{V}}$. Therefore,

$$\begin{aligned}
& \int_{\mathbb{R}^3} \int_0^{+\infty} Q_3^{react}(\mathbf{v}, I) \varphi_3(I) dI d\mathbf{v} \\
&= \frac{(m_3 m_4)^{\frac{3}{2}}}{(2\pi k_B T)^3} \left[\left(\frac{m_3 m_4}{m_1 m_2} \right)^{\frac{3}{2}} \frac{n_1^\varepsilon n_2^\varepsilon}{q_1(T) q_2(T)} \exp\left(-\frac{Q_R}{k_B T}\right) - \frac{n_3^\varepsilon n_4^\varepsilon}{q_3(T) q_4(T)} \right] \\
&\times \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_0^{+\infty} \int_0^{+\infty} \int_0^1 \int_0^1 \int_{\mathbb{S}^2} \exp\left(-\frac{M_{34} \tilde{X}^2 + \mu_{34} \tilde{V}^2}{2k_B T}\right) \exp\left(-\frac{I + I_4}{k_B T}\right) \\
&\times \frac{2 \cos \theta}{(m_3 m_4)^2} \tilde{V}^{\gamma-1} \Phi^{react}(I, I_j, R, r) b^{react}(\cos \theta) (1-R) d\boldsymbol{\sigma} dr dR dI_4 dI d\tilde{\mathbf{X}} d\tilde{\mathbf{V}} + O(\varepsilon),
\end{aligned} \quad (6.3.42)$$

Observe that

$$\begin{aligned}
& \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \tilde{V}^{\gamma-1} \exp\left(-\frac{M_{34} \tilde{X}^2 + \mu_{34} \tilde{V}^2}{2k_B T}\right) d\tilde{\mathbf{X}} d\tilde{\mathbf{V}} \\
&= \int_{\mathbb{R}^3} \exp\left(-\frac{M_{34} \tilde{X}^2}{2k_B T}\right) d\tilde{\mathbf{X}} \int_{\mathbb{R}^3} \tilde{V}^{\gamma-1} \exp\left(-\frac{\mu_{34} \tilde{V}^2}{2k_B T}\right) d\tilde{\mathbf{V}}.
\end{aligned} \quad (6.3.43)$$

The integral in $\widetilde{\mathbf{X}}$ above is similar to that given in equation (4.4.17). Therefore, following similar steps as those used in the computation of equation (4.4.17), we obtain:

$$\int_{\mathbb{R}^3} \exp\left(-\frac{M_{34}\widetilde{X}^2}{2k_B T}\right) d\widetilde{\mathbf{X}} = \left(\frac{2\pi k_B T}{M_{34}}\right)^{\frac{3}{2}}. \quad (6.3.44)$$

Writing integral in $\widetilde{\mathbf{V}}$ above in spherical coordinates and integrating, we obtain:

$$\begin{aligned} \int_{\mathbb{R}^3} \widetilde{V}^{\gamma-1} \exp\left(-\frac{\mu_{34}\widetilde{V}^2}{2k_B T}\right) d\widetilde{\mathbf{V}} &= \int_0^\infty \int_0^\pi \int_0^{2\pi} \widetilde{V}^{\gamma-1} \exp\left(-\frac{\mu_{34}\widetilde{V}^2}{2k_B T}\right) \widetilde{V}^2 \sin\theta \, d\phi \, d\theta \, d\widetilde{V} \\ &= \int_0^\infty \widetilde{V}^{\gamma+1} \exp\left(-\frac{\mu_{34}\widetilde{V}^2}{2k_B T}\right) d\widetilde{V} \underbrace{\int_0^\pi \sin\theta \, d\theta}_2 \underbrace{\int_0^{2\pi} d\phi}_{2\pi} \\ &= 4\pi \int_0^\infty \widetilde{V}^{\gamma+1} \exp\left(-\frac{\mu_{34}\widetilde{V}^2}{2k_B T}\right) d\widetilde{V}. \end{aligned}$$

Using the integral representation of gamma function given in equation (4.3.8), we obtain:

$$\begin{aligned} 4\pi \int_0^\infty \widetilde{V}^{\gamma+1} \exp\left(-\frac{\mu_{34}\widetilde{V}^2}{2k_B T}\right) d\widetilde{V} &= 4\pi \frac{1}{2} \Gamma\left(\frac{\gamma+1+1}{2}\right) \left(\frac{2k_B T}{\mu_{34}}\right)^{\frac{\gamma+1+1}{2}} \\ &= 2\pi \Gamma\left(\frac{\gamma+2}{2}\right) \left(\frac{2k_B T}{\mu_{34}}\right)^{\frac{\gamma+2}{2}}. \end{aligned}$$

Therefore,

$$\int_{\mathbb{R}^3} \widetilde{V}^{\gamma-1} \exp\left(-\frac{\mu_{34}\widetilde{V}^2}{2k_B T}\right) d\widetilde{\mathbf{V}} = 2\pi \Gamma\left(\frac{\gamma+2}{2}\right) \left(\frac{2k_B T}{\mu_{34}}\right)^{\frac{\gamma+2}{2}}. \quad (6.3.45)$$

Substituting equations (6.3.44) and (6.3.45) into equation (6.3.43) gives:

$$\int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \widetilde{V}^{\gamma-1} \exp\left(-\frac{M_{34}\widetilde{X}^2 + \mu_{34}\widetilde{V}^2}{2k_B T}\right) d\widetilde{\mathbf{X}} \, d\widetilde{\mathbf{V}} = \left(\frac{2\pi k_B T}{M_{34}}\right)^{\frac{3}{2}} 2\pi \Gamma\left(\frac{\gamma+2}{2}\right) \left(\frac{2k_B T}{\mu_{34}}\right)^{\frac{\gamma+2}{2}} \quad (6.3.46)$$

Substituting equation (6.3.46) into equation (6.3.42) gives:

$$\begin{aligned} A^\varepsilon &= \int_{\mathbb{R}^3} \int_0^{+\infty} Q_3^{react}(\mathbf{v}, I) \varphi_3(I) dI d\mathbf{v} \\ &= \frac{(m_3 m_4)^{\frac{3}{2}}}{(2\pi k_B T)^3} \left[\left(\frac{m_3 m_4}{m_1 m_2}\right)^{\frac{3}{2}} \frac{n_1^\varepsilon n_2^\varepsilon}{q_1(T) q_2(T)} \exp\left(-\frac{Q_R}{k_B T}\right) - \frac{n_3^\varepsilon n_4^\varepsilon}{q_3(T) q_4(T)} \right] \left(\frac{2\pi k_B T}{M_{34}}\right)^{\frac{3}{2}} \\ &\quad \times 2\pi \Gamma\left(\frac{\gamma+2}{2}\right) \left(\frac{2k_B T}{\mu_{34}}\right)^{\frac{\gamma+2}{2}} \int_0^{+\infty} \int_0^{+\infty} \int_0^1 \int_0^1 \int_{\mathbb{S}^2} \exp\left(-\frac{I+I_4}{k_B T}\right) \\ &\quad \times \frac{2 \cos \theta}{(m_3 m_4)^2} \Phi^{react}(I, I_j, R, r) b^{react}(\cos \theta) (1-R) d\boldsymbol{\sigma} \, dr \, dR \, dI_4 \, dI + O(\varepsilon). \end{aligned} \quad (6.3.47)$$

Observe that

$$\frac{(m_3 m_4)^{\frac{3}{2}}}{(2\pi k_B T)^3} \left(\frac{2\pi k_B T}{M_{34}}\right)^{\frac{3}{2}} 2\pi \Gamma\left(\frac{\gamma+2}{2}\right) \left(\frac{2k_B T}{\mu_{34}}\right)^{\frac{\gamma+2}{2}} = \frac{1}{(2\pi k_B T)^{\frac{3}{2}}} \left(\frac{m_3 m_4}{M_{34}}\right)^{\frac{3}{2}} 2\pi \Gamma\left(\frac{\gamma+2}{2}\right) \left(\frac{2k_B T}{\mu_{34}}\right)^{\frac{\gamma+2}{2}}$$

$$\begin{aligned}
&= \left(\frac{\mu_{34}}{2k_B T} \right)^{\frac{3}{2}} \frac{2}{\sqrt{\pi}} \Gamma\left(\frac{\gamma+2}{2}\right) \left(\frac{2k_B T}{\mu_{34}} \right)^{\frac{\gamma+2}{2}} \\
&= \frac{2}{\sqrt{\pi}} \Gamma\left(\frac{\gamma+2}{2}\right) \left(\frac{2k_B T}{\mu_{34}} \right)^{\frac{\gamma-1}{2}}.
\end{aligned} \tag{6.3.48}$$

Substituting equation (6.3.48) into equation (6.3.47) gives:

$$\begin{aligned}
A^\varepsilon &= \left[\left(\frac{m_3 m_4}{m_1 m_2} \right)^{3/2} \frac{n_1^\varepsilon n_2^\varepsilon}{q_1(T) q_2(T)} \exp\left(-\frac{Q_R}{k_B T}\right) - \frac{n_3^\varepsilon n_4^\varepsilon}{q_3(T) q_4(T)} \right] \\
&\times \frac{4}{\sqrt{\pi} (m_3 m_4)^2} \left(\frac{2k_B T}{\mu_{34}} \right)^{\frac{\gamma-1}{2}} \Gamma\left(\frac{\gamma+2}{2}\right) \int_0^{+\infty} \int_0^{+\infty} \int_0^1 \int_0^1 \int_{\mathbb{S}^2} \exp\left(-\frac{I + I_4}{k_B T}\right) \\
&\times \Phi^{react}(I, I_4, R, r) b^{react}(\cos \theta) \cos \theta (1 - R) d\boldsymbol{\sigma} dr dR dI_4 dI + O(\varepsilon).
\end{aligned}$$

Substituting the previous equation into the right-hand side of equation (6.3.38), then divide both sides of the resulting equation by ε and finally, taking the limit as $\varepsilon \rightarrow 0$ gives the desired result. $\square$

6.3.3 Moment of order one

From the scaled kinetic equations, the evolution equation for the momentum of each species in the reactive mixture, can be derived as stated in the following lemma.

Lemma 6.3.5. (i) *The balance equation for the momentum of each constituent in the reactive mixture can be written in the form*

$$\nabla_x (n_i k_B T) = m_i \mathbf{B}_i, \quad i = 1, 2, 3, 4, \tag{6.3.49}$$

where

$$n_i = \lim_{\varepsilon \rightarrow 0} n_i^\varepsilon, \quad T = \lim_{\varepsilon \rightarrow 0} (T + \varepsilon T_i^\varepsilon),$$

$\mathbf{B}_i$ is the production term associated to the momentum balance of the species, namely the formal limit for $\varepsilon \rightarrow 0$ of

$$\begin{aligned}
\mathbf{B}_i^\varepsilon &= \sum_{\substack{j=1 \\ j \neq i}}^4 \frac{m_j}{m_i + m_j} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_0^{+\infty} \int_0^{+\infty} \int_0^1 \int_0^1 \int_{\mathbb{S}^2} (\mathbf{a}_{ij} \cdot \widehat{\mathbf{V}}^*) \mathbf{v} M_i^\varepsilon M_j^\varepsilon \widehat{V}^{*\gamma-1} \\
&\quad \times 2 \Phi_{ij}(I, I_j, R, r) b_{ij}(\cos \theta) \cos \theta (1 - R) d\boldsymbol{\sigma} dr dR dI_j dI d\mathbf{v}_j d\mathbf{v} \\
&+ \sum_{\substack{j=1 \\ j \neq i}}^4 \frac{m_j}{m_i + m_j} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_0^{+\infty} \int_0^{+\infty} \int_0^1 \int_0^1 \int_{\mathbb{S}^2} (\mathbf{a}_{ij} \cdot \boldsymbol{\sigma}) \mathbf{v} \sqrt{\frac{2R\mathcal{E}}{\mu_{ij}}} M_i^\varepsilon M_j^\varepsilon \widehat{V}^{*\gamma-1} \\
&\quad \times 2 \Phi_{ij}(I, I_j, R, r) b_{ij}(\cos \theta) \cos \theta (1 - R) d\boldsymbol{\sigma} dr dR dI_j dI d\mathbf{v}_j d\mathbf{v} \\
&+ \sum_{\substack{j=1 \\ j \neq i}}^4 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_0^{+\infty} \int_0^{+\infty} \int_0^1 \int_0^1 \int_{\mathbb{S}^2} \mathbf{v} \left(\frac{T_i^\varepsilon}{k_B T^2} - \frac{T_j^\varepsilon}{k_B T^2} \right)
\end{aligned}$$

$$\begin{aligned}
& \times \left(\frac{m_i(\mathbf{v}'_i)^2}{2} - \frac{m_i(\mathbf{v})^2}{2} + I'_i - I \right) M_i^\varepsilon M_j^\varepsilon \widehat{V}^{*\gamma-1} \Phi_{ij}(I, I_j, R, r) \\
& \times 2 b_{ij}(\cos \theta) \cos \theta (1 - R) d\boldsymbol{\sigma} dr dR dI_j dI d\mathbf{v}_j d\mathbf{v} + O(\varepsilon).
\end{aligned} \tag{6.3.50}$$

(ii) Moreover, if the angular collision kernel of the elastic bi-species collision kernel is an odd function of $\cos \theta$, then the production term $\mathbf{B}_i$ is the formal limit for $\varepsilon \rightarrow 0$ of

$$\begin{aligned}
\mathbf{B}_i^\varepsilon &= - \sum_{\substack{j=1 \\ j \neq i}}^4 \left(\frac{m_j}{m_i + m_j} \right)^2 \left(\frac{m_i}{2\pi k_B T} \right)^{\frac{3}{2}} \left(\frac{m_j}{2\pi k_B T} \right)^{3/2} \frac{n_j^\varepsilon \mathbf{J}_i^\varepsilon - n_i^\varepsilon \mathbf{J}_j^\varepsilon}{q_i(T) q_j(T)} \\
& \times \frac{m_i}{k_B T} \left(\frac{2\pi k_B T}{m_i + m_j} \right)^{\frac{3}{2}} \frac{2\pi}{3} \Gamma \left(\frac{\gamma + 4}{2} \right) \left(\frac{2k_B T}{\mu_{ij}} \right)^{\frac{\gamma+4}{2}} \\
& \times \int_0^{+\infty} \int_0^{+\infty} \int_0^1 \int_0^1 \int_{\mathbb{S}^2} \exp \left(-\frac{I + I_j}{k_B T} \right) \\
& \times \Phi_{ij}(I, I_j, R, r) 2 \cos \theta (1 - R) b_{ij}(\cos \theta) d\boldsymbol{\sigma} dr dR dI_j dI + O(\varepsilon),
\end{aligned} \tag{6.3.51}$$

where $\mathbf{J}_i^\varepsilon$ denotes the molar diffusion flux of the species given by

$$\mathbf{J}_i^\varepsilon = n_i^\varepsilon (\mathbf{u}_i^\varepsilon - \mathbf{u}^\varepsilon). \tag{6.3.52}$$

Proof. (i) Multiplying the scaled kinetic equations given in equation (6.2.1) by $\mathbf{v} \varphi_i(I)$ and integrating the resulting equations with respect to $\mathbf{v} \in \mathbb{R}^3$ and $I \in \mathbb{R}_+$, we obtain:

$$\begin{aligned}
& \varepsilon \int_{\mathbb{R}^3} \int_0^{+\infty} \frac{\partial f_i^\varepsilon}{\partial t} \mathbf{v} \varphi_i(I) dI d\mathbf{v} + \int_{\mathbb{R}^3} \int_0^{+\infty} \mathbf{v} \cdot \nabla_{\mathbf{x}} f_i^\varepsilon \mathbf{v} \varphi_i(I) dI d\mathbf{v} \\
& = \frac{1}{\varepsilon} \sum_{j=1}^4 \int_{\mathbb{R}^3} \int_0^{+\infty} \mathbf{v} \varphi_i(I) Q_{ij}^e(f_i^\varepsilon, f_j^\varepsilon) dI d\mathbf{v} + \varepsilon \int_{\mathbb{R}^3} \int_0^{+\infty} \mathbf{v} \varphi_i(I) Q_i^{react} dI d\mathbf{v}.
\end{aligned}$$

Applying the Leibniz integral rule to the two terms on the left-hand side of the previous equation and splitting the elastic collision operator into the mono-species and the bi-species collision operators, we obtain:

$$\begin{aligned}
& \varepsilon \frac{\partial}{\partial t} \left(\int_{\mathbb{R}^3} \int_0^{+\infty} \mathbf{v} f_i^\varepsilon \varphi_i(I) dI d\mathbf{v} \right) + \nabla_{\mathbf{x}} \cdot \left(\int_{\mathbb{R}^3} \int_0^{+\infty} (\mathbf{v} \otimes \mathbf{v}) f_i^\varepsilon \varphi_i(I) dI d\mathbf{v} \right) \\
& = \frac{1}{\varepsilon} \int_{\mathbb{R}^3} \int_0^{+\infty} \mathbf{v} Q_{ii}^e(f_i^\varepsilon, f_i^\varepsilon) \varphi_i(I) dI d\mathbf{v} + \frac{1}{\varepsilon} \sum_{\substack{j=1 \\ j \neq i}}^4 \int_{\mathbb{R}^3} \int_0^{+\infty} \mathbf{v} Q_{ij}^e(f_i^\varepsilon, f_j^\varepsilon) \varphi_i(I) dI d\mathbf{v} \\
& \quad + \varepsilon \int_{\mathbb{R}^3} \int_0^{+\infty} \mathbf{v} Q_i^{react} \varphi_i(I) dI d\mathbf{v}, \tag{6.3.53}
\end{aligned}$$

The first integral on the left-hand side of equation (6.3.53) above has been previously evaluated and its value is given in equation (6.3.36). The second integral on the left-hand side of the same equation can be written as:

$$\begin{aligned}
\int_{\mathbb{R}^3} \int_0^{+\infty} (\mathbf{v} \otimes \mathbf{v}) f_i^\varepsilon \varphi_i(I) dI d\mathbf{v} &= \frac{n_i^\varepsilon}{q_i(T + \varepsilon T_i^\varepsilon)} \left(\frac{m_i}{2\pi k_B(T + \varepsilon T_i^\varepsilon)} \right)^{3/2} \\
&\times \int_{\mathbb{R}^3} \int_0^{+\infty} (\mathbf{v} \otimes \mathbf{v}) \exp \left(-\frac{m_i(\mathbf{v} - \varepsilon \mathbf{u}_i^\varepsilon)^2}{2k_B(T + \varepsilon T_i^\varepsilon)} \right) \\
&\times \exp \left(-\frac{I}{k_B(T + \varepsilon T_i^\varepsilon)} \right) \varphi_i(I) dI d\mathbf{v} \\
&= \frac{n_i^\varepsilon}{q_i(T + \varepsilon T_i^\varepsilon)} \left(\frac{m_i}{2\pi k_B(T + \varepsilon T_i^\varepsilon)} \right)^{3/2} \\
&\times \int_{\mathbb{R}^3} (\mathbf{v} \otimes \mathbf{v}) \exp \left(-\frac{m_i(\mathbf{v} - \varepsilon \mathbf{u}_i^\varepsilon)^2}{2k_B(T + \varepsilon T_i^\varepsilon)} \right) d\mathbf{v} \\
&\times \int_0^{+\infty} \varphi_i(I) \exp \left(-\frac{I}{k_B(T + \varepsilon T_i^\varepsilon)} \right) dI.
\end{aligned}$$

Using equation (6.3.29), the previous equation reduces to:

$$\begin{aligned}
\int_{\mathbb{R}^3} \int_0^{+\infty} (\mathbf{v} \otimes \mathbf{v}) f_i^\varepsilon \varphi_i(I) dI d\mathbf{v} \\
= n_i^\varepsilon \left(\frac{m_i}{2\pi k_B(T + \varepsilon T_i^\varepsilon)} \right)^{3/2} \int_{\mathbb{R}^3} (\mathbf{v} \otimes \mathbf{v}) \exp \left(-\frac{m_i(\mathbf{v} - \varepsilon \mathbf{u}_i^\varepsilon)^2}{2k_B(T + \varepsilon T_i^\varepsilon)} \right) d\mathbf{v}. \quad (6.3.54)
\end{aligned}$$

Using equation (6.3.30) together with the fact that

$$(\boldsymbol{\xi} + \varepsilon \mathbf{u}_i^\varepsilon) \otimes (\boldsymbol{\xi} + \varepsilon \mathbf{u}_i^\varepsilon) = \boldsymbol{\xi} \otimes \boldsymbol{\xi} + 2\varepsilon(\boldsymbol{\xi} \otimes \mathbf{u}_i^\varepsilon) + \varepsilon^2(\mathbf{u}_i^\varepsilon \otimes \mathbf{u}_i^\varepsilon),$$

we can rewrite equation (6.3.54) as given below:

$$\begin{aligned}
\int_{\mathbb{R}^3} \int_0^{+\infty} (\mathbf{v} \otimes \mathbf{v}) f_i^\varepsilon \varphi_i(I) dI d\mathbf{v} \\
= n_i^\varepsilon \left(\frac{m_i}{2\pi k_B(T + \varepsilon T_i^\varepsilon)} \right)^{3/2} \int_{\mathbb{R}^3} (\boldsymbol{\xi} \otimes \boldsymbol{\xi} + 2\varepsilon(\boldsymbol{\xi} \otimes \mathbf{u}_i^\varepsilon) + \varepsilon^2(\mathbf{u}_i^\varepsilon \otimes \mathbf{u}_i^\varepsilon)) \exp \left(-\frac{m_i(\boldsymbol{\xi})^2}{2k_B(T + \varepsilon T_i^\varepsilon)} \right) d\boldsymbol{\xi}.
\end{aligned}$$

Expanding, we obtain:

$$\begin{aligned}
\int_{\mathbb{R}^3} \int_0^{+\infty} (\mathbf{v} \otimes \mathbf{v}) f_i^\varepsilon \varphi_i(I) dI d\mathbf{v} \\
= n_i^\varepsilon \left(\frac{m_i}{2\pi k_B(T + \varepsilon T_i^\varepsilon)} \right)^{3/2} \int_{\mathbb{R}^3} (\boldsymbol{\xi} \otimes \boldsymbol{\xi}) \exp \left(-\frac{m_i(\boldsymbol{\xi})^2}{2k_B(T + \varepsilon T_i^\varepsilon)} \right) d\boldsymbol{\xi} \\
+ n_i^\varepsilon \left(\frac{m_i}{2\pi k_B(T + \varepsilon T_i^\varepsilon)} \right)^{3/2} 2\varepsilon \mathbf{u}_i^\varepsilon \otimes \int_{\mathbb{R}^3} \boldsymbol{\xi} \exp \left(-\frac{m_i(\boldsymbol{\xi})^2}{2k_B(T + \varepsilon T_i^\varepsilon)} \right) d\boldsymbol{\xi}
\end{aligned}$$

$$+ n_i^\varepsilon \left(\frac{m_i}{2\pi k_B(T + \varepsilon T_i^\varepsilon)} \right)^{3/2} \varepsilon^2 (\mathbf{u}_i^\varepsilon \otimes \mathbf{u}_i^\varepsilon) \int_{\mathbb{R}^3} \exp \left(- \frac{m_i(\boldsymbol{\xi})^2}{2k_B(T + \varepsilon T_i^\varepsilon)} \right) d\boldsymbol{\xi}.$$

The second and third integrals on the right-hand side of the previous equation have been previously evaluated, see equations (6.3.34) and (6.3.31), respectively for their values. Therefore

$$\begin{aligned} & \int_{\mathbb{R}^3} \int_0^{+\infty} (\mathbf{v} \otimes \mathbf{v}) f_i^\varepsilon \varphi_i(I) dI d\mathbf{v} \\ &= n_i^\varepsilon \left(\frac{m_i}{2\pi k_B(T + \varepsilon T_i^\varepsilon)} \right)^{3/2} \int_{\mathbb{R}^3} (\boldsymbol{\xi} \otimes \boldsymbol{\xi}) \exp \left(- \frac{m_i(\boldsymbol{\xi})^2}{2k_B(T + \varepsilon T_i^\varepsilon)} \right) d\boldsymbol{\xi} \\ &+ n_i^\varepsilon \left(\frac{m_i}{2\pi k_B(T + \varepsilon T_i^\varepsilon)} \right)^{3/2} 2\varepsilon \mathbf{u}_i^\varepsilon \otimes \mathbf{0} \\ &+ n_i^\varepsilon \left(\frac{m_i}{2\pi k_B(T + \varepsilon T_i^\varepsilon)} \right)^{3/2} \varepsilon^2 (\mathbf{u}_i^\varepsilon \otimes \mathbf{u}_i^\varepsilon) \left(\frac{2\pi k_B(T + \varepsilon T_i^\varepsilon)}{m_i} \right)^{\frac{3}{2}} \\ &= n_i^\varepsilon \left(\frac{m_i}{2\pi k_B(T + \varepsilon T_i^\varepsilon)} \right)^{3/2} \int_{\mathbb{R}^3} (\boldsymbol{\xi} \otimes \boldsymbol{\xi}) \exp \left(- \frac{m_i(\boldsymbol{\xi})^2}{2k_B(T + \varepsilon T_i^\varepsilon)} \right) d\boldsymbol{\xi} \\ &+ \varepsilon^2 n_i^\varepsilon (\mathbf{u}_i^\varepsilon \otimes \mathbf{u}_i^\varepsilon). \end{aligned}$$

The integral on the right-hand side of the last equality of the previous equation is similar to that whose value is given in equation (5.4.9). Therefore, following similar procedures as those used to obtain equation (5.4.9), we have that:

$$\int_{\mathbb{R}^3} (\boldsymbol{\xi} \otimes \boldsymbol{\xi}) \exp \left(- \frac{m_i(\boldsymbol{\xi})^2}{2k_B(T + \varepsilon T_i^\varepsilon)} \right) d\boldsymbol{\xi} = \mathbf{I} \left(\frac{2\pi k_B(T + \varepsilon T_i^\varepsilon)}{m_i} \right)^{\frac{3}{2}} \frac{k_B(T + \varepsilon T_i^\varepsilon)}{m_i}, \quad (6.3.55)$$

where $\mathbf{I}$ is the identity tensor. Thus

$$\begin{aligned} \int_{\mathbb{R}^3} \int_0^{+\infty} (\mathbf{v} \otimes \mathbf{v}) f_i^\varepsilon \varphi_i(I) dI d\mathbf{v} &= \mathbf{I} \frac{n_i^\varepsilon k_B(T + \varepsilon T_i^\varepsilon)}{m_i} + \varepsilon^2 n_i^\varepsilon (\mathbf{u}_i^\varepsilon \otimes \mathbf{u}_i^\varepsilon) \\ &= \frac{n_i^\varepsilon k_B(T + \varepsilon T_i^\varepsilon)}{m_i} + \varepsilon^2 n_i^\varepsilon (\mathbf{u}_i^\varepsilon \otimes \mathbf{u}_i^\varepsilon). \end{aligned} \quad (6.3.56)$$

Substituting equations (6.3.36) and (6.3.56) into equation (6.3.53), we obtain:

$$\begin{aligned} & \varepsilon^2 \frac{\partial}{\partial t} (n_i^\varepsilon \mathbf{u}_i^\varepsilon) + \nabla_{\mathbf{x}} \cdot \left(\frac{n_i^\varepsilon k_B(T + \varepsilon T_i^\varepsilon)}{m_i} + \varepsilon^2 n_i^\varepsilon (\mathbf{u}_i^\varepsilon \otimes \mathbf{u}_i^\varepsilon) \right) \\ &= \frac{1}{\varepsilon} \int_{\mathbb{R}^3} \int_0^{+\infty} \mathbf{v} Q_{ii}^\varepsilon(f_i^\varepsilon, f_i^\varepsilon) \varphi_i(I) dI d\mathbf{v} + \frac{1}{\varepsilon} \sum_{\substack{j=1 \\ j \neq i}}^4 \int_{\mathbb{R}^3} \int_0^{+\infty} \mathbf{v} Q_{ij}^\varepsilon(f_i^\varepsilon, f_j^\varepsilon) \varphi_i(I) dI d\mathbf{v} \\ &\quad + \varepsilon \int_{\mathbb{R}^3} \int_0^{+\infty} \mathbf{v} Q_i^{\text{react}} \varphi_i(I) dI d\mathbf{v}, \end{aligned} \quad (6.3.57)$$

Since the properties of the scaled collision operators are similar to their un-scaled version, the first integral on the right-hand side of the previous equation vanishes, that is

$$\int_{\mathbb{R}^3} \int_0^{+\infty} \mathbf{v} Q_{ii}^e \varphi_i(I) dI d\mathbf{v} = 0.$$

This can be seen if one set $\psi(\mathbf{v}, I) = \mathbf{v}$ in the weak form for the mono-species collision operator given in equation (2.4.67) and then apply the conservation of momentum for mono-species collision given in equation (2.2.6). Therefore, equation (6.3.57) reduces to:

$$\begin{aligned} \varepsilon^2 \frac{\partial}{\partial t} (n_i^\varepsilon \mathbf{u}_i^\varepsilon) + \nabla_{\mathbf{x}} \cdot \left(\frac{n_i^\varepsilon k_B (T + \varepsilon T_i^\alpha)}{m_i} + \varepsilon^2 n_i^\varepsilon (\mathbf{u}_i^\varepsilon \otimes \mathbf{u}_i^\varepsilon) \right) \\ = \frac{1}{\varepsilon} \sum_{\substack{j=1 \\ j \neq i}}^4 \int_{\mathbb{R}^3} \int_0^{+\infty} \mathbf{v} Q_{ij}^e (f_i^\varepsilon, f_j^\varepsilon) \varphi_i(I) dI d\mathbf{v} + \varepsilon \int_{\mathbb{R}^3} \int_0^{+\infty} \mathbf{v} Q_i^{react} \varphi_i(I) dI d\mathbf{v}. \end{aligned} \quad (6.3.58)$$

To evaluate the first integral on the right-hand side of equation (6.3.58) above, we use the elastic bi-species collision operator $Q_{ij}^e(f_i^\varepsilon, f_j^\varepsilon)$ in the form given in equation (6.3.21) and the decomposition of the elastic bi-species kernel indicated in equation (6.3.23) to obtain equation (6.3.50). Upon specifying $\Phi_{ij}(I, I_j, R, r)$, the integrals with respect to I, I_j, R, r, σ can be evaluated explicitly. The six fold integrals with respect to $\mathbf{v}, \mathbf{v}_j$ can be transformed to the centre of mass velocity and relative velocity, and the resulting integrals can be evaluated using the integral representation of gamma function given in equation (4.3.8).

To evaluate the second integral on the right-hand side of equation (6.3.58), we use the form of the reactive collision operator Q_i^{react} given in equation (6.3.22) and the decomposition of the reactive kernel given equation (6.3.24) to obtain:

$$\begin{aligned} \mathbf{C}_i^\varepsilon = \varepsilon \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_0^{+\infty} \int_0^{+\infty} \int_0^1 \int_0^1 \int_{\mathbb{S}^2} \mathbf{v} \left[\left(\frac{m_i m_j}{m_k m_l} \right)^3 M_k^{\varepsilon'} M_l^{\varepsilon'} - M_i^\varepsilon M_j^\varepsilon \right] \\ \times H_i 2 \cos \theta \widehat{V}^{*\gamma-1} \Phi^{react}(I, I_j, R, r) b^{react}(\cos \theta) (m_i m_j)^{-2} \\ \times (1 - R) d\sigma dr dR dI d\mathbf{v}_j d\mathbf{v} + O(\varepsilon^2). \end{aligned} \quad (6.3.59)$$

Again, upon specifying $\Phi^{react}(I, I_j, R, r)$, the integrals on the right hand side of equation (6.3.59) above can be computed. Specifically, the integrals with respect to I, I_j, R, r, σ can be evaluated explicitly, while the six fold integrals with respect to $\mathbf{v}, \mathbf{v}_j$ can be transformed to the centre of mass velocity and relative velocity, and the resulting integrals can either be evaluated using the integral representation of gamma function given in equation (4.3.8) or be represented by the incomplete gamma function given in equation (4.3.3).

Therefore, equation (6.3.58) reduces to:

$$\varepsilon^2 \frac{\partial}{\partial t} (n_i^\varepsilon \mathbf{u}_i^\varepsilon) + \nabla_{\mathbf{x}} \cdot \left(\frac{n_i^\varepsilon k_B (T + \varepsilon T_i^\alpha)}{m_i} + \varepsilon^2 n_i^\varepsilon (\mathbf{u}_i^\varepsilon \otimes \mathbf{u}_i^\varepsilon) \right) = \mathbf{B}_i^\varepsilon + \mathbf{C}_i^\varepsilon. \quad (6.3.60)$$

Finally, multiplying both side of equation (6.3.60) by m_i and taking the limit as $\varepsilon \rightarrow 0$, we obtain the

balance equation given in (6.3.49) for the momentum of each species, in which the production term $\mathbf{B}_i$ is the formal limit for $\varepsilon \rightarrow 0$ of the term $\mathbf{B}_i^\varepsilon$ given in equation (6.3.50). That the second term on the right-hand side of equation (6.3.60) vanishes is because the two terms on the right-hand side of equation (6.3.59) each contain ε coefficient.

(ii) Using the assumption that the angular collision kernel is an odd function of $\cos \theta$, one obtains that the second term on the right hand side of equation (6.3.50) vanishes. See Appendix C, section C.1 for details of the computation. Transforming the six fold integrals over $\mathbf{v}$ and $\mathbf{v}_j$ in the first and third terms on the right-hand side of equation (6.3.50) to the centre of mass velocity

$$\widehat{\mathbf{X}}^* = \frac{m_i \mathbf{v} + m_j \mathbf{v}_j}{m_i + m_j},$$

and relative velocity given as in equation (6.3.5), we have that following the steps used to obtain equations (2.4.10), (2.4.11) and (2.4.12), we obtain:

$$\mathbf{v} = \widehat{\mathbf{X}}^* - \frac{m_j \widehat{\mathbf{V}}^*}{m_i + m_j}, \quad (6.3.61)$$

$$\mathbf{v}_j = \widehat{\mathbf{X}}^* + \frac{m_i \widehat{\mathbf{V}}^*}{m_i + m_j}, \quad (6.3.62)$$

$$m_i(\mathbf{v})^2 + m_j(\mathbf{v}_j)^2 = M \widehat{X}^{*2} + \mu_{ij} \widehat{V}^{*2}, \quad (6.3.63)$$

where $M = m_i + m_j$, $\widehat{X}^* = \|\widehat{\mathbf{X}}^*\| = |\widehat{\mathbf{X}}^*|$ and $\widehat{V}^* = \|\widehat{\mathbf{V}}^*\| = |\widehat{\mathbf{V}}^*|$. Substituting equations (6.3.61), (6.3.62) and (6.3.63) into the integral given in the third term on the right-hand side of equation (6.3.50) and evaluating the resulting integrals in $\widehat{\mathbf{X}}^*$ and $\widehat{\mathbf{V}}^*$ using the integral representation of gamma function given in equation (4.3.8), we obtain that it vanishes. See Appendix C section C.2 for details of the computation. Furthermore, substituting equations (6.3.61), (6.3.62) and (6.3.63) into the integral given in the first term on the right-hand side of equation (6.3.50) and using the fact that the Jacobian of the transformation $(\mathbf{v}, \mathbf{v}_j) \mapsto (\widehat{\mathbf{X}}^*, \widehat{\mathbf{V}}^*)$ is unity which implies that $d\mathbf{v}d\mathbf{v}_j = d\widehat{\mathbf{X}}^* d\widehat{\mathbf{V}}^*$, we obtain that the integrals over $\mathbf{v}, \mathbf{v}_j$ can be rewritten as:

$$\begin{aligned} & \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} (\mathbf{a}_{ij} \cdot \widehat{\mathbf{V}}^*) \mathbf{v} M_i^\varepsilon M_j^\varepsilon \widehat{V}^{*\gamma-1} d\mathbf{v}_j d\mathbf{v} \\ &= \frac{n_i^\varepsilon n_j^\varepsilon (m_i m_j)^{3/2}}{q_i q_j (2\pi k_B T)^3} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} (\mathbf{a}_{ij} \cdot \widehat{\mathbf{V}}^*) \mathbf{v} \exp \left(-\frac{m_i(\mathbf{v}_i)^2 + m_j(\mathbf{v}_j)^2}{2k_B T} - \frac{I + I_j}{k_B T} \right) \\ & \quad \times \widehat{V}^{*\gamma-1} d\mathbf{v}_j d\mathbf{v} \\ &= \frac{n_i^\varepsilon n_j^\varepsilon (m_i m_j)^{3/2}}{q_i q_j (2\pi k_B T)^3} \exp \left(-\frac{I + I_j}{k_B T} \right) \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} (\mathbf{a}_{ij} \cdot \widehat{\mathbf{V}}^*) \left(\widehat{\mathbf{X}}^* - \frac{m_j \widehat{\mathbf{V}}^*}{m_i + m_j} \right) \\ & \quad \times \exp \left(-\frac{M \widehat{X}^{*2} + \mu_{ij} \widehat{V}^{*2}}{2k_B T} \right) \widehat{V}^{*\gamma-1} d\widehat{\mathbf{V}}^* d\widehat{\mathbf{X}}^* \\ &= \frac{n_i^\varepsilon n_j^\varepsilon (m_i m_j)^{3/2}}{q_i q_j (2\pi k_B T)^3} \exp \left(-\frac{I + I_j}{k_B T} \right) \end{aligned}$$

$$\times \left[\int_{\mathbb{R}^3} \widehat{\mathbf{X}}^* \exp \left(-\frac{M \widehat{X}^{*2}}{2k_B T} \right) d\widehat{\mathbf{X}}^* \int_{\mathbb{R}^3} (\mathbf{a}_{ij} \cdot \widehat{\mathbf{V}}^*) \exp \left(-\frac{\mu_{ij} \widehat{V}^{*2}}{2k_B T} \right) \widehat{V}^{*\gamma-1} d\widehat{\mathbf{V}}^* \right. \\ \left. - \int_{\mathbb{R}^3} \exp \left(-\frac{M \widehat{X}^{*2}}{2k_B T} \right) d\widehat{\mathbf{X}}^* \frac{m_j}{m_i + m_j} \int_{\mathbb{R}^3} \mathbf{V}^* (\mathbf{a}_{ij} \cdot \widehat{\mathbf{V}}^*) \exp \left(-\frac{\mu_{ij} \widehat{V}^{*2}}{2k_B T} \right) \widehat{V}^{*\gamma-1} d\widehat{\mathbf{V}}^* \right]. \quad (6.3.64)$$

The first integral in $\widehat{\mathbf{X}}^*$ on the right-hand side of the last equality of the previous equation is similar to that given in equation (4.4.20) and the second is similar to that given in equation (4.4.17). Therefore, we have that

$$\int_{\mathbb{R}^3} \widehat{\mathbf{X}}^* \exp \left(-\frac{M \widehat{X}^{*2}}{2k_B T} \right) d\widehat{\mathbf{X}}^* = 0 \quad \text{and} \quad \int_{\mathbb{R}^3} \exp \left(-\frac{M \widehat{X}^{*2}}{2k_B T} \right) d\widehat{\mathbf{X}}^* = \left(\frac{2\pi k_B T}{M} \right)^{\frac{3}{2}}. \quad (6.3.65)$$

The first integral in $\widehat{\mathbf{V}}^*$ appearing in the last equality of equation (6.3.64) can be written in spherical coordinates and then evaluated as given below:

$$\begin{aligned} & \int_{\mathbb{R}^3} (\mathbf{a}_{ij} \cdot \widehat{\mathbf{V}}^*) \exp \left(-\frac{\mu_{ij} \widehat{V}^{*2}}{2k_B T} \right) \widehat{V}^{*\gamma-1} d\widehat{\mathbf{V}}^* \\ &= \int_{\mathbb{R}^3} a_{ij} \widehat{V}^* \cos \theta \exp \left(-\frac{\mu_{ij} \widehat{V}^{*2}}{2k_B T} \right) \widehat{V}^{*\gamma-1} d\widehat{\mathbf{V}}^* \\ &= a_{ij} \int_0^\infty \int_0^\pi \int_0^{2\pi} \widehat{V}^* \cos \theta \exp \left(-\frac{\mu_{ij} \widehat{V}^{*2}}{2k_B T} \right) \widehat{V}^{*\gamma-1} \widehat{V}^{*2} \sin \theta d\phi d\theta d\widehat{V}^* \\ &= a_{ij} \int_0^\infty \widehat{V}^{*\gamma+2} \exp \left(-\frac{\mu_{ij} \widehat{V}^{*2}}{2k_B T} \right) d\widehat{V}^* \underbrace{\int_0^\pi \sin \theta \cos \theta d\theta}_0 \underbrace{\int_0^{2\pi} d\phi}_{2\pi}, \end{aligned}$$

where use have been made of the fact that $\mathbf{a}_{ij} \cdot \widehat{\mathbf{V}}^* = \|\mathbf{a}_{ij}\| \|\widehat{\mathbf{V}}^*\| \cos \theta = a_{ij} \widehat{V}^* \cos \theta$. Now using the integral representation of gamma function given in equation (4.3.8), we obtain:

$$\begin{aligned} \int_0^\infty \widehat{V}^{*\gamma+2} \exp \left(-\frac{\mu_{ij} \widehat{V}^{*2}}{2k_B T} \right) d\widehat{V}^* &= \frac{1}{2} \Gamma \left(\frac{\gamma+2+1}{2} \right) \left(\frac{2k_B T}{\mu_{ij}} \right)^{\frac{\gamma+2+1}{2}} \\ &= \frac{1}{2} \Gamma \left(\frac{\gamma+3}{2} \right) \left(\frac{2k_B T}{\mu_{ij}} \right)^{\frac{\gamma+3}{2}}. \end{aligned}$$

Therefore,

$$\begin{aligned} \int_{\mathbb{R}^3} (\mathbf{a}_{ij} \cdot \widehat{\mathbf{V}}^*) \exp \left(-\frac{\mu_{ij} \widehat{V}^{*2}}{2k_B T} \right) \widehat{V}^{*\gamma-1} d\widehat{\mathbf{V}}^* &= \frac{1}{2} \Gamma \left(\frac{\gamma+3}{2} \right) \left(\frac{2k_B T}{\mu_{ij}} \right)^{\frac{\gamma+3}{2}} (0 \times 2\pi) \\ &= 0. \end{aligned} \quad (6.3.66)$$

The second integral in $\widehat{\mathbf{V}}^*$ appearing in the last equality of equation (6.3.64) can be evaluated using the fact that any vector $\widehat{\mathbf{V}}^*$ can be written in terms of a unit vector as: $\widehat{\mathbf{V}}^* = \widehat{V}^* \vec{v}$, where $\widehat{V}^* = \|\widehat{\mathbf{V}}^*\|$ and $\vec{v}$ is a unit vector. Therefore,

$$\int_{\mathbb{R}^3} (\mathbf{a}_{ij} \cdot \hat{\mathbf{V}}^*) \hat{\mathbf{V}}^* \exp\left(-\frac{\mu_{ij} \hat{V}^{*2}}{2k_B T}\right) \hat{V}^{*\gamma-1} d\hat{\mathbf{V}}^* = \int_{\mathbb{R}^3} (a_{ij} \hat{V}^* \cos \theta) \hat{\mathbf{V}}^* \vec{\nu} \exp\left(-\frac{\mu_{ij} \hat{V}^{*2}}{2k_B T}\right) \hat{V}^{*\gamma-1} d\hat{\mathbf{V}}^*.$$

Writing the previous equation in spherical coordinates and integrating gives:

$$\begin{aligned} & \int_{\mathbb{R}^3} (a_{ij} \hat{V}^* \cos \theta) \hat{\mathbf{V}}^* \vec{\nu} \exp\left(-\frac{\mu_{ij} \hat{V}^{*2}}{2k_B T}\right) \hat{V}^{*\gamma-1} d\hat{\mathbf{V}}^* \\ &= \int_0^\infty \int_0^\pi \int_0^{2\pi} (a_{ij} \hat{V}^* \cos \theta) \hat{\mathbf{V}}^* (\hat{\mathbf{x}} \sin \theta \cos \phi + \hat{\mathbf{y}} \sin \theta \sin \phi + \hat{\mathbf{z}} \cos \theta) \hat{V}^{*\gamma-1} \\ & \quad \times \exp\left(-\frac{\mu_{ij} \hat{V}^{*2}}{2k_B T}\right) \hat{V}^{*2} \sin \theta d\phi d\theta d\hat{V}^* \\ &= a_{ij} \hat{\mathbf{x}} \int_0^\infty \hat{V}^{*\gamma+3} \exp\left(-\frac{\mu_{ij} \hat{V}^{*2}}{2k_B T}\right) d\hat{V}^* \underbrace{\int_0^\pi \sin^2 \theta \cos \theta d\theta}_0 \underbrace{\int_0^{2\pi} \cos \phi d\phi}_0 \\ & \quad + a_{ij} \hat{\mathbf{y}} \int_0^\infty \hat{V}^{*\gamma+3} \exp\left(-\frac{\mu_{ij} \hat{V}^{*2}}{2k_B T}\right) d\hat{V}^* \underbrace{\int_0^\pi \sin^2 \theta \cos \theta d\theta}_0 \underbrace{\int_0^{2\pi} \sin \phi d\phi}_0 \\ & \quad + a_{ij} \hat{\mathbf{z}} \int_0^\infty \hat{V}^{*\gamma+3} \exp\left(-\frac{\mu_{ij} \hat{V}^{*2}}{2k_B T}\right) d\hat{V}^* \underbrace{\int_0^\pi \sin \theta \cos^2 \theta d\theta}_{\frac{2}{3}} \underbrace{\int_0^{2\pi} d\phi}_{2\pi}. \end{aligned}$$

Using the integral representation of gamma function given in equation (4.3.8), we obtain:

$$\begin{aligned} \int_0^\infty \hat{V}^{*\gamma+3} \exp\left(-\frac{\mu_{ij} \hat{V}^{*2}}{2k_B T}\right) d\hat{V}^* &= \frac{1}{2} \Gamma\left(\frac{\gamma+3+1}{2}\right) \left(\frac{2k_B T}{\mu_{ij}}\right)^{\frac{\gamma+3+1}{2}} \\ &= \frac{1}{2} \Gamma\left(\frac{\gamma+4}{2}\right) \left(\frac{2k_B T}{\mu_{ij}}\right)^{\frac{\gamma+4}{2}}. \end{aligned}$$

Therefore,

$$\begin{aligned} & \int_{\mathbb{R}^3} (\mathbf{a}_{ij} \cdot \hat{\mathbf{V}}^*) \hat{\mathbf{V}}^* \exp\left(-\frac{\mu_{ij} \hat{V}^{*2}}{2k_B T}\right) \hat{V}^{*(\gamma-1)} d\hat{\mathbf{V}}^* \\ &= a_{ij} \frac{1}{2} \Gamma\left(\frac{\gamma+4}{2}\right) \left(\frac{2k_B T}{\mu_{ij}}\right)^{\frac{\gamma+4}{2}} \left[\hat{\mathbf{x}}(0) + \hat{\mathbf{y}}(0) + \hat{\mathbf{z}}\left(\frac{2}{3} \times 2\pi\right) \right] \\ &= \frac{2\pi}{3} a_{ij} \Gamma\left(\frac{\gamma+4}{2}\right) \left(\frac{2k_B T}{\mu_{ij}}\right)^{\frac{\gamma+4}{2}}. \end{aligned} \tag{6.3.67}$$

Substituting equations (6.3.65), (6.3.66) and (6.3.67) into (6.3.64), we obtain:

$$\begin{aligned} & \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} (\mathbf{a}_{ij} \cdot \hat{\mathbf{V}}^*) \mathbf{v} M_i^\varepsilon M_j^\varepsilon \hat{V}^{*\gamma-1} d\mathbf{v}_j d\mathbf{v} \\ &= -\frac{n_i^\varepsilon n_j^\varepsilon (m_i m_j)^{3/2}}{q_i q_j (2\pi k_B T)^3} \exp\left(-\frac{I + I_j}{k_B T}\right) \left(\frac{2\pi k_B T}{M}\right)^{\frac{3}{2}} \frac{m_j}{m_i + m_j} \frac{2\pi}{3} a_{ij} \Gamma\left(\frac{\gamma+4}{2}\right) \left(\frac{2k_B T}{\mu_{ij}}\right)^{\frac{\gamma+4}{2}}. \end{aligned}$$

Using the definition of $\mathbf{a}_{ij}$ given in equation (6.3.10) and setting $n_i^\varepsilon \mathbf{u}_i^\varepsilon = \mathbf{J}_i^\varepsilon + n_i^\varepsilon \mathbf{u}^\varepsilon$, we obtain:

$$\begin{aligned} \frac{n_i^\varepsilon n_j^\varepsilon}{q_i q_j} \mathbf{a}_{ij} &= \frac{n_i^\varepsilon n_j^\varepsilon m_i (\mathbf{u}_i^\varepsilon - \mathbf{u}_j^\varepsilon)}{q_i q_j k_B T} \\ &= \frac{m_i}{k_B T q_i q_j} (n_i^\varepsilon n_j^\varepsilon \mathbf{u}_i^\varepsilon - n_i^\varepsilon n_j^\varepsilon \mathbf{u}_j^\varepsilon) \\ &= \frac{m_i}{k_B T q_i q_j} (n_j^\varepsilon (\mathbf{J}_i^\varepsilon + n_i^\varepsilon \mathbf{u}^\varepsilon) - n_i^\varepsilon (\mathbf{J}_j^\varepsilon + n_j^\varepsilon \mathbf{u}^\varepsilon)) \\ &= \frac{m_i}{k_B T q_i q_j} (n_j^\varepsilon \mathbf{J}_i^\varepsilon - n_i^\varepsilon \mathbf{J}_j^\varepsilon). \end{aligned}$$

Therefore,

$$\begin{aligned} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} (\mathbf{a}_{ij} \cdot \widehat{\mathbf{V}}^*) \mathbf{v} M_i^\varepsilon M_j^\varepsilon \widehat{V}^{*\gamma-1} d\mathbf{v}_j d\mathbf{v} \\ = -\frac{(m_i m_j)^{3/2}}{(2\pi k_B T)^3} \exp\left(-\frac{I + I_j}{k_B T}\right) \left(\frac{2\pi k_B T}{M}\right)^{\frac{3}{2}} \\ \times \frac{m_j}{m_i + m_j} \frac{2\pi}{3} \Gamma\left(\frac{\gamma+4}{2}\right) \left(\frac{2k_B T}{\mu_{ij}}\right)^{\frac{\gamma+4}{2}} \frac{m_i}{k_B T} \frac{(n_j^\varepsilon \mathbf{J}_i^\varepsilon - n_i^\varepsilon \mathbf{J}_j^\varepsilon)}{q_i q_j}. \end{aligned} \quad (6.3.68)$$

Finally, substituting equation (6.3.68) into the first addend in equation (6.3.50) and using the fact that the second and third addends vanish, we obtain the desired result. $\square$

Remark 6.3.6. Observe that the production term $\mathbf{B}_i^\varepsilon$ given in equation (6.3.51) has the Maxwell-Stefan structure [29, 68]. The remaining integrals involved in equation (6.3.51), when evaluated, will only contribute to the definition of the diffusion coefficients. $\square$

6.3.4 Conservation of energy

From the scaled equations given in equation (6.2.1), the evolution equation for the energy of the mixture can be obtained as given in the following lemma.

Lemma 6.3.7. The balance equation for the energy of the reactive mixture can be written in the form

$$\frac{\partial}{\partial t} \left[\sum_{i=1}^4 \left(\frac{3}{2} n_i k_B T + n_i \frac{q_i^*(T)}{q_i(T)} \right) \right] + \nabla_{\mathbf{x}} \cdot \left[\sum_{i=1}^4 \left(\frac{5}{2} n_i k_B T \mathbf{u}_i + n_i \mathbf{u}_i \frac{q_i^*(T)}{q_i(T)} \right) \right] = -Q_R A, \quad (6.3.69)$$

where

$$n_i = \lim_{\varepsilon \rightarrow 0} n_i^\varepsilon, \quad \mathbf{u}_i = \lim_{\varepsilon \rightarrow 0} \mathbf{u}_i^\varepsilon, \quad T = \lim_{\varepsilon \rightarrow 0} (T + \varepsilon T_i^\varepsilon), \quad (6.3.70)$$

$q_i^*(T)$ has been defined in equation (6.3.11), and A is the production term defined as in subsection 6.3.2.

Proof. Multiplying the scaled kinetic equations given in Eq. (6.2.1) by $\left[\frac{m_i(\mathbf{v})^2}{2} + I \right] \varphi_i(I)$ and integrate the resulting equations with respect to $\mathbf{v} \in \mathbb{R}^3$, $I \in \mathbb{R}_+$, and then sum over the species $i = 1, 2, 3, 4$, we

obtain:

$$\begin{aligned}
& \varepsilon \sum_{i=1}^4 \int_{\mathbb{R}^3} \int_0^{+\infty} \frac{\partial f_i^\varepsilon}{\partial t} \left[\frac{m_i(\mathbf{v})^2}{2} + I \right] \varphi_i(I) dI d\mathbf{v} + \sum_{i=1}^4 \int_{\mathbb{R}^3} \int_0^{+\infty} \mathbf{v} \cdot \nabla_{\mathbf{x}} f_i^\varepsilon \left[\frac{m_i(\mathbf{v})^2}{2} + I \right] \varphi_i(I) dI d\mathbf{v} \\
&= \frac{1}{\varepsilon} \sum_{i=1}^4 \sum_{j=1}^4 \int_{\mathbb{R}^3} \int_0^{+\infty} Q_{ij}^e(f_i^\varepsilon, f_j^\varepsilon) \left[\frac{m_i(\mathbf{v})^2}{2} + I \right] \varphi_i(I) dI d\mathbf{v} \\
&\quad + \varepsilon \sum_{i=1}^4 \int_{\mathbb{R}^3} \int_0^{+\infty} Q_i^{react} \left[\frac{m_i(\mathbf{v})^2}{2} + I \right] \varphi_i(I) dI d\mathbf{v}
\end{aligned}$$

Applying the Leibniz integral rule to the two terms on the left-hand side of the previous equation and splitting the elastic collision operator into the mono-species and the bi-species collision operators, we obtain:

$$\begin{aligned}
& \varepsilon \frac{\partial}{\partial t} \sum_{i=1}^4 \left(\int_{\mathbb{R}^3} \int_0^{+\infty} \left[\frac{m_i(\mathbf{v})^2}{2} + I \right] \varphi_i(I) f_i^\varepsilon dI d\mathbf{v} \right) \\
&+ \nabla_{\mathbf{x}} \cdot \sum_{i=1}^4 \left(\int_{\mathbb{R}^3} \int_0^{+\infty} \left[\frac{m_i(\mathbf{v})^2}{2} + I \right] \varphi_i(I) \mathbf{v} f_i^\varepsilon dI d\mathbf{v} \right) = \mathcal{D}^\varepsilon + \mathcal{E}^\varepsilon + \mathcal{F}^\varepsilon, \quad (6.3.71)
\end{aligned}$$

where

$$\begin{aligned}
\mathcal{D}^\varepsilon &= \frac{1}{\varepsilon} \sum_{i=1}^4 \int_{\mathbb{R}^3} \int_0^{+\infty} \left[\frac{m_i(\mathbf{v})^2}{2} + I \right] \varphi_i(I) Q_{ii}^e(f_i^\varepsilon, f_i^\varepsilon) dI d\mathbf{v}, \\
\mathcal{E}^\varepsilon &= \frac{1}{\varepsilon} \sum_{i=1}^4 \sum_{j=1, j \neq i}^4 \int_{\mathbb{R}^3} \int_0^{+\infty} \left[\frac{m_i(\mathbf{v})^2}{2} + I \right] \varphi_i(I) Q_{ij}^e(f_i^\varepsilon, f_j^\varepsilon) dI d\mathbf{v}, \\
\mathcal{F}^\varepsilon &= \varepsilon \sum_{i=1}^4 \int_{\mathbb{R}^3} \int_0^{+\infty} \left[\frac{m_i v^2}{2} + I \right] \varphi_i(I) Q_i^{react} dI d\mathbf{v}.
\end{aligned}$$

Using the definition of the distribution functions given in equation (6.2.4), the first integral on the left-hand side of equation (6.3.71) can be written as:

$$\begin{aligned}
& \int_{\mathbb{R}^3} \int_0^{+\infty} \left[\frac{m_i(\mathbf{v})^2}{2} + I \right] \varphi_i(I) f_i^\varepsilon dI d\mathbf{v} \\
&= \frac{n_i^\varepsilon}{q_i(T + \varepsilon T_i^\varepsilon)} \left(\frac{m_i}{2\pi k_B(T + \varepsilon T_i^\varepsilon)} \right)^{3/2} \\
&\times \int_{\mathbb{R}^3} \int_0^{+\infty} \left[\frac{m_i(\mathbf{v})^2}{2} + I \right] \exp \left(- \frac{m_i(\mathbf{v} - \varepsilon \mathbf{u}_i^\varepsilon)^2}{2k_B(T + \varepsilon T_i^\varepsilon)} \right) \exp \left(- \frac{I}{k_B(T + \varepsilon T_i^\varepsilon)} \right) \varphi_i(I) dI d\mathbf{v} \\
&= \frac{n_i^\varepsilon}{q_i(T + \varepsilon T_i^\varepsilon)} \left(\frac{m_i}{2\pi k_B(T + \varepsilon T_i^\varepsilon)} \right)^{3/2} \\
&\times \int_{\mathbb{R}^3} \int_0^{+\infty} \frac{m_i(\mathbf{v})^2}{2} \exp \left(- \frac{m_i(\mathbf{v} - \varepsilon \mathbf{u}_i^\varepsilon)^2}{2k_B(T + \varepsilon T_i^\varepsilon)} \right) \exp \left(- \frac{I}{k_B(T + \varepsilon T_i^\varepsilon)} \right) \varphi_i(I) dI d\mathbf{v}
\end{aligned}$$

$$\begin{aligned}
& + \frac{n_i^\varepsilon}{q_i(T + \varepsilon T_i^\varepsilon)} \left(\frac{m_i}{2\pi k_B(T + \varepsilon T_i^\varepsilon)} \right)^{3/2} \\
& \times \int_{\mathbb{R}^3} \int_0^{+\infty} I \exp \left(- \frac{m_i(\mathbf{v} - \varepsilon \mathbf{u}_i^\varepsilon)^2}{2k_B(T + \varepsilon T_i^\varepsilon)} \right) \exp \left(- \frac{I}{k_B(T + \varepsilon T_i^\varepsilon)} \right) \varphi_i(I) dI d\mathbf{v} \\
& = \frac{n_i^\varepsilon}{q_i(T + \varepsilon T_i^\varepsilon)} \left(\frac{m_i}{2\pi k_B(T + \varepsilon T_i^\varepsilon)} \right)^{3/2} \\
& \times \frac{m_i}{2} \int_{\mathbb{R}^3} (\mathbf{v})^2 \exp \left(- \frac{m_i(\mathbf{v} - \varepsilon \mathbf{u}_i^\varepsilon)^2}{2k_B(T + \varepsilon T_i^\varepsilon)} \right) d\mathbf{v} \int_0^{+\infty} \exp \left(- \frac{I}{k_B(T + \varepsilon T_i^\varepsilon)} \right) \varphi_i(I) dI \\
& + \frac{n_i^\varepsilon}{q_i(T + \varepsilon T_i^\varepsilon)} \left(\frac{m_i}{2\pi k_B(T + \varepsilon T_i^\varepsilon)} \right)^{3/2} \\
& \times \int_{\mathbb{R}^3} \exp \left(- \frac{m_i(\mathbf{v} - \varepsilon \mathbf{u}_i^\varepsilon)^2}{2k_B(T + \varepsilon T_i^\varepsilon)} \right) d\mathbf{v} \int_0^{+\infty} I \exp \left(- \frac{I}{k_B(T + \varepsilon T_i^\varepsilon)} \right) \varphi_i(I) dI.
\end{aligned}$$

Using equation (6.3.29) and the fact that

$$q_i^*(T + \varepsilon T_i^\varepsilon) = \int_0^{+\infty} I \exp \left(- \frac{I}{k_B(T + \varepsilon T_i^\varepsilon)} \right) \varphi_i(I) dI, \quad (6.3.72)$$

we obtain:

$$\begin{aligned}
& \int_{\mathbb{R}^3} \int_0^{+\infty} \left[\frac{m_i(\mathbf{v})^2}{2} + I \right] \varphi_i(I) f_i^\varepsilon dI d\mathbf{v} \\
& = n_i^\varepsilon \left(\frac{m_i}{2\pi k_B(T + \varepsilon T_i^\varepsilon)} \right)^{3/2} \frac{m_i}{2} \int_{\mathbb{R}^3} (\mathbf{v})^2 \exp \left(- \frac{m_i(\mathbf{v} - \varepsilon \mathbf{u}_i^\varepsilon)^2}{2k_B(T + \varepsilon T_i^\varepsilon)} \right) d\mathbf{v} \\
& + n_i^\varepsilon \frac{q_i^*(T + \varepsilon T_i^\varepsilon)}{q_i(T + \varepsilon T_i^\varepsilon)} \left(\frac{m_i}{2\pi k_B(T + \varepsilon T_i^\varepsilon)} \right)^{3/2} \int_{\mathbb{R}^3} \exp \left(- \frac{m_i(\mathbf{v} - \varepsilon \mathbf{u}_i^\varepsilon)^2}{2k_B(T + \varepsilon T_i^\varepsilon)} \right) d\mathbf{v}.
\end{aligned}$$

Using equation (6.3.30), we can rewrite the previous equation as follows:

$$\begin{aligned}
& \int_{\mathbb{R}^3} \int_0^{+\infty} \left[\frac{m_i(\mathbf{v})^2}{2} + I \right] \varphi_i(I) f_i^\varepsilon dI d\mathbf{v} \\
& = n_i^\varepsilon \left(\frac{m_i}{2\pi k_B(T + \varepsilon T_i^\varepsilon)} \right)^{3/2} \frac{m_i}{2} \int_{\mathbb{R}^3} (\boldsymbol{\xi} + \varepsilon \mathbf{u}_i^\varepsilon)^2 \exp \left(- \frac{m_i(\boldsymbol{\xi})^2}{2k_B(T + \varepsilon T_i^\varepsilon)} \right) d\boldsymbol{\xi} \\
& + n_i^\varepsilon \frac{q_i^*(T + \varepsilon T_i^\varepsilon)}{q_i(T + \varepsilon T_i^\varepsilon)} \left(\frac{m_i}{2\pi k_B(T + \varepsilon T_i^\varepsilon)} \right)^{3/2} \int_{\mathbb{R}^3} \exp \left(- \frac{m_i(\boldsymbol{\xi})^2}{2k_B(T + \varepsilon T_i^\varepsilon)} \right) d\boldsymbol{\xi}. \quad (6.3.73)
\end{aligned}$$

Observe that

$$(\boldsymbol{\xi} + \varepsilon \mathbf{u}_i^\varepsilon)^2 = (\boldsymbol{\xi})^2 + 2\varepsilon (\boldsymbol{\xi} \cdot \mathbf{u}_i^\varepsilon) + \varepsilon^2 (\mathbf{u}_i^\varepsilon)^2. \quad (6.3.74)$$

Substituting equation (6.3.74) above into the first integral on the right-hand side of equation (6.3.73) and

equation (6.3.31) which is the value of the second integral on the right-hand side of the same equation, we obtain:

$$\begin{aligned}
& \int_{\mathbb{R}^3} \int_0^{+\infty} \left[\frac{m_i(\mathbf{v})^2}{2} + I \right] \varphi_i(I) f_i^\varepsilon dI d\mathbf{v} \\
&= n_i^\varepsilon \left(\frac{m_i}{2\pi k_B(T + \varepsilon T_i^\varepsilon)} \right)^{3/2} \frac{m_i}{2} \int_{\mathbb{R}^3} ((\boldsymbol{\xi})^2 + 2\varepsilon(\boldsymbol{\xi} \cdot \mathbf{u}_i^\varepsilon) + \varepsilon^2(\mathbf{u}_i^\varepsilon)^2) \exp\left(-\frac{m_i(\boldsymbol{\xi})^2}{2k_B(T + \varepsilon T_i^\varepsilon)}\right) d\boldsymbol{\xi} \\
&+ n_i^\varepsilon \frac{q_i^*(T + \varepsilon T_i^\varepsilon)}{q_i(T + \varepsilon T_i^\varepsilon)} \left(\frac{m_i}{2\pi k_B(T + \varepsilon T_i^\varepsilon)} \right)^{3/2} \left(\frac{2\pi k_B(T + \varepsilon T_i^\varepsilon)}{m_i} \right)^{\frac{3}{2}} \\
&= n_i^\varepsilon \left(\frac{m_i}{2\pi k_B(T + \varepsilon T_i^\varepsilon)} \right)^{3/2} \frac{m_i}{2} \int_{\mathbb{R}^3} (\boldsymbol{\xi})^2 \exp\left(-\frac{m_i(\boldsymbol{\xi})^2}{2k_B(T + \varepsilon T_i^\varepsilon)}\right) d\boldsymbol{\xi} \\
&+ n_i^\varepsilon \left(\frac{m_i}{2\pi k_B(T + \varepsilon T_i^\varepsilon)} \right)^{3/2} m_i \varepsilon \mathbf{u}_i \cdot \int_{\mathbb{R}^3} \boldsymbol{\xi} \exp\left(-\frac{m_i(\boldsymbol{\xi})^2}{2k_B(T + \varepsilon T_i^\varepsilon)}\right) d\boldsymbol{\xi} \\
&+ n_i^\varepsilon \left(\frac{m_i}{2\pi k_B(T + \varepsilon T_i^\varepsilon)} \right)^{3/2} \frac{m_i}{2} \varepsilon^2 (\mathbf{u}_i^\varepsilon)^2 \int_{\mathbb{R}^3} \exp\left(-\frac{m_i(\boldsymbol{\xi})^2}{2k_B(T + \varepsilon T_i^\varepsilon)}\right) d\boldsymbol{\xi} \\
&+ n_i^\varepsilon \frac{q_i^*(T + \varepsilon T_i^\varepsilon)}{q_i(T + \varepsilon T_i^\varepsilon)}. \tag{6.3.75}
\end{aligned}$$

The first integral in the last equality of the previous equation can be evaluated in spherical coordinates as given below:

$$\begin{aligned}
& \int_{\mathbb{R}^3} (\boldsymbol{\xi})^2 \exp\left(-\frac{m_i(\boldsymbol{\xi})^2}{2k_B(T + \varepsilon T_i^\varepsilon)}\right) d\boldsymbol{\xi} \\
&= \int_0^\infty \int_0^\pi \int_0^{2\pi} (\boldsymbol{\xi})^2 \exp\left(-\frac{m_i(\boldsymbol{\xi})^2}{2k_B(T + \varepsilon T_i^\varepsilon)}\right) (\boldsymbol{\xi})^2 \sin\theta d\phi d\theta d\xi \\
&= \int_0^\infty \xi^4 \exp\left(-\frac{m_i(\boldsymbol{\xi})^2}{2k_B(T + \varepsilon T_i^\varepsilon)}\right) d\xi \underbrace{\int_0^\pi \sin\theta d\theta}_2 \underbrace{\int_0^{2\pi} d\phi}_{2\pi} \\
&= 4\pi \int_0^\infty \xi^4 \exp\left(-\frac{m_i(\boldsymbol{\xi})^2}{2k_B(T + \varepsilon T_i^\varepsilon)}\right) d\xi.
\end{aligned}$$

Using the integral representation of gamma function given in equation (4.3.8), we obtain:

$$\begin{aligned}
& \int_{\mathbb{R}^3} (\boldsymbol{\xi})^2 \exp\left(-\frac{m_i(\boldsymbol{\xi})^2}{2k_B(T + \varepsilon T_i^\varepsilon)}\right) d\boldsymbol{\xi} = 4\pi \frac{1}{2} \Gamma\left(\frac{5}{2}\right) \left(\frac{2k_B(T + \varepsilon T_i^\varepsilon)}{m_i}\right)^{\frac{5}{2}} \\
&= 4\pi \frac{1}{2} \frac{3\sqrt{\pi}}{4} \left(\frac{2k_B(T + \varepsilon T_i^\varepsilon)}{m_i}\right)^{\frac{5}{2}} \\
&= \left(\frac{2\pi k_B(T + \varepsilon T_i^\varepsilon)}{m_i}\right)^{\frac{3}{2}} \frac{3k_B(T + \varepsilon T_i^\varepsilon)}{m_i}. \tag{6.3.76}
\end{aligned}$$

The value of the second integral in the last equality of equation (6.3.75) is given in equation (6.3.34), while the value of the last integral is given in equation (6.3.31). Therefore, substituting equations (6.3.31), (6.3.34) and (6.3.76) into equation (6.3.75) we obtain:

$$\begin{aligned}
& \int_{\mathbb{R}^3} \int_0^{+\infty} \left[\frac{m_i(\mathbf{v})^2}{2} + I \right] \varphi_i(I) f_i^\varepsilon dI d\mathbf{v} \\
&= n_i^\varepsilon \left(\frac{m_i}{2\pi k_B(T + \varepsilon T_i^\varepsilon)} \right)^{3/2} \frac{m_i}{2} \left(\frac{2\pi k_B(T + \varepsilon T_i^\varepsilon)}{m_i} \right)^{\frac{3}{2}} \frac{3k_B(T + \varepsilon T_i^\varepsilon)}{m_i} \\
&+ n_i^\varepsilon \left(\frac{m_i}{2\pi k_B(T + \varepsilon T_i^\varepsilon)} \right)^{3/2} m_i \varepsilon \mathbf{u}_i \cdot \mathbf{0} \\
&+ n_i^\varepsilon \left(\frac{m_i}{2\pi k_B(T + \varepsilon T_i^\varepsilon)} \right)^{3/2} \frac{m_i}{2} \varepsilon^2 (\mathbf{u}_i^\varepsilon)^2 \left(\frac{2\pi k_B(T + \varepsilon T_i^\varepsilon)}{m_i} \right)^{\frac{3}{2}} \\
&+ n_i^\varepsilon \frac{q_i^*(T + \varepsilon T_i^\varepsilon)}{q_i(T + \varepsilon T_i^\varepsilon)}.
\end{aligned}$$

Thus

$$\begin{aligned}
& \int_{\mathbb{R}^3} \int_0^{+\infty} \left[\frac{m_i(\mathbf{v})^2}{2} + I \right] \varphi_i(I) f_i^\varepsilon dI d\mathbf{v} \\
&= \frac{3}{2} n_i^\varepsilon k_B(T + \varepsilon T_i^\varepsilon) + n_i^\varepsilon \frac{m_i}{2} \varepsilon^2 (\mathbf{u}_i^\varepsilon)^2 + n_i^\varepsilon \frac{q_i^*(T + \varepsilon T_i^\varepsilon)}{q_i(T + \varepsilon T_i^\varepsilon)}. \quad (6.3.77)
\end{aligned}$$

The second integral on the left-hand side of equation (6.3.71) can be written as:

$$\begin{aligned}
& \int_{\mathbb{R}^3} \int_0^{+\infty} \left[\frac{m_i(\mathbf{v})^2}{2} + I \right] \varphi_i(I) \mathbf{v} f_i^\varepsilon dI d\mathbf{v} \\
&= \frac{n_i^\varepsilon}{q_i(T + \varepsilon T_i^\varepsilon)} \left(\frac{m_i}{2\pi k_B(T + \varepsilon T_i^\varepsilon)} \right)^{3/2} \\
&\times \int_{\mathbb{R}^3} \int_0^{+\infty} \mathbf{v} \left[\frac{m_i(\mathbf{v})^2}{2} + I \right] \exp \left(- \frac{m_i(\mathbf{v} - \varepsilon \mathbf{u}_i^\varepsilon)^2}{2k_B(T + \varepsilon T_i^\varepsilon)} \right) \exp \left(- \frac{I}{k_B(T + \varepsilon T_i^\varepsilon)} \right) \varphi_i(I) dI d\mathbf{v} \\
&= \frac{n_i^\varepsilon}{q_i(T + \varepsilon T_i^\varepsilon)} \left(\frac{m_i}{2\pi k_B(T + \varepsilon T_i^\varepsilon)} \right)^{3/2} \\
&\times \int_{\mathbb{R}^3} \int_0^{+\infty} \mathbf{v} \frac{m_i(\mathbf{v})^2}{2} \exp \left(- \frac{m_i(\mathbf{v} - \varepsilon \mathbf{u}_i^\varepsilon)^2}{2k_B(T + \varepsilon T_i^\varepsilon)} \right) \exp \left(- \frac{I}{k_B(T + \varepsilon T_i^\varepsilon)} \right) \varphi_i(I) dI d\mathbf{v} \\
&+ \frac{n_i^\varepsilon}{q_i(T + \varepsilon T_i^\varepsilon)} \left(\frac{m_i}{2\pi k_B(T + \varepsilon T_i^\varepsilon)} \right)^{3/2} \\
&\times \int_{\mathbb{R}^3} \int_0^{+\infty} \mathbf{v} I \exp \left(- \frac{m_i(\mathbf{v} - \varepsilon \mathbf{u}_i^\varepsilon)^2}{2k_B(T + \varepsilon T_i^\varepsilon)} \right) \exp \left(- \frac{I}{k_B(T + \varepsilon T_i^\varepsilon)} \right) \varphi_i(I) dI d\mathbf{v} \\
&= \frac{n_i^\varepsilon}{q_i(T + \varepsilon T_i^\varepsilon)} \left(\frac{m_i}{2\pi k_B(T + \varepsilon T_i^\varepsilon)} \right)^{3/2}
\end{aligned}$$

$$\begin{aligned}
& \times \frac{m_i}{2} \int_{\mathbb{R}^3} \mathbf{v}(\mathbf{v})^2 \exp \left(-\frac{m_i(\mathbf{v} - \varepsilon \mathbf{u}_i^\varepsilon)^2}{2k_B(T + \varepsilon T_i^\varepsilon)} \right) d\mathbf{v} \int_0^{+\infty} \exp \left(-\frac{I}{k_B(T + \varepsilon T_i^\varepsilon)} \right) \varphi_i(I) dI \\
& + \frac{n_i^\varepsilon}{q_i(T + \varepsilon T_i^\varepsilon)} \left(\frac{m_i}{2\pi k_B(T + \varepsilon T_i^\varepsilon)} \right)^{3/2} \\
& \times \int_{\mathbb{R}^3} \mathbf{v} \exp \left(-\frac{m_i(\mathbf{v} - \varepsilon \mathbf{u}_i^\varepsilon)^2}{2k_B(T + \varepsilon T_i^\varepsilon)} \right) d\mathbf{v} \int_0^{+\infty} I \exp \left(-\frac{I}{k_B(T + \varepsilon T_i^\varepsilon)} \right) \varphi_i(I) dI.
\end{aligned}$$

Using equations (6.3.29) and (6.3.72), we obtain:

$$\begin{aligned}
& \int_{\mathbb{R}^3} \int_0^\infty \left[\frac{m_i(\mathbf{v})^2}{2} + I \right] \varphi_i(I) \mathbf{v} f_i^\varepsilon dI d\mathbf{v} \\
& = n_i^\varepsilon \left(\frac{m_i}{2\pi k_B(T + \varepsilon T_i^\varepsilon)} \right)^{3/2} \frac{m_i}{2} \int_{\mathbb{R}^3} \mathbf{v}(\mathbf{v})^2 \exp \left(-\frac{m_i(\mathbf{v} - \varepsilon \mathbf{u}_i^\varepsilon)^2}{2k_B(T + \varepsilon T_i^\varepsilon)} \right) d\mathbf{v} \\
& + n_i^\varepsilon \frac{q_i^*(T + \varepsilon T_i^\varepsilon)}{q_i(T + \varepsilon T_i^\varepsilon)} \left(\frac{m_i}{2\pi k_B(T + \varepsilon T_i^\varepsilon)} \right)^{3/2} \int_{\mathbb{R}^3} \mathbf{v} \exp \left(-\frac{m_i(\mathbf{v} - \varepsilon \mathbf{u}_i^\varepsilon)^2}{2k_B(T + \varepsilon T_i^\varepsilon)} \right) d\mathbf{v}.
\end{aligned}$$

The value of the second integral on the right-hand side of the previous equation is given in equation (6.3.35).

Therefore,

$$\begin{aligned}
& \int_{\mathbb{R}^3} \int_0^\infty \left[\frac{m_i(\mathbf{v})^2}{2} + I \right] \varphi_i(I) \mathbf{v} f_i^\varepsilon dI d\mathbf{v} \\
& = n_i^\varepsilon \left(\frac{m_i}{2\pi k_B(T + \varepsilon T_i^\varepsilon)} \right)^{3/2} \frac{m_i}{2} \int_{\mathbb{R}^3} \mathbf{v}(\mathbf{v})^2 \exp \left(-\frac{m_i(\mathbf{v} - \varepsilon \mathbf{u}_i^\varepsilon)^2}{2k_B(T + \varepsilon T_i^\varepsilon)} \right) d\mathbf{v} \quad (6.3.78) \\
& + n_i^\varepsilon \frac{q_i^*(T + \varepsilon T_i^\varepsilon)}{q_i(T + \varepsilon T_i^\varepsilon)} \left(\frac{m_i}{2\pi k_B(T + \varepsilon T_i^\varepsilon)} \right)^{3/2} \varepsilon \mathbf{u}_i^\varepsilon \left(\frac{2\pi k_B(T + \varepsilon T_i^\varepsilon)}{m_i} \right)^{\frac{3}{2}}.
\end{aligned}$$

Using equation (6.3.30) we can rewrite the integral on the right-hand side of the previous equation as given below:

$$\begin{aligned}
& \int_{\mathbb{R}^3} \mathbf{v}(\mathbf{v})^2 \exp \left(-\frac{m_i(\mathbf{v} - \varepsilon \mathbf{u}_i^\varepsilon)^2}{2k_B(T + \varepsilon T_i^\varepsilon)} \right) d\mathbf{v} \\
& = \int_{\mathbb{R}^3} (\boldsymbol{\xi} + \varepsilon \mathbf{u}_i^\varepsilon)(\boldsymbol{\xi} + \varepsilon \mathbf{u}_i^\varepsilon)^2 \exp \left(-\frac{m_i(\boldsymbol{\xi})^2}{2k_B(T + \varepsilon T_i^\varepsilon)} \right) d\boldsymbol{\xi} \quad (6.3.79)
\end{aligned}$$

Using (6.3.74), observe that

$$\begin{aligned}
& (\boldsymbol{\xi} + \varepsilon \mathbf{u}_i^\varepsilon)(\boldsymbol{\xi} + \varepsilon \mathbf{u}_i^\varepsilon)^2 = (\boldsymbol{\xi} + \varepsilon \mathbf{u}_i^\varepsilon)((\boldsymbol{\xi})^2 + 2\varepsilon(\boldsymbol{\xi} \cdot \mathbf{u}_i^\varepsilon) + \varepsilon^2(\mathbf{u}_i^\varepsilon)^2) \\
& = \boldsymbol{\xi}(\boldsymbol{\xi})^2 + 2\varepsilon \boldsymbol{\xi}(\boldsymbol{\xi} \cdot \mathbf{u}_i^\varepsilon) + \varepsilon^2 \boldsymbol{\xi}(\mathbf{u}_i^\varepsilon)^2 + \varepsilon \mathbf{u}_i^\varepsilon(\boldsymbol{\xi})^2 + 2\varepsilon^2 \mathbf{u}_i^\varepsilon(\boldsymbol{\xi} \cdot \mathbf{u}_i^\varepsilon) + \varepsilon^3 \mathbf{u}_i^\varepsilon(\mathbf{u}_i^\varepsilon)^2.
\end{aligned}$$

Substituting the previous equation into the integral of the right-hand side of equation (6.3.79) and expanding the resulting equation gives:

$$\begin{aligned}
\int_{\mathbb{R}^3} \mathbf{v}(\mathbf{v})^2 \exp \left(-\frac{m_i(\mathbf{v} - \varepsilon \mathbf{u}_i^\varepsilon)^2}{2k_B(T + \varepsilon T_i^\varepsilon)} \right) d\mathbf{v} &= \int_{\mathbb{R}^3} \boldsymbol{\xi}(\boldsymbol{\xi})^2 \exp \left(-\frac{m_i(\boldsymbol{\xi})^2}{2k_B(T + \varepsilon T_i^\varepsilon)} \right) d\boldsymbol{\xi} \\
&+ 2\varepsilon \mathbf{u}_i^\varepsilon \cdot \int_{\mathbb{R}^3} (\boldsymbol{\xi} \otimes \boldsymbol{\xi}) \exp \left(-\frac{m_i(\boldsymbol{\xi})^2}{2k_B(T + \varepsilon T_i^\varepsilon)} \right) d\boldsymbol{\xi} \\
&+ \varepsilon^2 (\mathbf{u}_i^\varepsilon)^2 \int_{\mathbb{R}^3} \boldsymbol{\xi} \exp \left(-\frac{m_i(\boldsymbol{\xi})^2}{2k_B(T + \varepsilon T_i^\varepsilon)} \right) d\boldsymbol{\xi} \\
&+ \varepsilon \mathbf{u}_i^\varepsilon \int_{\mathbb{R}^3} (\boldsymbol{\xi})^2 \exp \left(-\frac{m_i(\boldsymbol{\xi})^2}{2k_B(T + \varepsilon T_i^\varepsilon)} \right) d\boldsymbol{\xi} \\
&+ (2\varepsilon^2 \mathbf{u}_i^\varepsilon) \mathbf{u}_i^\varepsilon \cdot \int_{\mathbb{R}^3} \boldsymbol{\xi} \exp \left(-\frac{m_i(\boldsymbol{\xi})^2}{2k_B(T + \varepsilon T_i^\varepsilon)} \right) d\boldsymbol{\xi} \\
&+ \varepsilon^3 \mathbf{u}_i^\varepsilon (\mathbf{u}_i^\varepsilon)^2 \int_{\mathbb{R}^3} \exp \left(-\frac{m_i(\boldsymbol{\xi})^2}{2k_B(T + \varepsilon T_i^\varepsilon)} \right) d\boldsymbol{\xi}.
\end{aligned}$$

The values of the second, third, fourth, fifth and sixth integrals on the right-hand side of the previous equation are respectively given in equations (6.3.55), (6.3.34), (6.3.76), (6.3.34) and (6.3.31). Therefore,

$$\begin{aligned}
\int_{\mathbb{R}^3} \mathbf{v}(\mathbf{v})^2 \exp \left(-\frac{m_i(\mathbf{v} - \varepsilon \mathbf{u}_i^\varepsilon)^2}{2k_B(T + \varepsilon T_i^\varepsilon)} \right) d\mathbf{v} &= \int_{\mathbb{R}^3} \boldsymbol{\xi}(\boldsymbol{\xi})^2 \exp \left(-\frac{m_i(\boldsymbol{\xi})^2}{2k_B(T + \varepsilon T_i^\varepsilon)} \right) d\boldsymbol{\xi} \\
&+ 2\varepsilon \mathbf{u}_i^\varepsilon \mathbf{l} \left(\frac{2\pi k_B(T + \varepsilon T_i^\varepsilon)}{m_i} \right)^{\frac{3}{2}} \frac{k_B(T + \varepsilon T_i^\varepsilon)}{m_i} \\
&+ \varepsilon^2 (\mathbf{u}_i^\varepsilon)^2 \times \mathbf{0} \\
&+ \varepsilon \mathbf{u}_i^\varepsilon \left(\frac{2\pi k_B(T + \varepsilon T_i^\varepsilon)}{m_i} \right)^{\frac{3}{2}} \frac{3k_B(T + \varepsilon T_i^\varepsilon)}{m_i} \\
&+ (2\varepsilon^2 \mathbf{u}_i^\varepsilon) \mathbf{u}_i^\varepsilon \cdot \mathbf{0} \\
&+ \varepsilon^3 \mathbf{u}_i^\varepsilon (\mathbf{u}_i^\varepsilon)^2 \left(\frac{2\pi k_B(T + \varepsilon T_i^\varepsilon)}{m_i} \right)^{\frac{3}{2}}.
\end{aligned} \tag{6.3.80}$$

Using the fact that any vector can be written in terms of a unit vector, we have that $\boldsymbol{\xi}$ can be written as $\boldsymbol{\xi} = \xi \vec{\mathbf{v}}$, where $\xi = \|\boldsymbol{\xi}\| = |\boldsymbol{\xi}|$ and $\vec{\mathbf{v}}$ is a unit vector. Therefore, the integral on the right-hand side of the previous equation can be written as given below:

$$\int_{\mathbb{R}^3} \boldsymbol{\xi}(\boldsymbol{\xi})^2 \exp \left(-\frac{m_i(\boldsymbol{\xi})^2}{2k_B(T + \varepsilon T_i^\varepsilon)} \right) d\boldsymbol{\xi} = \int_{\mathbb{R}^3} \xi \vec{\mathbf{v}}(\xi^2) \exp \left(-\frac{m_i(\boldsymbol{\xi})^2}{2k_B(T + \varepsilon T_i^\varepsilon)} \right) d\boldsymbol{\xi}.$$

Writing the previous integral in spherical coordinates and integrating, we obtain:

$$\begin{aligned}
&\int_{\mathbb{R}^3} \xi \vec{\mathbf{v}}(\xi^2) \exp \left(-\frac{m_i(\boldsymbol{\xi})^2}{2k_B(T + \varepsilon T_i^\varepsilon)} \right) d\boldsymbol{\xi} \\
&= \int_0^\infty \int_0^\pi \int_0^{2\pi} \xi (\hat{\mathbf{x}} \sin \theta \cos \phi + \hat{\mathbf{y}} \sin \theta \sin \phi + \hat{\mathbf{z}} \cos \theta) \xi^2
\end{aligned}$$

$$\begin{aligned}
& \times \exp \left(-\frac{m_i(\boldsymbol{\xi})^2}{2k_B(T + \varepsilon T_i^\varepsilon)} \right) \xi^2 \sin \theta \, d\phi \, d\theta \, d\xi \\
& = \int_0^\infty \xi^5 \exp \left(-\frac{m_i(\boldsymbol{\xi})^2}{2k_B(T + \varepsilon T_i^\varepsilon)} \right) d\xi \left(\hat{\mathbf{x}} \underbrace{\int_0^\pi \sin^2 \theta \, d\theta}_{\frac{\pi}{2}} \underbrace{\int_0^{2\pi} \cos \phi \, d\phi}_0 \right. \\
& \quad \left. + \hat{\mathbf{y}} \underbrace{\int_0^\pi \sin^2 \theta \, d\theta}_{\frac{\pi}{2}} \underbrace{\int_0^{2\pi} \sin \phi \, d\phi}_0 + \hat{\mathbf{z}} \underbrace{\int_0^\pi \cos \theta \sin \theta \, d\theta}_0 \underbrace{\int_0^{2\pi} d\phi}_{2\pi} \right),
\end{aligned}$$

where $\hat{\mathbf{x}}, \hat{\mathbf{y}}, \hat{\mathbf{z}}$ are the Cartesian unit vectors in $\mathbb{R}^3$. The integral in ξ can be evaluated using the integral representation of gamma given in equation (4.3.8) as follows:

$$\begin{aligned}
\int_0^\infty \xi^5 \exp \left(-\frac{m_i(\boldsymbol{\xi})^2}{2k_B(T + \varepsilon T_i^\varepsilon)} \right) d\xi &= \frac{1}{2} \Gamma(3) \left(\frac{2k_B(T + \varepsilon T_i^\varepsilon)}{m_i} \right)^3 \\
&= \frac{1}{2} 2! \left(\frac{2k_B(T + \varepsilon T_i^\varepsilon)}{m_i} \right)^3 \\
&= \left(\frac{2k_B(T + \varepsilon T_i^\varepsilon)}{m_i} \right)^3.
\end{aligned}$$

Therefore,

$$\begin{aligned}
& \int_{\mathbb{R}^3} \boldsymbol{\xi}(\boldsymbol{\xi})^2 \exp \left(-\frac{m_i(\boldsymbol{\xi})^2}{2k_B(T + \varepsilon T_i^\varepsilon)} \right) d\boldsymbol{\xi} \\
&= \left(\frac{2k_B(T + \varepsilon T_i^\varepsilon)}{m_i} \right)^3 \left[\hat{\mathbf{x}} \left(\frac{\pi}{2} \times 0 \right) + \hat{\mathbf{y}} \left(\frac{\pi}{2} \times 0 \right) + \hat{\mathbf{z}} (0 \times 2\pi) \right] \\
&= \left(\frac{2k_B(T + \varepsilon T_i^\varepsilon)}{m_i} \right)^3 \times \mathbf{0} \\
&= \mathbf{0}.
\end{aligned} \tag{6.3.81}$$

Substituting equation (6.3.81) into equation (6.3.80), we obtain:

$$\begin{aligned}
\int_{\mathbb{R}^3} \mathbf{v}(\mathbf{v})^2 \exp \left(-\frac{m_i(\mathbf{v} - \varepsilon \mathbf{u}_i^\varepsilon)^2}{2k_B(T + \varepsilon T_i^\varepsilon)} \right) d\mathbf{v} &= 2\varepsilon \mathbf{u}_i^\varepsilon \left(\frac{2\pi k_B(T + \varepsilon T_i^\varepsilon)}{m_i} \right)^{\frac{3}{2}} \frac{k_B(T + \varepsilon T_i^\varepsilon)}{m_i} \\
&+ \varepsilon \mathbf{u}_i^\varepsilon \left(\frac{2\pi k_B(T + \varepsilon T_i^\varepsilon)}{m_i} \right)^{\frac{3}{2}} \frac{3k_B(T + \varepsilon T_i^\varepsilon)}{m_i} \\
&+ \varepsilon^3 \mathbf{u}_i^\varepsilon (\mathbf{u}_i^\varepsilon)^2 \left(\frac{2\pi k_B(T + \varepsilon T_i^\varepsilon)}{m_i} \right)^{\frac{3}{2}}.
\end{aligned} \tag{6.3.82}$$

Substituting equation (6.3.82) into equation (6.3.78), we obtain:

$$\int_{\mathbb{R}^3} \int_0^\infty \left[\frac{m_i(\mathbf{v})^2}{2} + I \right] \varphi_i(I) \mathbf{v} f_i^\varepsilon dI d\mathbf{v}$$

$$\begin{aligned}
&= n_i^\varepsilon \left(\frac{m_i}{2\pi k_B(T + \varepsilon T_i^\varepsilon)} \right)^{3/2} \frac{m_i}{2} \left(2\varepsilon \mathbf{u}_i^\varepsilon \mathbf{I} \left(\frac{2\pi k_B(T + \varepsilon T_i^\varepsilon)}{m_i} \right)^{\frac{3}{2}} \frac{k_B(T + \varepsilon T_i^\alpha)}{m_i} \right. \\
&+ \varepsilon \mathbf{u}_i^\varepsilon \left(\frac{2\pi k_B(T + \varepsilon T_i^\varepsilon)}{m_i} \right)^{\frac{3}{2}} \frac{3k_B(T + \varepsilon T_i^\varepsilon)}{m_i} + \varepsilon^3 \mathbf{u}_i^\varepsilon (\mathbf{u}_i^\varepsilon)^2 \left(\frac{2\pi k_B(T + \varepsilon T_i^\varepsilon)}{m_i} \right)^{\frac{3}{2}} \Bigg) \\
&+ n_i^\varepsilon \frac{q_i^*(T + \varepsilon T_i^\varepsilon)}{q_i(T + \varepsilon T_i^\varepsilon)} \left(\frac{m_i}{2\pi k_B(T + \varepsilon T_i^\varepsilon)} \right)^{3/2} \varepsilon \mathbf{u}_i^\varepsilon \left(\frac{2\pi k_B(T + \varepsilon T_i^\varepsilon)}{m_i} \right)^{\frac{3}{2}}.
\end{aligned}$$

Therefore,

$$\begin{aligned}
&\int_{\mathbb{R}^3} \int_0^\infty \left[\frac{m_i(\mathbf{v})^2}{2} + I \right] \varphi_i(I) \mathbf{v} f_i^\varepsilon dI d\mathbf{v} \\
&= \varepsilon n_i^\varepsilon \mathbf{u}_i^\varepsilon k_B(T + \varepsilon T_i^\alpha) + \varepsilon n_i^\varepsilon \mathbf{u}_i^\varepsilon \frac{3k_B(T + \varepsilon T_i^\varepsilon)}{2} + \varepsilon^3 \frac{m_i}{2} n_i^\varepsilon \mathbf{u}_i^\varepsilon (\mathbf{u}_i^\varepsilon)^2 + \varepsilon n_i^\varepsilon \mathbf{u}_i^\varepsilon \frac{q_i^*(T + \varepsilon T_i^\varepsilon)}{q_i(T + \varepsilon T_i^\varepsilon)} \\
&= \varepsilon \frac{5}{2} n_i^\varepsilon \mathbf{u}_i^\varepsilon k_B(T + \varepsilon T_i^\alpha) + \varepsilon^3 \frac{m_i}{2} n_i^\varepsilon \mathbf{u}_i^\varepsilon (\mathbf{u}_i^\varepsilon)^2 + \varepsilon n_i^\varepsilon \mathbf{u}_i^\varepsilon \frac{q_i^*(T + \varepsilon T_i^\varepsilon)}{q_i(T + \varepsilon T_i^\varepsilon)}. \tag{6.3.83}
\end{aligned}$$

Substituting equations (6.3.77) and (6.3.83) into equation (6.3.71), we obtain:

$$\begin{aligned}
&\varepsilon \frac{\partial}{\partial t} \sum_{i=1}^4 \left(\frac{3}{2} n_i^\varepsilon k_B(T + \varepsilon T_i^\varepsilon) + \frac{m_i}{2} \varepsilon^2 n_i^\varepsilon (\mathbf{u}_i^\varepsilon)^2 + n_i^\varepsilon \frac{q_i^*(T + \varepsilon T_i^\varepsilon)}{q_i(T + \varepsilon T_i^\varepsilon)} \right) \\
&+ \nabla_{\mathbf{x}} \cdot \sum_{i=1}^4 \left(\varepsilon \frac{5}{2} n_i^\varepsilon \mathbf{u}_i^\varepsilon k_B(T + \varepsilon T_i^\alpha) + \varepsilon^3 \frac{m_i}{2} n_i^\varepsilon \mathbf{u}_i^\varepsilon (\mathbf{u}_i^\varepsilon)^2 + \varepsilon n_i^\varepsilon \mathbf{u}_i^\varepsilon \frac{q_i^*(T + \varepsilon T_i^\varepsilon)}{q_i(T + \varepsilon T_i^\varepsilon)} \right) = \mathcal{D}^\varepsilon + \mathcal{E}^\varepsilon + \mathcal{F}^\varepsilon, \tag{6.3.84}
\end{aligned}$$

Since the properties of the scaled collision operators are similar to their un-scaled version, using the weak forms of the mono-species, bi-species and reactive collision operators given in equations (2.4.67), (2.4.69) and (2.4.70), respectively, with $\psi(\mathbf{v}, I) = \left[\frac{m_i(\mathbf{v})^2}{2} + I \right]$, together with the conservation laws of total energy for mono-species (i.e., equation (2.4.2) with j replaced by i_*), bi-species given in equation (2.4.2) and reactive collisions given in equation (2.4.5), respectively, we obtain:

$$\mathcal{D}^\varepsilon = 0, \quad \mathcal{E}^\varepsilon = 0 \quad \text{and} \quad \mathcal{F}^\varepsilon = -\varepsilon Q_R A^\varepsilon, \tag{6.3.85}$$

with A^ε defined as given in equation (6.3.27). Substituting equation (6.3.85) into (6.3.84) and dividing both sides by ε , we obtain:

$$\begin{aligned}
&\frac{\partial}{\partial t} \sum_{i=1}^4 \left(\frac{3}{2} n_i^\varepsilon k_B(T + \varepsilon T_i^\varepsilon) + \frac{m_i}{2} \varepsilon^2 n_i^\varepsilon (\mathbf{u}_i^\varepsilon \otimes \mathbf{u}_i^\varepsilon) + n_i^\varepsilon \frac{q_i^*(T + \varepsilon T_i^\varepsilon)}{q_i(T + \varepsilon T_i^\varepsilon)} \right) \\
&+ \nabla_{\mathbf{x}} \cdot \sum_{i=1}^4 \left(\frac{5}{2} n_i^\varepsilon \mathbf{u}_i^\varepsilon k_B(T + \varepsilon T_i^\alpha) + \varepsilon^2 \frac{m_i}{2} n_i^\varepsilon \mathbf{u}_i^\varepsilon (\mathbf{u}_i^\varepsilon)^2 + n_i^\varepsilon \mathbf{u}_i^\varepsilon \frac{q_i^*(T + \varepsilon T_i^\varepsilon)}{q_i(T + \varepsilon T_i^\varepsilon)} \right) = -Q_R A^\varepsilon.
\end{aligned}$$

Taking the limit as $\varepsilon \rightarrow 0$ and using equation (6.3.70), we obtain the balance equation for the energy of the mixture in the form of equation (6.3.69). $\square$

6.4 Limit Equations

In this section a summary of the results obtained in section 6.3 will be given. Also, the limit equations when the angular collision kernels of both the elastic bi-species and the reactive operators are odd functions of $\cos \theta$ will be given. Furthermore, observe that from (6.3.52) one has that $n_i^\varepsilon \mathbf{u}_i^\varepsilon = \mathbf{J}_i^\varepsilon + \mathbf{u}^\varepsilon$. Due to assumption (b) given in subsection 6.2.2, in the limit as $\varepsilon \rightarrow 0$, we have that $\mathbf{J}_i = n_i \mathbf{u}_i$, for all $i = 1, 2, 3, 4$. Putting together the balance equations (6.3.25) and (6.3.49) for the number densities and momentum of the constituents as well as the balance equation (6.3.69) for the total energy of the mixture, we obtain the following macroscopic system of non-isothermal reaction-diffusion equations,

$$\begin{aligned} \frac{\partial n_i}{\partial t} + \nabla_{\mathbf{x}} \cdot \mathbf{J}_i &= -\lambda_i A, \quad i = 1, 2, 3, 4, \\ \nabla_{\mathbf{x}} \left(n_i k_B T \right) &= - \sum_{\substack{j=1 \\ j \neq i}}^4 \frac{n_j \mathbf{J}_i - n_i \mathbf{J}_j}{D_{ij}}, \quad i = 1, 2, 3, 4, \\ \frac{\partial}{\partial t} \left[\sum_{i=1}^4 n_i \left(\frac{3}{2} k_B T + \frac{q_i^*(T)}{q_i(T)} \right) \right] + \nabla_{\mathbf{x}} \cdot \left[\sum_{i=1}^4 \left(\frac{5}{2} k_B T + \frac{q_i^*(T)}{q_i(T)} \right) \mathbf{J}_i \right] &= -Q_R A, \end{aligned} \quad (6.4.1)$$

where A is the formal limit for $\varepsilon \rightarrow 0$ of the production term given in equation (6.3.27). Moreover, D_{ij} , for $i = 1, 2, 3, 4$, and $i \neq j$, are diffusion coefficients that can be recovered from the production term $\mathbf{B}_i$ which is the formal limit for $\varepsilon \rightarrow 0$ of $\mathbf{B}_i^\varepsilon$ given in (6.3.51). The production term A is given by

$$\begin{aligned} A &= \left[\left(\frac{m_3 m_4}{m_1 m_2} \right)^{3/2} \frac{n_1 n_2}{q_1(T) q_2(T)} \exp \left(-\frac{Q_R}{k_B T} \right) - \frac{n_3 n_4}{q_3(T) q_4(T)} \right] \frac{4}{\sqrt{\pi} (m_3 m_4)^2} \\ &\times \Gamma \left(\frac{\gamma + 2}{2} \right) \left(\frac{2 k_B T}{\mu_{34}} \right)^{(\gamma-1)/2} \int_0^{+\infty} \int_0^{+\infty} \int_0^1 \int_0^1 \int_{\mathbb{S}^2} \exp \left(-\frac{I + I_4}{k_B T} \right) \\ &\times \Phi^{react}(I, I_4, R, r) b^{react}(\cos \theta) \cos \theta (1 - R) d\sigma dr dR dI_4 dI, \end{aligned} \quad (6.4.2)$$

and the diffusion coefficients D_{ij} are defined as

$$\begin{aligned} \frac{1}{D_{ij}} &= \frac{4}{3\sqrt{\pi}} \mu_{ij}^{\frac{(3-\gamma)}{2}} (2 k_B T)^{\frac{(\gamma-1)}{2}} \frac{1}{q_i(T) q_j(T)} \Gamma \left(\frac{\gamma + 4}{2} \right) \\ &\times \int_0^{+\infty} \int_0^{+\infty} \int_0^1 \int_0^1 \int_{\mathbb{S}^2} \exp \left(-\frac{I + I_j}{k_B T} \right) \Phi_{ij}(I, I_j, R, r) \cos \theta (1 - R) \\ &\times b_{ij}(\cos \theta) d\sigma dr dR dI_j dI. \end{aligned} \quad (6.4.3)$$

The equations in the second row of (6.4.1) are the MS equations for the reactive mixture of polyatomic gases considered in this chapter. Upon specifying the kinetic and the angular kernels, the integrals appearing in equations (6.4.2) and (6.4.3) can be evaluated explicitly and detailed expressions for the reactive production terms A , $Q_R A$ and the diffusion coefficients D_{ij} can be obtained.

6.5 Conclusion

In this chapter, a set of non-isothermal reaction-diffusion equations of MS type was derived from a Maxwell-Boltzmann type kinetic model that describe a chemically reactive gaseous mixture composed of polyatomic species, which takes into account both the presence of internal energy degrees as well as the chemical mass transfer among the constituents.

The starting point has been the kinetic model for reactive polyatomic gases proposed by Desvillettes, Monaco and Salvarani [45], which has been studied here under the standard diffusive scaling.

The form of the limiting equations obtained (see equation (6.4.1)) shows the influence of both the chemical reaction and the polyatomic structure of the mixture on the evolution of the number densities of the constituents, as well as on the evolution of the energy of the mixture. Moreover, the evolution equation of the momentum of each constituent also show the influence of the polyatomic structure of the mixture, through the diffusion coefficients D_{ij} , but it is not affected by the chemical reaction. This is due to the fact that the considered chemical regime corresponds to a slow reaction, in which the reactive process, in comparison with diffusion, has a small effect in the evolution.

Furthermore, it is important to mention that the target equations obtained here take into account the effect of chemical reactions, which impose to work in the non-isothermal setting. Notice that the sum over the index i of the right-hand sides of the four (vectorial) equations appearing in the second line of the system of equations (6.4.1) vanishes. Therefore they do not constitute a set of independent equations for the fluxes $\mathbf{J}_i$.

The limit equations obtained are compatible with the internal energy law of polyatomic gases and the law of mass action. At the equilibrium, from both equation (6.4.1) and the formulation of the source term for the species given by equation (6.4.2), the law of mass action reads

$$\frac{n_1 n_2}{n_3 n_4} = \left(\frac{m_1 m_2}{m_3 m_4} \right)^{3/2} \frac{q_1(T) q_2(T)}{q_3(T) q_4(T)} \exp \left(\frac{Q_R}{k_B T} \right),$$

which is exactly the same as in [45].

Of course, all the computations heavily depend on the choice of the functional forms of the weights φ_i which can be – in principle – freely chosen, provided that they induce a macroscopic behaviour consistent with the physical situation under investigation.

In the case of polytropic gases, the weights φ_i have the form $\varphi_i(I) = I^{\alpha_i}$, where $\alpha_i = (k - 2) \in \mathbb{N}$ and k is the number of atoms of the species i . The special case $\alpha_i = 0$ corresponds to diatomic molecules [45, 91]. Thanks to this choice of the weights φ_i one can compute

$$q_i(T) = \int_0^{+\infty} I^{\alpha_i} e^{-I/(k_B T)} dI = [k_B T]^{\alpha_i+1} (\alpha_i!),$$

with the convention $0! = 1$, and analogously

$$q_i^*(T) = \int_0^{+\infty} I^{\alpha_i+1} e^{-I/(k_B T)} dI = [k_B T]^{\alpha_i+2} (\alpha_i + 1)!.$$

The model is thus consistent with the energy law of polytropic molecules, which provides a linear dependence on temperature T . More precisely, the total energy at the equilibrium state becomes

$$\sum_{i=1}^4 n_i \left(\frac{3}{2} k_B T + \frac{q_i^*(T)}{q_i(T)} \right) = \sum_{i=1}^4 n_i \left(\frac{3}{2} + \alpha_i + 1 \right) k_B T.$$

Because of the total conservation of mass during the chemical reaction (i.e. $\alpha_1 + \alpha_2 = \alpha_3 + \alpha_4$), we can conclude that

$$\frac{q_1(T)q_2(T)}{q_3(T)q_4(T)} = \frac{(\alpha_1!)(\alpha_2!)}{(\alpha_3!)(\alpha_4!)} ,$$

which is a constant and does not depend on the temperature. In particular, it is equal to one as soon as $(\alpha_1!)(\alpha_2!) = (\alpha_3!)(\alpha_4!)$.

Of course, more complicated weights φ_i should be chosen to reproduce situations with non-polytropic gases, for which total energy is made up also by exponential functions of the global temperature, as it occurs for instance in the kinetic description involving a set of discrete internal energies for each gas [17].

Chapter 7

Conclusion

In this thesis, the hydrodynamic limits of the Maxwell-Boltzmann type equations for reactive multi-species mixtures of monatomic and polyatomic gases have been studied.

In chapter one, the subject of hydrodynamic limits was introduced. In chapter two, a non-reactive multicomponent mixture was considered and the MBEs which describe how the mixture is influenced as a result of free streaming and collisions was obtained. Also the properties of the collision operators for the non-reactive MBEs were given and the macroscopic equations associated with the MBEs were presented. Furthermore, the MBEs for reactive multi-species systems was presented. More precisely, the SRS kinetic model which describe a reactive mixture of monatomic-like gases and a kinetic model which describe a reactive mixture of polyatomic gases with a continuous structure of internal energy were presented together with the properties of their collision operators. In chapter three, the continuum physics description of diffusion in multicomponent mixtures was presented. In particular, diffusion models where the diffusion processes are modelled by the MS equations and the Fick's law, respectively, were presented. This was followed by the description of the kinetic theory approach for deriving hydrodynamic models and the problems studied in this thesis. Although there were no new contributions to the subject of hydrodynamic limits in these chapters, however, some of the properties presented in chapter two were used in chapters four, five and six to obtain the results presented there in.

In chapter four, a reaction-diffusion system of MS type was derived as a hydrodynamic limit of the SRS kinetic model. This result was achieved by studying a scaling of the kinetic model which correspond to a situation where the dominant role in the evolution of the species is played by mechanical interaction (non-reactive interactions) and chemical reactions are assumed to be very slow. The scaled kinetic equations were studied under isothermal condition. The isothermal condition assumption was met by the fact that the chemical reactions are assumed to be slow enough to allow the surroundings to continually compensate for the difference in reaction heat between the reactants and products of the chemical reaction. As a consequence of the isothermal assumption, the macroscopic equations are obtained from the concentration and momentum balance equations for the species only. By applying the moment method to the scaled kinetic equations and using distribution functions that are local maxwellians centred at the average velocity of the species together with the assumption that the bulk velocity of the mixture is small

and vanishes in the limit as the scaling parameter goes to zero, the reaction-diffusion system where the diffusion process is modelled by the MS equations was derived as a hydrodynamic limit of the concentration and momentum balance equations.

In chapter five, an extension to the MS diffusion theory was derived. More precisely, the isothermal and non-isothermal reactive MS equations were derived from the SRS kinetic model. The reactive MS equations derived contain additional terms when compared with the original version derived by Maxwell and Stefan. This is because the original MS equations were derived from a non-reactive multicomponent mixture where only mechanical interactions occur. Therefore, the MS equations in this case describe the diffusion of the non-reactive species in the mixture. However, in a reactive mixture, both mechanical and chemical interactions occur. Therefore, the additional terms in the reactive MS equations describe the diffusion of the reactive species. The derivation of the reactive MS equations was achieved by considering a scaling of the kinetic equations which corresponds to a physical situation in which both mechanical collisions and chemical reactions have comparable relaxation times, which are much smaller than the characteristic times of the flow. Then using distribution functions which are local Maxwellians centred at the average velocity of the species together with the assumption that the average velocity of the mixture vanishes in the limit as the scaling parameter goes to zero, the reactive MS equations were derived as a hydrodynamic limit of the momentum balance equations for the species.

In chapter six, a set of non-isothermal reaction-diffusion system was derived from a kinetic model that describe a reactive mixture of polyatomic gases with a continuous structure of internal energy, under non-isothermal condition. The starting point for the derivation was a scaling of the kinetic model in which mechanical interactions are dominant with respect to chemical interactions. As a consequence of the non-isothermal condition, the required macroscopic equations are obtained from the species number density balance equations, the species momentum balance equations and the energy balance equation of the mixture. The moment method was applied to the scaled kinetic equations together with the assumptions that the distribution functions are local Maxwellians centred at the average velocity of the species and that the bulk velocity of the mixture is small and vanishes in the limit as the scaling parameter goes to zero. The non-isothermal reaction-diffusion system where the diffusion process is modelled by the MS equations was obtained as a hydrodynamic limit of the scaled kinetic equations. This non-isothermal reaction-diffusion system is composed of the number density balance equations for the species, the MS equations obtained from the momentum balance equations for the species and the energy balance equation for the mixture.

It is important to highlight that the results mentioned above were obtained at the formal level. To the best of my knowledge, these results are the first results in these directions, in terms of the kinetic theory of chemically reactive gaseous mixtures.

Finally, in the diffusion models derived in this thesis from the kinetic theory of chemically reactive gaseous mixtures, the driving force of the MS equations is either a function of the species concentration as in the case of isothermal setting or a function of the species concentrations and the temperature of the mixture as in the case of non-isothermal setting. It will be interesting to study the case in which the driving force is defined in terms of the species chemical potential. The chemical potential is a function

of concentration, temperature and pressure. In addition, convective effects were neglected by assuming that the bulk velocity of the mixture is small and vanishes in the limit equations. It will be interesting to study the case with convective effects together with the driving force of the MS equations defined in terms of the chemical potential of the species. This of course will lead to a better macroscopic description of the fluid. In this case, the unknowns for this macroscopic system of equations are the concentration or number density of the species, the molar diffusion flux of the species, the average velocity of the mixture, the temperature of the mixture and pressure.

Appendix A

Evaluation of the Integrals: $\bar{\mathcal{E}}$, $\mathcal{F}$ and $Q_i^{(1)}$ Given in Chapter 4

Here, the integrals $\bar{\mathcal{E}}$, $\mathcal{F}$ and $Q_i^{(1)}$ given in the proof of Lemma 4.3.1 for the concentration balance equations of the species in the reactive mixture, will be evaluated.

A.1 Evaluation of the Integral $\bar{\mathcal{E}}$

Expanding the integral $\bar{\mathcal{E}}$ given in equation (4.3.18) gives:

$$\begin{aligned}\bar{\mathcal{E}} = & \sigma_{ij}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} \left(\frac{\mu_{ij}}{\mu_{kl}} \right)^2 M_k^{\alpha\circ} M_l^{\alpha\circ} (\mathbf{a}_k \cdot \mathbf{v}_k^\circ) \Theta(\langle \boldsymbol{\epsilon}, c_0 \mathbf{v}_i - c_0 \mathbf{v}_j \rangle - \Xi_{ij}) \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_j \rangle d\boldsymbol{\epsilon} d\mathbf{v}_j d\mathbf{v}_i \\ & + \sigma_{ij}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} \left(\frac{\mu_{ij}}{\mu_{kl}} \right)^2 M_k^{\alpha\circ} M_l^{\alpha\circ} (\mathbf{a}_l \cdot \mathbf{v}_l^\circ) \Theta(\langle \boldsymbol{\epsilon}, c_0 \mathbf{v}_i - c_0 \mathbf{v}_j \rangle - \Xi_{ij}) \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_j \rangle d\boldsymbol{\epsilon} d\mathbf{v}_j d\mathbf{v}_i.\end{aligned}$$

To evaluate the integrals given in $\bar{\mathcal{E}}$ above, it will be convenient to transform them from $(\mathbf{v}_i, \mathbf{v}_j)$ to $(\mathbf{v}_k^\circ, \mathbf{v}_l^\circ)$. This is achieved by using equation (2.3.20) together with the Jacobian of this transformation given in equation (4.4.42) which imply equation (4.4.43), to obtain:

$$\begin{aligned}\bar{\mathcal{E}} = & \sigma_{ij}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} \left(\frac{\mu_{ij}}{\mu_{kl}} \right)^2 M_k^{\alpha\circ} M_l^{\alpha\circ} (\mathbf{a}_k \cdot \mathbf{v}_k^\circ) \Theta(\langle \boldsymbol{\epsilon}, c_0 \mathbf{v}_k^\circ - c_0 \mathbf{v}_l^\circ \rangle - \Xi_{kl}) \\ & \times \left(\frac{\mu_{kl}}{\mu_{ij}} \right)^{\frac{1}{2}} \omega^+ \left(\frac{\mu_{kl}}{\mu_{ij}} \right)^{\frac{3}{2}} \frac{\langle \boldsymbol{\epsilon}, \mathbf{v}_k^\circ - \mathbf{v}_l^\circ \rangle}{\omega^+} d\boldsymbol{\epsilon} d\mathbf{v}_k^\circ d\mathbf{v}_l^\circ \\ & + \sigma_{ij}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} \left(\frac{\mu_{ij}}{\mu_{kl}} \right)^2 M_k^{\alpha\circ} M_l^{\alpha\circ} (\mathbf{a}_l \cdot \mathbf{v}_l^\circ) \Theta(\langle \boldsymbol{\epsilon}, c_0 \mathbf{v}_k^\circ - c_0 \mathbf{v}_l^\circ \rangle - \Xi_{kl}) \\ & \times \left(\frac{\mu_{kl}}{\mu_{ij}} \right)^{\frac{1}{2}} \omega^+ \left(\frac{\mu_{kl}}{\mu_{ij}} \right)^{\frac{3}{2}} \frac{\langle \boldsymbol{\epsilon}, \mathbf{v}_k^\circ - \mathbf{v}_l^\circ \rangle}{\omega^+} d\boldsymbol{\epsilon} d\mathbf{v}_k^\circ d\mathbf{v}_l^\circ.\end{aligned}$$

Therefore, the integral $\bar{\mathcal{E}}$ above reduces to:

$$\begin{aligned}
\bar{\mathcal{E}} = & \sigma_{ij}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} M_k^{\alpha\circ} M_l^{\alpha\circ} (\mathbf{a}_k \cdot \mathbf{v}_k^\circ) \Theta(\langle \boldsymbol{\epsilon}, c_0 \mathbf{v}_k^\circ - c_0 \mathbf{v}_l^\circ \rangle - \Xi_{kl}) \langle \boldsymbol{\epsilon}, \mathbf{v}_k^\circ - \mathbf{v}_l^\circ \rangle d\boldsymbol{\epsilon} d\mathbf{v}_k^\circ d\mathbf{v}_l^\circ \\
& + \sigma_{ij}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} M_k^{\alpha\circ} M_l^{\alpha\circ} (\mathbf{a}_l \cdot \mathbf{v}_l^\circ) \Theta(\langle \boldsymbol{\epsilon}, c_0 \mathbf{v}_k^\circ - c_0 \mathbf{v}_l^\circ \rangle - \Xi_{kl}) \langle \boldsymbol{\epsilon}, \mathbf{v}_k^\circ - \mathbf{v}_l^\circ \rangle d\boldsymbol{\epsilon} d\mathbf{v}_k^\circ d\mathbf{v}_l^\circ.
\end{aligned} \tag{A.1.1}$$

Using the definition of the distribution function given in equation (4.2.3), the above integrals can be written as follows:

$$\begin{aligned}
\bar{\mathcal{E}} = & \sigma_{ij}^2 \frac{(m_k m_l)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_k^\alpha c_l^\alpha \mathbf{a}_k \cdot \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} \mathbf{v}_k^\circ \exp\left(-\frac{m_k(\mathbf{v}_k^\circ)^2 + m_l(\mathbf{v}_l^\circ)^2}{2k_B T}\right) \\
& \times \Theta(\langle \boldsymbol{\epsilon}, c_0 \mathbf{v}_k^\circ - c_0 \mathbf{v}_l^\circ \rangle - \Xi_{kl}) \langle \boldsymbol{\epsilon}, \mathbf{v}_k^\circ - \mathbf{v}_l^\circ \rangle d\boldsymbol{\epsilon} d\mathbf{v}_k^\circ d\mathbf{v}_l^\circ \\
& + \sigma_{ij}^2 \frac{(m_k m_l)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_k^\alpha c_l^\alpha \mathbf{a}_l \cdot \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} \mathbf{v}_l^\circ \exp\left(-\frac{m_k(\mathbf{v}_k^\circ)^2 + m_l(\mathbf{v}_l^\circ)^2}{2k_B T}\right) \\
& \times \Theta(\langle \boldsymbol{\epsilon}, c_0 \mathbf{v}_k^\circ - c_0 \mathbf{v}_l^\circ \rangle - \Xi_{kl}) \langle \boldsymbol{\epsilon}, \mathbf{v}_k^\circ - \mathbf{v}_l^\circ \rangle d\boldsymbol{\epsilon} d\mathbf{v}_k^\circ d\mathbf{v}_l^\circ.
\end{aligned} \tag{A.1.2}$$

Observe that the integral over $\mathbb{S}_+^2$ is similar to that evaluated in (4.3.20). Therefore,

$$\int_{\mathbb{S}_+^2} \Theta(\langle \boldsymbol{\epsilon}, c_0 \mathbf{v}_k^\circ - c_0 \mathbf{v}_l^\circ \rangle - \Xi_{kl}) \langle \boldsymbol{\epsilon}, \mathbf{v}_k^\circ - \mathbf{v}_l^\circ \rangle d\boldsymbol{\epsilon} = \pi \bar{V} \Theta\left(\bar{V} - \frac{\Xi_{kl}}{c_0}\right) \left[1 - \left(\frac{\Xi_{kl}}{c_0 \bar{V}}\right)^2\right],$$

where

$$\bar{V} = \|\bar{\mathbf{V}}\| = \|\mathbf{v}_l^\circ - \mathbf{v}_k^\circ\| = \|-(\mathbf{v}_k^\circ - \mathbf{v}_l^\circ)\| = |-1| \|\mathbf{v}_k^\circ - \mathbf{v}_l^\circ\| = \|\mathbf{v}_k^\circ - \mathbf{v}_l^\circ\|.$$

Therefore,

$$\begin{aligned}
\bar{\mathcal{E}} = & \pi \sigma_{ij}^2 \frac{(m_k m_l)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_k^\alpha c_l^\alpha \mathbf{a}_k \cdot \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \mathbf{v}_k^\circ \exp\left(-\frac{m_k(\mathbf{v}_k^\circ)^2 + m_l(\mathbf{v}_l^\circ)^2}{2k_B T}\right) \\
& \times \bar{V} \Theta\left(\bar{V} - \frac{\Xi_{kl}}{c_0}\right) \left[1 - \left(\frac{\Xi_{kl}}{c_0 \bar{V}}\right)^2\right] d\mathbf{v}_k^\circ d\mathbf{v}_l^\circ \\
& + \pi \sigma_{ij}^2 \frac{(m_k m_l)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_k^\alpha c_l^\alpha \mathbf{a}_l \cdot \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \mathbf{v}_l^\circ \exp\left(-\frac{m_k(\mathbf{v}_k^\circ)^2 + m_l(\mathbf{v}_l^\circ)^2}{2k_B T}\right) \\
& \times \bar{V} \Theta\left(\bar{V} - \frac{\Xi_{kl}}{c_0}\right) \left[1 - \left(\frac{\Xi_{kl}}{c_0 \bar{V}}\right)^2\right] d\mathbf{v}_k^\circ d\mathbf{v}_l^\circ.
\end{aligned}$$

Next, we transform the above integrals from $\mathbf{v}_k^\circ$ and $\mathbf{v}_l^\circ$ to the centre of mass velocity $\bar{\mathbf{X}}$ and relative velocity $\bar{\mathbf{V}}$ defined respectively as given below:

$$\bar{\mathbf{x}} = \frac{m_k \mathbf{v}_k^\circ + m_l \mathbf{v}_l^\circ}{m_k + m_l}, \quad \bar{\mathbf{V}} = \mathbf{v}_l^\circ - \mathbf{v}_k^\circ. \tag{A.1.3}$$

Following the steps used to obtain equations (2.4.10), (2.4.11) and (2.4.12), one obtains that:

$$\mathbf{v}_k^\circ = \bar{\mathbf{X}} - \frac{m_l \bar{\mathbf{V}}}{m_k + m_l}, \tag{A.1.4}$$

$$\mathbf{v}_l^\circ = \bar{\mathbf{X}} + \frac{m_k \bar{\mathbf{V}}}{m_k + m_l}, \quad (\text{A.1.5})$$

$$m_k (\mathbf{v}_k^\circ)^2 + m_l (\mathbf{v}_l^\circ)^2 = M \bar{X}^2 + \mu_{kl} \bar{V}^2, \quad (\text{A.1.6})$$

where $M = (m_k + m_l)$. Using equations (A.1.4), (A.1.5) and (A.1.6) together with the fact that the Jacobian of the transformation $(\mathbf{v}_k^\circ, \mathbf{v}_l^\circ) \mapsto (\bar{\mathbf{X}}, \bar{\mathbf{V}})$ is unity which implies that

$$d\mathbf{v}_k^\circ d\mathbf{v}_l^\circ = d\bar{\mathbf{X}} d\bar{\mathbf{V}},$$

we can rewrite the the integral $\bar{\mathcal{E}}$ as follows:

$$\begin{aligned} \bar{\mathcal{E}} &= \pi \sigma_{ij}^2 \frac{(m_k m_l)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_k^\alpha c_l^\alpha \mathbf{a}_k \cdot \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \left(\bar{\mathbf{X}} - \frac{m_l \bar{\mathbf{V}}}{M} \right) \exp \left(-\frac{M \bar{X}^2 + \mu_{kl} \bar{V}^2}{2k_B T} \right) \\ &\quad \times \bar{V} \Theta \left(\bar{V} - \frac{\Xi_{kl}}{c_0} \right) \left[1 - \left(\frac{\Xi_{kl}}{c_0 \bar{V}} \right)^2 \right] d\bar{\mathbf{X}} d\bar{\mathbf{V}} \\ &+ \pi \sigma_{ij}^2 \frac{(m_k m_l)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_k^\alpha c_l^\alpha \mathbf{a}_l \cdot \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \left(\bar{\mathbf{X}} + \frac{m_k \bar{\mathbf{V}}}{M} \right) \exp \left(-\frac{M \bar{X}^2 + \mu_{kl} \bar{V}^2}{2k_B T} \right) \\ &\quad \times \bar{V} \Theta \left(\bar{V} - \frac{\Xi_{kl}}{c_0} \right) \left[1 - \left(\frac{\Xi_{kl}}{c_0 \bar{V}} \right)^2 \right] d\bar{\mathbf{X}} d\bar{\mathbf{V}} \\ &= \pi \sigma_{ij}^2 \frac{(m_k m_l)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_k^\alpha c_l^\alpha \mathbf{a}_k \cdot \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \left(\bar{\mathbf{X}} - \frac{m_l \bar{\mathbf{V}}}{M} \right) \exp \left(-\frac{M \bar{X}^2 + \mu_{kl} \bar{V}^2}{2k_B T} \right) \\ &\quad \times \bar{V} \Theta \left(\bar{V} - \frac{\Xi_{kl}}{c_0} \right) d\bar{\mathbf{X}} d\bar{\mathbf{V}} \\ &- \pi \sigma_{ij}^2 \frac{(m_k m_l)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_k^\alpha c_l^\alpha \mathbf{a}_k \cdot \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \left(\bar{\mathbf{X}} - \frac{m_l \bar{\mathbf{V}}}{M} \right) \exp \left(-\frac{M \bar{X}^2 + \mu_{kl} \bar{V}^2}{2k_B T} \right) \\ &\quad \times \bar{V} \Theta \left(\bar{V} - \frac{\Xi_{kl}}{c_0} \right) \left(\frac{\Xi_{kl}}{c_0 \bar{V}} \right)^2 d\bar{\mathbf{X}} d\bar{\mathbf{V}} \\ &+ \pi \sigma_{ij}^2 \frac{(m_k m_l)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_k^\alpha c_l^\alpha \mathbf{a}_l \cdot \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \left(\bar{\mathbf{X}} + \frac{m_k \bar{\mathbf{V}}}{M} \right) \exp \left(-\frac{M \bar{X}^2 + \mu_{kl} \bar{V}^2}{2k_B T} \right) \\ &\quad \times \bar{V} \Theta \left(\bar{V} - \frac{\Xi_{kl}}{c_0} \right) d\bar{\mathbf{X}} d\bar{\mathbf{V}} \\ &- \pi \sigma_{ij}^2 \frac{(m_k m_l)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_k^\alpha c_l^\alpha \mathbf{a}_l \cdot \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \left(\bar{\mathbf{X}} + \frac{m_k \bar{\mathbf{V}}}{M} \right) \exp \left(-\frac{M \bar{X}^2 + \mu_{kl} \bar{V}^2}{2k_B T} \right) \\ &\quad \times \bar{V} \Theta \left(\bar{V} - \frac{\Xi_{kl}}{c_0} \right) \left(\frac{\Xi_{kl}}{c_0 \bar{V}} \right)^2 d\bar{\mathbf{X}} d\bar{\mathbf{V}} \\ &= \pi \sigma_{ij}^2 \frac{(m_k m_l)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_k^\alpha c_l^\alpha \mathbf{a}_k \cdot \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \bar{\mathbf{X}} \exp \left(-\frac{M \bar{X}^2 + \mu_{kl} \bar{V}^2}{2k_B T} \right) \\ &\quad \times \bar{V} \Theta \left(\bar{V} - \frac{\Xi_{kl}}{c_0} \right) d\bar{\mathbf{X}} d\bar{\mathbf{V}} \\ &- \pi \sigma_{ij}^2 \frac{(m_k m_l)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_k^\alpha c_l^\alpha \frac{m_l}{M} \mathbf{a}_k \cdot \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \bar{\mathbf{V}} \exp \left(-\frac{M \bar{X}^2 + \mu_{kl} \bar{V}^2}{2k_B T} \right) \end{aligned}$$

$$\begin{aligned}
& \times \bar{V} \Theta \left(\bar{V} - \frac{\Xi_{kl}}{c_0} \right) d\bar{\mathbf{X}} d\bar{V} \\
& - \pi \sigma_{ij}^2 \frac{(m_k m_l)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_k^\alpha c_l^\alpha \mathbf{a}_k \cdot \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \bar{\mathbf{X}} \exp \left(-\frac{M \bar{X}^2 + \mu_{kl} \bar{V}^2}{2k_B T} \right) \\
& \quad \times \bar{V} \Theta \left(\bar{V} - \frac{\Xi_{kl}}{c_0} \right) \left(\frac{\Xi_{kl}}{c_0 \bar{V}} \right)^2 d\bar{\mathbf{X}} d\bar{V} \\
& + \pi \sigma_{ij}^2 \frac{(m_k m_l)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_k^\alpha c_l^\alpha \frac{m_l}{M} \mathbf{a}_k \cdot \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \bar{\mathbf{V}} \exp \left(-\frac{M \bar{X}^2 + \mu_{kl} \bar{V}^2}{2k_B T} \right) \\
& \quad \times \bar{V} \Theta \left(\bar{V} - \frac{\Xi_{kl}}{c_0} \right) \left(\frac{\Xi_{kl}}{c_0 \bar{V}} \right)^2 d\bar{\mathbf{X}} d\bar{V} \\
& + \pi \sigma_{ij}^2 \frac{(m_k m_l)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_k^\alpha c_l^\alpha \mathbf{a}_l \cdot \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \bar{\mathbf{X}} \exp \left(-\frac{M \bar{X}^2 + \mu_{kl} \bar{V}^2}{2k_B T} \right) \\
& \quad \times \bar{V} \Theta \left(\bar{V} - \frac{\Xi_{kl}}{c_0} \right) d\bar{\mathbf{X}} d\bar{V} \\
& + \pi \sigma_{ij}^2 \frac{(m_k m_l)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_k^\alpha c_l^\alpha \frac{m_k}{M} \mathbf{a}_l \cdot \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \bar{\mathbf{V}} \exp \left(-\frac{M \bar{X}^2 + \mu_{kl} \bar{V}^2}{2k_B T} \right) \\
& \quad \times \bar{V} \Theta \left(\bar{V} - \frac{\Xi_{kl}}{c_0} \right) d\bar{\mathbf{X}} d\bar{V} \\
& - \pi \sigma_{ij}^2 \frac{(m_k m_l)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_k^\alpha c_l^\alpha \mathbf{a}_l \cdot \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \bar{\mathbf{X}} \exp \left(-\frac{M \bar{X}^2 + \mu_{kl} \bar{V}^2}{2k_B T} \right) \\
& \quad \times \bar{V} \Theta \left(\bar{V} - \frac{\Xi_{kl}}{c_0} \right) \left(\frac{\Xi_{kl}}{c_0 \bar{V}} \right)^2 d\bar{\mathbf{X}} d\bar{V} \\
& - \pi \sigma_{ij}^2 \frac{(m_k m_l)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_k^\alpha c_l^\alpha \frac{m_k}{M} \mathbf{a}_l \cdot \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \bar{\mathbf{V}} \exp \left(-\frac{M \bar{X}^2 + \mu_{kl} \bar{V}^2}{2k_B T} \right) \\
& \quad \times \bar{V} \Theta \left(\bar{V} - \frac{\Xi_{kl}}{c_0} \right) \left(\frac{\Xi_{kl}}{c_0 \bar{V}} \right)^2 d\bar{\mathbf{X}} d\bar{V} \\
& = \pi \sigma_{ij}^2 \frac{(m_k m_l)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_k^\alpha c_l^\alpha \\
& \quad \times \mathbf{a}_k \cdot \int_{\mathbb{R}^3} \bar{\mathbf{X}} \exp \left(-\frac{M \bar{X}^2}{2k_B T} \right) d\bar{\mathbf{X}} \underbrace{\int_{\mathbb{R}^3} \exp \left(-\frac{\mu_{kl} \bar{V}^2}{2k_B T} \right) \bar{V} \Theta \left(\bar{V} - \frac{\Xi_{kl}}{c_0} \right) d\bar{V}}_{\mathcal{E}_1} \\
& - \pi \sigma_{ij}^2 \frac{(m_k m_l)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_k^\alpha c_l^\alpha \frac{m_l}{M} \\
& \quad \times \mathbf{a}_k \cdot \int_{\mathbb{R}^3} \exp \left(-\frac{M \bar{X}^2}{2k_B T} \right) d\bar{\mathbf{X}} \underbrace{\int_{\mathbb{R}^3} \bar{\mathbf{V}} \exp \left(-\frac{\mu_{kl} \bar{V}^2}{2k_B T} \right) \bar{V} \Theta \left(\bar{V} - \frac{\Xi_{kl}}{c_0} \right) d\bar{V}}_{\mathcal{E}_2} \\
& - \pi \sigma_{ij}^2 \frac{(m_k m_l)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_k^\alpha c_l^\alpha \\
& \quad \times \mathbf{a}_k \cdot \int_{\mathbb{R}^3} \bar{\mathbf{X}} \exp \left(-\frac{M \bar{X}^2}{2k_B T} \right) d\bar{\mathbf{X}} \underbrace{\int_{\mathbb{R}^3} \exp \left(-\frac{\mu_{kl} \bar{V}^2}{2k_B T} \right) \bar{V} \Theta \left(\bar{V} - \frac{\Xi_{kl}}{c_0} \right) \left(\frac{\Xi_{kl}}{c_0 \bar{V}} \right)^2 d\bar{V}}_{\mathcal{E}_3}
\end{aligned}$$

$$\begin{aligned}
& + \pi \sigma_{ij}^2 \frac{(m_k m_l)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_k^\alpha c_l^\alpha \frac{m_l}{M} \\
& \quad \times \mathbf{a}_k \cdot \underbrace{\int_{\mathbb{R}^3} \exp\left(-\frac{M \bar{X}^2}{2k_B T}\right) d\bar{\mathbf{X}} \int_{\mathbb{R}^3} \bar{\mathbf{V}} \exp\left(-\frac{\mu_{kl} \bar{V}^2}{2k_B T}\right) \bar{V} \Theta\left(\bar{V} - \frac{\Xi_{kl}}{c_0}\right) \left(\frac{\Xi_{kl}}{c_0 \bar{V}}\right)^2 d\bar{\mathbf{V}}}_{\mathcal{E}_4} \\
& + \pi \sigma_{ij}^2 \frac{(m_k m_l)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_k^\alpha c_l^\alpha \\
& \quad \times \mathbf{a}_l \cdot \underbrace{\int_{\mathbb{R}^3} \bar{\mathbf{X}} \exp\left(-\frac{M \bar{X}^2}{2k_B T}\right) d\bar{\mathbf{X}} \int_{\mathbb{R}^3} \exp\left(-\frac{\mu_{kl} \bar{V}^2}{2k_B T}\right) \bar{V} \Theta\left(\bar{V} - \frac{\Xi_{kl}}{c_0}\right) d\bar{\mathbf{V}}}_{\mathcal{E}_1} \\
& + \pi \sigma_{ij}^2 \frac{(m_k m_l)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_k^\alpha c_l^\alpha \frac{m_k}{M} \\
& \quad \times \mathbf{a}_l \cdot \underbrace{\int_{\mathbb{R}^3} \exp\left(-\frac{M \bar{X}^2}{2k_B T}\right) d\bar{\mathbf{X}} \int_{\mathbb{R}^3} \bar{\mathbf{V}} \exp\left(-\frac{\mu_{kl} \bar{V}^2}{2k_B T}\right) \bar{V} \Theta\left(\bar{V} - \frac{\Xi_{kl}}{c_0}\right) d\bar{\mathbf{V}}}_{\mathcal{E}_2} \\
& - \pi \sigma_{ij}^2 \frac{(m_k m_l)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_k^\alpha c_l^\alpha \\
& \quad \times \mathbf{a}_l \cdot \underbrace{\int_{\mathbb{R}^3} \bar{\mathbf{X}} \exp\left(-\frac{M \bar{X}^2}{2k_B T}\right) d\bar{\mathbf{X}} \int_{\mathbb{R}^3} \exp\left(-\frac{\mu_{kl} \bar{V}^2}{2k_B T}\right) \bar{V} \Theta\left(\bar{V} - \frac{\Xi_{kl}}{c_0}\right) \left(\frac{\Xi_{kl}}{c_0 \bar{V}}\right)^2 d\bar{\mathbf{V}}}_{\mathcal{E}_3} \\
& - \pi \sigma_{ij}^2 \frac{(m_k m_l)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_k^\alpha c_l^\alpha \frac{m_k}{M} \\
& \quad \times \mathbf{a}_l \cdot \underbrace{\int_{\mathbb{R}^3} \exp\left(-\frac{M \bar{X}^2}{2k_B T}\right) d\bar{\mathbf{X}} \int_{\mathbb{R}^3} \bar{\mathbf{V}} \exp\left(-\frac{\mu_{kl} \bar{V}^2}{2k_B T}\right) \bar{V} \Theta\left(\bar{V} - \frac{\Xi_{kl}}{c_0}\right) \left(\frac{\Xi_{kl}}{c_0 \bar{V}}\right)^2 d\bar{\mathbf{V}}}_{\mathcal{E}_4}.
\end{aligned}$$

The integrals in $\bar{\mathbf{X}}$ above are similar to those whose values are given in equations (4.4.17) and (4.4.20). Therefore,

$$\int_{\mathbb{R}^3} \exp\left(-\frac{M \bar{X}^2}{2k_B T}\right) d\bar{\mathbf{X}} = \left(\frac{2\pi k_B T}{M}\right)^{\frac{3}{2}} \quad \text{and} \quad \int_{\mathbb{R}^3} \bar{\mathbf{X}} \exp\left(-\frac{M \bar{X}^2}{2k_B T}\right) d\bar{\mathbf{x}} = \mathbf{0}. \quad (\text{A.1.7})$$

Now let us evaluate the integrals $\mathcal{E}_1$, $\mathcal{E}_2$, $\mathcal{E}_3$ and $\mathcal{E}_4$. Writing the integral $\mathcal{E}_1$ in spherical coordinates and integrating, we obtain:

$$\begin{aligned}
\mathcal{E}_1 &= \int_0^\infty \int_0^\pi \int_0^{2\pi} \bar{V} \exp\left(-\frac{\mu_{kl} \bar{V}^2}{2k_B T}\right) \Theta\left(\bar{V} - \frac{\Xi_{kl}}{c_0}\right) \bar{V}^2 \sin \theta d\phi d\theta d\bar{V} \\
&= \int_{\bar{V} \geq \frac{\Xi_{kl}}{c_0}}^\infty \bar{V}^3 \exp\left(-\frac{\mu_{kl} \bar{V}^2}{2k_B T}\right) d\bar{V} \underbrace{\int_0^\pi \sin \theta d\theta}_2 \underbrace{\int_0^{2\pi} d\phi}_{2\pi}.
\end{aligned}$$

Using a change of variable similar to that given in equation (4.3.23), one obtains equations similar to equations (4.3.24) and (4.3.25). Therefore, the integral in $\bar{V}$ above can be rewritten as follows:

$$\begin{aligned}
\int_{\bar{V} \geq \frac{\Xi_{kl}}{c_0}}^{\infty} \bar{V}^3 \exp\left(-\frac{\mu_{kl} \bar{V}^2}{2k_B T}\right) d\bar{V} &= \int_{z_{i*}}^{\infty} z_*^{\frac{3}{2}} \left(\frac{2k_B T}{\mu_{kl}}\right)^{\frac{3}{2}} \exp(-z_*) \frac{1}{2z_*^{\frac{1}{2}}} \left(\frac{2k_B T}{\mu_{kl}}\right)^{\frac{1}{2}} dz_* \\
&= \frac{1}{2} \left(\frac{2k_B T}{\mu_{kl}}\right)^2 \int_{z_{i*}}^{\infty} z_* \exp(-z_*) dz_*,
\end{aligned}$$

where z_{i*} is obtained by replacing the subscripts i, j by k, l in equation (4.3.25). Using the incomplete Euler gamma function given in equation (4.3.3) with $\eta - 1 = 1$ i.e $\eta = 2$, we obtain:

$$\int_{\bar{V} \geq \frac{\Xi_{kl}}{c_0}}^{\infty} \bar{V}^3 \exp\left(-\frac{\mu_{kl} \bar{V}^2}{2k_B T}\right) d\bar{V} = \frac{1}{2} \left(\frac{2k_B T}{\mu_{kl}}\right)^2 \Gamma\left(2, z_{i*}\right). \quad (\text{A.1.8})$$

Therefore

$$\begin{aligned}
\mathcal{E}_1 &= \int_{\mathbb{R}^3} \exp\left(-\frac{\mu_{kl} \bar{V}^2}{2k_B T}\right) \bar{V} \Theta\left(\bar{V} - \frac{\Xi_{kl}}{c_0}\right) d\bar{\mathbf{V}} = 4\pi \frac{1}{2} \left(\frac{2k_B T}{\mu_{kl}}\right)^2 \Gamma\left(2, z_{i*}\right) \\
&= 2\pi \left(\frac{2k_B T}{\mu_{kl}}\right)^2 \Gamma\left(2, z_{i*}\right). \quad (\text{A.1.9})
\end{aligned}$$

Next let us evaluate the integral $\mathcal{E}_2$. Using the fact that any vector $\bar{\mathbf{V}}$ can be written in terms of a unit vector as $\bar{\mathbf{V}} = \bar{V} \bar{\mathbf{v}}$, with $\bar{V} = \|\bar{\mathbf{V}}\|$ and $\bar{\mathbf{v}}$ a unit vector, we can rewrite the integral $\mathcal{E}_2$ as given below:

$$\int_{\mathbb{R}^3} \bar{\mathbf{V}} \exp\left(-\frac{\mu_{kl} \bar{V}^2}{2k_B T}\right) \bar{V} \Theta\left(\bar{V} - \frac{\Xi_{kl}}{c_0}\right) d\bar{\mathbf{V}} = \int_{\mathbb{R}^3} \bar{V} \bar{\mathbf{v}} \exp\left(-\frac{\mu_{kl} \bar{V}^2}{2k_B T}\right) \bar{V} \Theta\left(\bar{V} - \frac{\Xi_{kl}}{c_0}\right) d\bar{\mathbf{V}}.$$

Writing the above integral in spherical coordinates and integrating gives:

$$\begin{aligned}
\mathcal{E}_2 &= \int_0^{\infty} \int_0^{\pi} \int_0^{2\pi} \bar{V} (\hat{\mathbf{x}} \sin \theta \cos \phi + \hat{\mathbf{y}} \sin \theta \sin \phi + \hat{\mathbf{z}} \cos \theta) \\
&\quad \times \exp\left(-\frac{\mu_{kl} \bar{V}^2}{2k_B T}\right) \bar{V} \Theta\left(\bar{V} - \frac{\Xi_{kl}}{c_0}\right) \bar{V}^2 \sin \theta d\phi d\theta d\bar{V} \\
&= \int_{\bar{V} \geq \frac{\Xi_{kl}}{c_0}}^{\infty} \bar{V}^4 \exp\left(-\frac{\mu_{kl} \bar{V}^2}{2k_B T}\right) d\bar{V} \left(\hat{\mathbf{x}} \underbrace{\int_0^{\pi} \sin^2 \theta d\theta}_{\frac{\pi}{2}} \underbrace{\int_0^{2\pi} \cos \phi d\phi}_0 \right. \\
&\quad \left. + \hat{\mathbf{y}} \underbrace{\int_0^{\pi} \sin^2 \theta d\theta}_{\frac{\pi}{2}} \underbrace{\int_0^{2\pi} \sin \phi d\phi}_0 + \hat{\mathbf{z}} \underbrace{\int_0^{\pi} \sin \theta \cos \theta d\theta}_0 \underbrace{\int_0^{2\pi} d\phi}_{2\pi} \right),
\end{aligned}$$

where $\hat{\mathbf{x}}, \hat{\mathbf{y}}, \hat{\mathbf{z}}$ are the Cartesian unit vectors in $\mathbb{R}^3$. The integral in $\bar{V}$ above is similar to that given in equation (4.4.29). Therefore, the integral $\mathcal{E}_2$ reduces to:

$$\begin{aligned}
\int_{\mathbb{R}^3} \bar{\mathbf{V}} \exp\left(-\frac{\mu_{kl} \bar{V}^2}{2k_B T}\right) \bar{V} \Theta\left(\bar{V} - \frac{\Xi_{kl}}{c_0}\right) d\bar{\mathbf{V}} &= \frac{1}{2} \left(\frac{2k_B T}{\mu_{kl}}\right)^{\frac{5}{2}} \Gamma\left(\frac{5}{2}, z_{i*}\right) (\hat{\mathbf{x}}(0) + \hat{\mathbf{y}}(0) + \hat{\mathbf{z}}(0)) \\
&= \mathbf{0}. \quad (\text{A.1.10})
\end{aligned}$$

Next let us evaluate the integral $\mathcal{E}_3$. Writing it in spherical coordinates and integrating gives:

$$\begin{aligned}\mathcal{E}_3 &= \int_0^\infty \int_0^\pi \int_0^{2\pi} \bar{V} \exp\left(-\frac{\mu_{kl}\bar{V}^2}{2k_B T}\right) \Theta\left(\bar{V} - \frac{\Xi_{kl}}{c_0}\right) \left(\frac{\Xi_{kl}}{c_0\bar{V}}\right)^2 \bar{V}^2 \sin\theta d\phi d\theta d\bar{V} \\ &= \left(\frac{\Xi_{kl}}{c_0}\right)^2 \int_{\bar{V} \geq \frac{\Xi_{kl}}{c_0}}^\infty \bar{V} \exp\left(-\frac{\mu_{kl}\bar{V}^2}{2k_B T}\right) d\bar{V} \underbrace{\int_0^\pi \sin\theta d\theta}_2 \underbrace{\int_0^{2\pi} d\phi}_{2\pi}.\end{aligned}$$

The integral in $\bar{V}$ above is similar to that given in equation (4.4.31). Therefore, the integral $\mathcal{E}_3$ reduces to:

$$\int_{\mathbb{R}^3} \exp\left(-\frac{\mu_{kl}\bar{V}^2}{2k_B T}\right) \bar{V} \Theta\left(\bar{V} - \frac{\Xi_{kl}}{c_0}\right) \left(\frac{\Xi_{kl}}{c_0\bar{V}}\right)^2 d\bar{V} = \left(\frac{\Xi_{kl}}{c_0}\right)^2 2\pi \left(\frac{2k_B T}{\mu_{kl}}\right) \Gamma(1, z_{i*}). \quad (\text{A.1.11})$$

Finally, using the fact that any vector $\bar{\mathbf{V}}$ can be written in terms of a unit vector as $\bar{\mathbf{V}} = \bar{V} \bar{\mathbf{v}}$, with $\bar{V} = \|\bar{\mathbf{V}}\|$ and $\bar{\mathbf{v}}$ a unit vector, we can rewrite the integral $\mathcal{E}_4$ as given below:

$$\mathcal{E}_4 = \int_{\mathbb{R}^3} \bar{V} \bar{\mathbf{v}} \exp\left(-\frac{\mu_{kl}\bar{V}^2}{2k_B T}\right) \bar{V} \Theta\left(\bar{V} - \frac{\Xi_{kl}}{c_0}\right) \left(\frac{\Xi_{kl}}{c_0\bar{V}}\right)^2 d\bar{\mathbf{V}}.$$

Writing the above integral in spherical coordinates and integrating gives:

$$\begin{aligned}\mathcal{E}_4 &= \int_0^\infty \int_0^\pi \int_0^{2\pi} \bar{V} (\hat{\mathbf{x}} \sin\theta \cos\phi + \hat{\mathbf{y}} \sin\theta \sin\phi + \hat{\mathbf{z}} \cos\theta) \exp\left(-\frac{\mu_{kl}\bar{V}^2}{2k_B T}\right) \\ &\quad \times \bar{V} \Theta\left(\bar{V} - \frac{\Xi_{kl}}{c_0}\right) \left(\frac{\Xi_{kl}}{c_0\bar{V}}\right)^2 \bar{V}^2 \sin\theta d\phi d\theta d\bar{V} \\ &= \left(\frac{\Xi_{kl}}{c_0}\right)^2 \int_{\bar{V} \geq \frac{\Xi_{kl}}{c_0}}^\infty \bar{V}^2 \exp\left(-\frac{\mu_{kl}\bar{V}^2}{2k_B T}\right) d\bar{V} \left(\hat{\mathbf{x}} \underbrace{\int_0^\pi \sin^2\theta d\theta}_{\frac{\pi}{2}} \underbrace{\int_0^{2\pi} \cos\phi d\phi}_0 \right. \\ &\quad \left. + \hat{\mathbf{y}} \underbrace{\int_0^\pi \sin^2\theta d\theta}_{\frac{\pi}{2}} \underbrace{\int_0^{2\pi} \sin\phi d\phi}_0 + \hat{\mathbf{z}} \underbrace{\int_0^\pi \sin\theta \cos\theta d\theta}_0 \underbrace{\int_0^{2\pi} d\phi}_{2\pi} \right),\end{aligned}$$

where $\hat{\mathbf{x}}, \hat{\mathbf{y}}, \hat{\mathbf{z}}$ are the Cartesian unit vectors in $\mathbb{R}^3$. The integral in $\bar{V}$ above is similar to that given in equation (4.4.35). Therefore, the integral $\mathcal{E}_4$ reduces to:

$$\begin{aligned}\int_{\mathbb{R}^3} \bar{\mathbf{V}} \exp\left(-\frac{\mu_{kl}\bar{V}^2}{2k_B T}\right) \bar{V} \Theta\left(\bar{V} - \frac{\Xi_{kl}}{c_0}\right) \left(\frac{\Xi_{kl}}{c_0\bar{V}}\right)^2 d\bar{\mathbf{V}} \\ = \frac{1}{2} \left(\frac{2k_B T}{\mu_{kl}}\right)^{\frac{3}{2}} \Gamma\left(\frac{3}{2}, z_{i*}\right) \left[\hat{\mathbf{x}} \left(\frac{\pi}{2} \times 0\right) + \hat{\mathbf{y}} \left(\frac{\pi}{2} \times 0\right) + \hat{\mathbf{z}} (0 \times 2\pi) \right] \\ = \mathbf{0}.\end{aligned} \quad (\text{A.1.12})$$

Substituting equations (A.1.7), (A.1.9), (A.1.10), (A.1.11) and (A.1.12) into the integral $\bar{\mathcal{E}}$, we obtain:

$$\bar{\mathcal{E}} = 0. \quad (\text{A.1.13})$$

A.2 Evaluation of the Integral $\mathcal{F}$

Expanding the integral $\mathcal{F}$ given in equation (4.3.18), we obtain:

$$\begin{aligned} \mathcal{F} = & -\sigma_{ij}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} M_i^\alpha M_j^\alpha (\mathbf{a}_i \cdot \mathbf{v}_i) \Theta(\langle \boldsymbol{\epsilon}, c_0 \mathbf{v}_i - c_0 \mathbf{v}_j \rangle - \Xi_{ij}) \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_j \rangle d\boldsymbol{\epsilon} d\mathbf{v}_j d\mathbf{v}_i \\ & -\sigma_{ij}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} M_i^\alpha M_j^\alpha (\mathbf{a}_j \cdot \mathbf{v}_j) \Theta(\langle \boldsymbol{\epsilon}, c_0 \mathbf{v}_i - c_0 \mathbf{v}_j \rangle - \Xi_{ij}) \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_j \rangle d\boldsymbol{\epsilon} d\mathbf{v}_j d\mathbf{v}_i. \end{aligned}$$

The above integrals are similar to the integrals $\bar{\mathcal{E}}$ given in equation (A.1.1) whose value is given in equation (A.1.13). Therefore, following the steps used in the computation of the integral $\bar{\mathcal{E}}$, one obtains that

$$\mathcal{F} = 0. \quad (\text{A.2.1})$$

A.3 Evaluation of the Integral $\mathcal{Q}_i^{(1)}$

Substituting equation (4.3.19) into the integral $\mathcal{Q}_i^{(1)}$ given in equation (4.4.40), we obtain:

$$\begin{aligned} \mathcal{Q}_i^{(1)} = & \alpha \beta_{ij} \sigma_{ij}^2 \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} \left[\left(\frac{\mu_{ij}}{\mu_{kl}} \right)^{\frac{1}{2}} c_k^\alpha c_l^\alpha \exp\left(\frac{Q_R}{k_B T}\right) - c_i^\alpha c_j^\alpha \right] \\ & \times \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} \mathbf{v}_i \exp\left(-\frac{m_i(\mathbf{v}_i)^2 + m_j(\mathbf{v}_j)^2}{2k_B T}\right) \Theta(\langle \boldsymbol{\epsilon}, c_0 \mathbf{v}_i - c_0 \mathbf{v}_j \rangle - \Xi_{ij}) \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_j \rangle d\boldsymbol{\epsilon} d\mathbf{v}_j d\mathbf{v}_i. \end{aligned}$$

The above integral is similar to the integrals on the right-hand side of $\bar{\mathcal{E}}$ given in equation (A.1.2) which both vanish upon evaluation. Therefore, following the same steps as those used in the computation of the integrals on the right-hand side of equation (A.1.2), we obtain:

$$\mathcal{Q}_i^{(1)} = 0.$$

Appendix B

Evaluation of the Integrals: $\tilde{\mathcal{O}}_i^{(2)}$, $\tilde{\mathcal{P}}_i^{(2)}$, $\tilde{\mathcal{Q}}_i^{(1)}$, $\tilde{\mathcal{Q}}_i^{(3)}$ and $\tilde{\mathcal{Q}}_i^{(4)}$ Given in Chapter 5

Here the integrals: $\tilde{\mathcal{O}}_i^{(2)}$, $\tilde{\mathcal{P}}_i^{(2)}$, $\tilde{\mathcal{Q}}_i^{(1)}$, $\tilde{\mathcal{Q}}_i^{(3)}$ and $\tilde{\mathcal{Q}}_i^{(4)}$, given in the proof of Lemma 5.4.1 for the momentum balance equations of the species in the reactive mixture, will be evaluated.

B.1 Evaluation of the Integral $\tilde{\mathcal{O}}_i^{(2)}$

In this section, the integral $\tilde{\mathcal{O}}_i^{(2)}$ given in equation (5.4.13), will be evaluated. To do this observe that from equation (2.3.8), we have that

$$\begin{aligned}
 (\mathbf{v}'_i)^2 &= \left(\mathbf{v}_i - \frac{2\mu_{is}}{m_i} \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_s \rangle \boldsymbol{\epsilon} \right)^2 \\
 &= \left(\mathbf{v}_i - \frac{2\mu_{is}}{m_i} \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_s \rangle \boldsymbol{\epsilon} \right) \left(\mathbf{v}_i - \frac{2\mu_{is}}{m_i} \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_s \rangle \boldsymbol{\epsilon} \right) \\
 &= \mathbf{v}_i \left(\mathbf{v}_i - \frac{2\mu_{is}}{m_i} \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_s \rangle \boldsymbol{\epsilon} \right) - \frac{2\mu_{is}}{m_i} \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_s \rangle \boldsymbol{\epsilon} \left(\mathbf{v}_i - \frac{2\mu_{is}}{m_i} \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_s \rangle \boldsymbol{\epsilon} \right) \\
 &= (\mathbf{v}_i)^2 - \frac{2\mu_{is}}{m_i} \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_s \rangle \boldsymbol{\epsilon} \cdot \mathbf{v}_i - \frac{2\mu_{is}}{m_i} \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_s \rangle \boldsymbol{\epsilon} \cdot \mathbf{v}_i + \left(\frac{2\mu_{is}}{m_i} \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_s \rangle \right)^2 \\
 &= (\mathbf{v}_i)^2 - \frac{4\mu_{is}}{m_i} \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_s \rangle \boldsymbol{\epsilon} \cdot \mathbf{v}_i + \left(\frac{2\mu_{is}}{m_i} \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_s \rangle \right)^2,
 \end{aligned}$$

where the fact that $\boldsymbol{\epsilon} \cdot \boldsymbol{\epsilon} = 1$ have been used. Therefore,

$$\begin{aligned}
 (\mathbf{v}'_i)^2 - (\mathbf{v}_i)^2 &= -\frac{4\mu_{is}}{m_i} \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_s \rangle \boldsymbol{\epsilon} \cdot \mathbf{v}_i + \left(\frac{2\mu_{is}}{m_i} \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_s \rangle \right)^2 \\
 &= -\frac{4\mu_{is}}{m_i} \|\mathbf{v}_i - \mathbf{v}_s\| \cos \theta \frac{(\mathbf{v}_i - \mathbf{v}_s)}{\|\mathbf{v}_i - \mathbf{v}_s\|} \cdot \mathbf{v}_i + \frac{4\mu_{is}^2}{m_i^2} (\|\mathbf{v}_i - \mathbf{v}_s\| \cos \theta)^2 \\
 &= \frac{4\mu_{is}}{m_i} \cos \theta (\mathbf{v}_s - \mathbf{v}_i) \cdot \mathbf{v}_i + \frac{4\mu_{is}^2}{m_i^2} (\|\mathbf{v}_i - \mathbf{v}_s\| \cos \theta)^2. \tag{B.1.1}
 \end{aligned}$$

Substituting equation (B.1.1) into the integral $\tilde{\mathcal{O}}_i^{(2)}$ given in equation (5.4.13) gives:

$$\begin{aligned}
\tilde{\mathcal{O}}_i^{(2)} &= \frac{\alpha}{k_B T^2} \sum_{\substack{s=1 \\ s \neq i}}^4 \sigma_{is}^2 (T_i^\alpha - T_s^\alpha) \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} m_i \mathbf{v}_i M_i^\alpha M_s^\alpha \frac{m_i}{2} \left(\frac{4\mu_{is}}{m_i} \cos \theta (\mathbf{v}_s - \mathbf{v}_i) \cdot \mathbf{v}_i \right. \\
&\quad \left. + \frac{4\mu_{is}^2}{m_i^2} (\|\mathbf{v}_i - \mathbf{v}_s\| \cos \theta)^2 \right) \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_s \rangle d\boldsymbol{\epsilon} d\mathbf{v}_s d\mathbf{v}_i \\
&= \frac{2\alpha}{k_B T^2} \sum_{\substack{s=1 \\ s \neq i}}^4 \sigma_{is}^2 (T_i^\alpha - T_s^\alpha) m_i \mu_{is} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} \mathbf{v}_i M_i^\alpha M_s^\alpha ((\mathbf{v}_s - \mathbf{v}_i) \cdot \mathbf{v}_i) \\
&\quad \times \cos \theta \|\mathbf{v}_i - \mathbf{v}_s\| \cos \theta d\boldsymbol{\epsilon} d\mathbf{v}_s d\mathbf{v}_i \\
&\quad + \frac{2\alpha}{k_B T^2} \sum_{\substack{s=1 \\ s \neq i}}^4 \sigma_{is}^2 (T_i^\alpha - T_s^\alpha) \mu_{is}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} \mathbf{v}_i M_i^\alpha M_s^\alpha (\|\mathbf{v}_i - \mathbf{v}_s\| \cos \theta)^2 \\
&\quad \times \|\mathbf{v}_i - \mathbf{v}_s\| \cos \theta d\boldsymbol{\epsilon} d\mathbf{v}_s d\mathbf{v}_i \\
&= \frac{2\alpha}{k_B T^2} \sum_{\substack{s=1 \\ s \neq i}}^4 \sigma_{is}^2 (T_i^\alpha - T_s^\alpha) m_i \mu_{is} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_0^{\frac{\pi}{2}} \int_0^{2\pi} \mathbf{v}_i M_i^\alpha M_s^\alpha ((\mathbf{v}_s - \mathbf{v}_i) \cdot \mathbf{v}_i) \\
&\quad \times \|\mathbf{v}_i - \mathbf{v}_s\| \cos^2 \theta \sin \theta d\phi d\theta d\mathbf{v}_s d\mathbf{v}_i \\
&\quad + \frac{2\alpha}{k_B T^2} \sum_{\substack{s=1 \\ s \neq i}}^4 \sigma_{is}^2 (T_i^\alpha - T_s^\alpha) \mu_{is}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_0^{\frac{\pi}{2}} \int_0^{2\pi} \mathbf{v}_i M_i^\alpha M_s^\alpha (\|\mathbf{v}_i - \mathbf{v}_s\| \cos \theta)^2 \\
&\quad \times \|\mathbf{v}_i - \mathbf{v}_s\| \cos \theta \sin \theta d\phi d\theta d\mathbf{v}_s d\mathbf{v}_i \\
&= \frac{2\alpha}{k_B T^2} \sum_{\substack{s=1 \\ s \neq i}}^4 \sigma_{is}^2 (T_i^\alpha - T_s^\alpha) m_i \mu_{is} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \mathbf{v}_i M_i^\alpha M_s^\alpha ((\mathbf{v}_s - \mathbf{v}_i) \cdot \mathbf{v}_i) \|\mathbf{v}_i - \mathbf{v}_s\| d\mathbf{v}_s d\mathbf{v}_i \\
&\quad \times \underbrace{\int_0^{\frac{\pi}{2}} \cos^2 \theta \sin \theta d\theta}_{\frac{1}{3}} \underbrace{\int_0^{2\pi} d\phi}_{2\pi} \\
&\quad + \frac{2\alpha}{k_B T^2} \sum_{\substack{s=1 \\ s \neq i}}^4 \sigma_{is}^2 (T_i^\alpha - T_s^\alpha) \mu_{is}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \mathbf{v}_i M_i^\alpha M_s^\alpha \|\mathbf{v}_i - \mathbf{v}_s\|^3 d\mathbf{v}_s d\mathbf{v}_i \underbrace{\int_0^{\frac{\pi}{2}} \cos^3 \theta \sin \theta d\theta}_{\frac{1}{4}} \underbrace{\int_0^{2\pi} d\phi}_{2\pi} \\
&= \alpha \frac{4\pi}{3k_B T^2} \sum_{\substack{s=1 \\ s \neq i}}^4 \sigma_{is}^2 (T_i^\alpha - T_s^\alpha) m_i \mu_{is} \frac{(m_i m_s)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_s^\alpha \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \mathbf{v}_i \exp \left(- \frac{m_i (\mathbf{v}_i)^2 + m_s (\mathbf{v}_s)^2}{2k_B T} \right) \\
&\quad \times ((\mathbf{v}_s - \mathbf{v}_i) \cdot \mathbf{v}_i) \|\mathbf{v}_i - \mathbf{v}_s\| d\mathbf{v}_s d\mathbf{v}_i \\
&\quad + \alpha \frac{\pi}{k_B T^2} \sum_{\substack{s=1 \\ s \neq i}}^4 \sigma_{is}^2 (T_i^\alpha - T_s^\alpha) \mu_{is}^2 \frac{(m_i m_s)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_s^\alpha \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \mathbf{v}_i \exp \left(- \frac{m_i (\mathbf{v}_i)^2 + m_s (\mathbf{v}_s)^2}{2k_B T} \right) \\
&\quad \times \|\mathbf{v}_i - \mathbf{v}_s\|^3 d\mathbf{v}_s d\mathbf{v}_i.
\end{aligned}$$

Next we transform the above six fold integrals from $\mathbf{v}_i$ and $\mathbf{v}_s$ to the centre of mass velocity $\mathbf{X}_*$ and relative velocity $\mathbf{V}_*$ defined as given in equations (4.4.11) and (4.4.12), respectively. More precisely, using equations (4.4.12), (4.4.13), (4.4.15) with $m_i + m_s = M_{is}$ and (4.4.16), one can rewrite the integral $\tilde{\mathcal{O}}_i^{(2)}$ as follows:

$$\begin{aligned}
\tilde{\mathcal{O}}_i^{(2)} &= \frac{\alpha 4\pi}{3k_B T^2} \sum_{\substack{s=1 \\ s \neq i}}^4 \sigma_{is}^2 (T_i^\alpha - T_s^\alpha) m_i \mu_{is} \frac{(m_i m_s)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_s^\alpha \\
&\quad \times \underbrace{\int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \left(\mathbf{X}_* - \frac{m_s \mathbf{V}_*}{M_{is}} \right) \exp \left(- \frac{M_{is} X_*^2 + \mu_{is} V_*^2}{2k_B T} \right) \left[\mathbf{V}_* \cdot \left(\mathbf{X}_* - \frac{m_s \mathbf{V}_*}{M_{is}} \right) \right] V_* d\mathbf{X}_* d\mathbf{V}_*}_{\mathcal{V}} \\
&\quad + \frac{\alpha \pi}{k_B T^2} \sum_{\substack{s=1 \\ s \neq i}}^4 \sigma_{is}^2 (T_i^\alpha - T_s^\alpha) \mu_{is}^2 \frac{(m_i m_s)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_s^\alpha \\
&\quad \times \underbrace{\int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \left(\mathbf{X}_* - \frac{m_s \mathbf{V}_*}{M_{is}} \right) \exp \left(- \frac{M_{is} X_*^2 + \mu_{is} V_*^2}{2k_B T} \right) V_*^3 d\mathbf{X}_* d\mathbf{V}_*}_{\mathcal{W}}, \tag{B.1.2}
\end{aligned}$$

where the fact that

$$\mathbf{v}_i - \mathbf{v}_s = -\mathbf{V}_* \quad \text{and} \quad \|\mathbf{V}_*\| = \|\mathbf{v}_i - \mathbf{v}_s\| = \|\mathbf{V}_*\| = V_*,$$

have been used to obtain the above equation. Observe that

$$\begin{aligned}
&\left(\mathbf{X}_* - \frac{m_s \mathbf{V}_*}{M_{is}} \right) \left[\mathbf{V}_* \cdot \left(\mathbf{X}_* - \frac{m_s \mathbf{V}_*}{M_{is}} \right) \right] \\
&= \left(\mathbf{X}_* - \frac{m_s \mathbf{V}_*}{M_{is}} \right) \left[\mathbf{V}_* \cdot \mathbf{X}_* - \frac{m_s V_*^2}{M_{is}} \right] \\
&= \mathbf{X}_* (\mathbf{V}_* \cdot \mathbf{X}_*) - \mathbf{X}_* \frac{m_s V_*^2}{M_{is}} - \frac{m_s \mathbf{V}_*}{M_{is}} (\mathbf{V}_* \cdot \mathbf{X}_*) + \left(\frac{m_s V_*}{M_{is}} \right)^2 \mathbf{V}_*.
\end{aligned}$$

Therefore, the integral $\mathcal{V}$ above becomes:

$$\begin{aligned}
\mathcal{V} &= \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \left[\mathbf{X}_* (\mathbf{V}_* \cdot \mathbf{X}_*) - \frac{m_s V_*^2}{M_{is}} \mathbf{X}_* - \frac{m_s \mathbf{V}_*}{M_{is}} (\mathbf{V}_* \cdot \mathbf{X}_*) + \left(\frac{m_s V_*}{M_{is}} \right)^2 \mathbf{V}_* \right] \\
&\quad \times \exp \left(- \frac{M_{is} X_*^2 + \mu_{is} V_*^2}{2k_B T} \right) V_* d\mathbf{X}_* d\mathbf{V}_* \\
&= \underbrace{\int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \mathbf{X}_* (\mathbf{V}_* \cdot \mathbf{X}_*) \exp \left(- \frac{M_{is} X_*^2 + \mu_{is} V_*^2}{2k_B T} \right) V_* d\mathbf{X}_* d\mathbf{V}_*}_{\mathcal{V}_1}
\end{aligned}$$

$$\begin{aligned}
& - \underbrace{\frac{m_s}{M_{is}} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \mathbf{X}_* \exp \left(- \frac{M_{is} X_*^2 + \mu_{is} V_*^2}{2k_B T} \right) V_*^3 d\mathbf{X}_* d\mathbf{V}_*}_{\mathcal{V}_2} \\
& - \underbrace{\frac{m_s}{M_{is}} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \mathbf{V}_* (\mathbf{V}_* \cdot \mathbf{X}_*) \exp \left(- \frac{M_{is} X_*^2 + \mu_{is} V_*^2}{2k_B T} \right) V_* d\mathbf{X}_* d\mathbf{V}_*}_{\mathcal{V}_3} \\
& + \underbrace{\left(\frac{m_s}{M_{is}} \right)^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \mathbf{V}_* \exp \left(- \frac{M_{is} X_*^2 + \mu_{is} V_*^2}{2k_B T} \right) V_*^3 d\mathbf{X}_* d\mathbf{V}_*}_{\mathcal{V}_4}.
\end{aligned}$$

Now let us evaluate the integrals $\mathcal{V}_1$, $\mathcal{V}_2$, $\mathcal{V}_3$ and $\mathcal{V}_4$. The integral $\mathcal{V}_1$ can be rewritten as:

$$\mathcal{V}_1 = \int_{\mathbb{R}^3} \mathbf{X}_* \exp \left(- \frac{M_{is} X_*^2}{2k_B T} \right) \left(\mathbf{X}_* \cdot \int_{\mathbb{R}^3} \mathbf{V}_* \exp \left(- \frac{\mu_{is} V_*^2}{2k_B T} \right) V_* d\mathbf{V}_* \right) d\mathbf{X}_*.$$

Using the fact that any vector $\mathbf{V}_*$ can be written in terms of a unit vector as $\mathbf{V}_* = V_* \vec{v}$, with $V_* = \|\mathbf{V}_*\|$ and $\vec{v}$ a unit vector, we can write the integral in $\mathbf{V}_*$ above as follows:

$$\int_{\mathbb{R}^3} \mathbf{V}_* \exp \left(- \frac{\mu_{is} V_*^2}{2k_B T} \right) V_* d\mathbf{V}_* = \int_{\mathbb{R}^3} V_* \vec{v} \exp \left(- \frac{\mu_{is} V_*^2}{2k_B T} \right) V_* d\mathbf{V}_*.$$

Writing the right-hand side of the previous equation in spherical coordinates and integrating gives:

$$\begin{aligned}
& \int_{\mathbb{R}^3} V_* \vec{v} \exp \left(- \frac{\mu_{is} V_*^2}{2k_B T} \right) V_* d\mathbf{V}_* \\
& = \int_0^\infty \int_0^\pi \int_0^{2\pi} V_* (\hat{\mathbf{x}} \sin \theta \cos \phi + \hat{\mathbf{y}} \sin \theta \sin \phi + \hat{\mathbf{z}} \cos \theta) \exp \left(- \frac{\mu_{is} V_*^2}{2k_B T} \right) V_*^3 \sin \theta d\phi d\theta dV_* \\
& = \int_0^\infty V_*^4 \exp \left(- \frac{\mu_{is} V_*^2}{2k_B T} \right) dV_* \left(\hat{\mathbf{x}} \underbrace{\int_0^\pi \sin^2 \theta d\theta}_{\frac{\pi}{2}} \underbrace{\int_0^{2\pi} \cos \phi d\phi}_0 + \hat{\mathbf{y}} \underbrace{\int_0^\pi \sin^2 \theta d\theta}_{\frac{\pi}{2}} \underbrace{\int_0^{2\pi} \sin \phi d\phi}_0 \right. \\
& \quad \left. + \hat{\mathbf{z}} \underbrace{\int_0^\pi \sin \theta \cos \theta d\theta}_0 \underbrace{\int_0^{2\pi} d\phi}_{2\pi} \right),
\end{aligned}$$

where $\hat{\mathbf{x}}, \hat{\mathbf{y}}, \hat{\mathbf{z}}$ are the Cartesian unit vectors in $\mathbb{R}^3$. The value of the integral in V_* above is given in equation (4.4.18). Therefore,

$$\begin{aligned}
\int_{\mathbb{R}^3} \mathbf{V}_* \exp \left(- \frac{\mu_{is} V_*^2}{2k_B T} \right) V_* d\mathbf{V}_* & = \frac{3\sqrt{\pi}}{8} \left(\frac{2k_B T}{\mu_{is}} \right)^{\frac{5}{2}} \left[\hat{\mathbf{x}} \left(\frac{\pi}{2} \times 0 \right) + \hat{\mathbf{y}} \left(\frac{\pi}{2} \times 0 \right) + \hat{\mathbf{z}} (0 \times 2\pi) \right] \\
& = \frac{3\sqrt{\pi}}{8} \left(\frac{2k_B T}{\mu_{is}} \right)^{\frac{5}{2}} \times \mathbf{0} \\
& = \mathbf{0}.
\end{aligned} \tag{B.1.3}$$

Substituting equation (B.1.3) into the integral $\mathcal{V}_1$ gives:

$$\begin{aligned}
& \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \mathbf{X}(\mathbf{V}_* \cdot \mathbf{X}_*) \exp\left(-\frac{M_{is}X_*^2 + \mu_{is}V_*^2}{2k_B T}\right) V_* d\mathbf{X}_* d\mathbf{V}_* \\
&= \int_{\mathbb{R}^3} \mathbf{X}_* \exp\left(-\frac{M_{is}X_*^2}{2k_B T}\right) (\mathbf{X}_* \cdot \mathbf{0}) d\mathbf{X}_* \\
&= \int_{\mathbb{R}^3} \left[\mathbf{X}_* \exp\left(-\frac{M_{is}X_*^2}{2k_B T}\right) \times 0 \right] d\mathbf{X}_* \\
&= \int_0^\infty \int_0^\pi \int_0^{2\pi} 0 X_*^2 \sin \theta d\phi d\theta dX_* \\
&= \underbrace{\int_0^\infty 0 dX_*}_0 \underbrace{\int_0^\pi \sin \theta d\theta}_2 \underbrace{\int_0^{2\pi} d\phi}_{2\pi} \\
&= 0.
\end{aligned} \tag{B.1.4}$$

The integral $\mathcal{V}_2$ can be rewritten as

$$\mathcal{V}_2 = \int_{\mathbb{R}^3} \mathbf{X}_* \exp\left(-\frac{M_{is}X_*^2}{2k_B T}\right) d\mathbf{X}_* \int_{\mathbb{R}^3} V_*^3 \exp\left(-\frac{\mu_{is}V_*^2}{2k_B T}\right) d\mathbf{V}_*. \tag{B.1.5}$$

The value of the integral in $\mathbf{X}_*$ above is given in equation (4.4.20). The integral in $\mathbf{V}_*$ can be written in spherical coordinates and integrated as follows:

$$\begin{aligned}
\int_{\mathbb{R}^3} V_*^3 \exp\left(-\frac{\mu_{is}V_*^2}{2k_B T}\right) d\mathbf{V}_* &= \int_0^\infty \int_0^\pi \int_0^{2\pi} V_*^3 \exp\left(-\frac{\mu_{is}V_*^2}{2k_B T}\right) V_*^2 \sin \theta d\phi d\theta dV_* \\
&= \int_0^\infty V_*^5 \exp\left(-\frac{\mu_{is}V_*^2}{2k_B T}\right) dV_* \underbrace{\int_0^\pi \sin \theta d\theta}_2 \underbrace{\int_0^{2\pi} d\phi}_{2\pi}.
\end{aligned}$$

The value of the integral in V_* above is given in equation (4.4.21). Therefore,

$$\int_{\mathbb{R}^3} V_*^3 \exp\left(-\frac{\mu_{is}V_*^2}{2k_B T}\right) d\mathbf{V}_* = 4\pi \left(\frac{2k_B T}{\mu_{is}}\right)^3. \tag{B.1.6}$$

Substituting equations (B.1.6) and (4.4.20) into equation (B.1.5) gives:

$$\int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \mathbf{X}_* \exp\left(-\frac{M_{is}X_*^2 + \mu_{is}V_*^2}{2k_B T}\right) V_*^3 d\mathbf{X}_* d\mathbf{V}_* = \mathbf{0} \times 4\pi \left(\frac{2k_B T}{\mu_{is}}\right)^3 = \mathbf{0}. \tag{B.1.7}$$

The integral $\mathcal{V}_3$ can be rewritten as

$$\mathcal{V}_3 = \int_{\mathbb{R}^3} \mathbf{V}_* \exp\left(-\frac{\mu_{is}V_*^2}{2k_B T}\right) V_* \left(\mathbf{V}_* \cdot \int_{\mathbb{R}^3} \mathbf{X}_* \exp\left(-\frac{M_{is}X_*^2}{2k_B T}\right) d\mathbf{X}_* \right) d\mathbf{V}_*$$

The value of the integral in $\mathbf{X}_*$ above is given in equation (4.4.20). Therefore,

$$\begin{aligned}
& \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \mathbf{V}_* (\mathbf{V}_* \cdot \mathbf{X}_*) \exp \left(-\frac{M_{is} X_*^2 + \mu_{is} V_*^2}{2k_B T} \right) V_* d\mathbf{X}_* d\mathbf{V}_* \\
&= \int_{\mathbb{R}^3} \mathbf{V}_* \exp \left(-\frac{\mu_{is} V_*^2}{2k_B T} \right) V_* (\mathbf{V}_* \cdot \mathbf{0}) d\mathbf{V}_* \\
&= \int_{\mathbb{R}^3} \left[\left(\mathbf{V}_* \exp \left(-\frac{\mu_{is} V_*^2}{2k_B T} \right) V_* \right) \times \mathbf{0} \right] d\mathbf{V}_* \\
&= \int_0^\infty \int_0^\pi \int_0^{2\pi} 0 V_*^2 \sin \theta d\phi d\theta dV_* \\
&= \underbrace{\int_0^\infty 0 dV_*}_0 \underbrace{\int_0^\pi \sin \theta d\theta}_2 \underbrace{\int_0^{2\pi} d\phi}_{2\pi} \\
&= 0.
\end{aligned} \tag{B.1.8}$$

The integral $\mathcal{V}_4$ can be rewritten as

$$\mathcal{V}_4 = \int_{\mathbb{R}^3} \exp \left(-\frac{M_{is} X_*^2}{2k_B T} \right) d\mathbf{X}_* \int_{\mathbb{R}^3} \mathbf{V}_* \exp \left(-\frac{\mu_{is} V_*^2}{2k_B T} \right) V_*^3 d\mathbf{V}_*$$

The value of integral in $\mathbf{X}_*$ above is given in equation (4.4.17). Therefore,

$$\mathcal{V}_4 = \left(\frac{2\pi k_B T}{M_{is}} \right)^{\frac{3}{2}} \int_{\mathbb{R}^3} \mathbf{V}_* \exp \left(-\frac{\mu_{is} V_*^2}{2k_B T} \right) V_*^3 d\mathbf{V}_*. \tag{B.1.9}$$

Using the fact that any vector $\mathbf{V}_*$ can be written in terms of a unit vector as $\mathbf{V}_* = V_* \vec{v}$, with $V_* = \|\mathbf{V}_*\|$ and $\vec{v}$ a unit vector, one can write the previous integral as follows:

$$\int_{\mathbb{R}^3} \mathbf{V}_* \exp \left(-\frac{\mu_{is} V_*^2}{2k_B T} \right) V_*^3 d\mathbf{V}_* = \int_{\mathbb{R}^3} V_* \vec{v} \exp \left(-\frac{\mu_{is} V_*^2}{2k_B T} \right) V_*^3 d\mathbf{V}_*.$$

Writing the right-hand side of the previous equation in spherical coordinates and integrating gives:

$$\begin{aligned}
& \int_{\mathbb{R}^3} V_* \vec{v} \exp \left(-\frac{\mu_{is} V_*^2}{2k_B T} \right) V_*^3 d\mathbf{V}_* \\
&= \int_0^\infty \int_0^\pi \int_0^{2\pi} V_* (\hat{x} \sin \theta \cos \phi + \hat{y} \sin \theta \sin \phi + \hat{z} \cos \theta) \exp \left(-\frac{\mu_{is} V_*^2}{2k_B T} \right) V_*^5 \sin \theta d\phi d\theta dV_* \\
&= \int_0^\infty V_*^6 \exp \left(-\frac{\mu_{is} V_*^2}{2k_B T} \right) dV_* \left(\underbrace{\hat{x} \int_0^\pi \sin^2 \theta d\theta}_{\frac{\pi}{2}} \underbrace{\int_0^{2\pi} \cos \phi d\phi}_0 + \underbrace{\hat{y} \int_0^\pi \sin^2 \theta d\theta}_{\frac{\pi}{2}} \underbrace{\int_0^{2\pi} \sin \phi d\phi}_0 \right)
\end{aligned}$$

$$+ \underbrace{\hat{z} \int_0^\pi \sin \theta \cos \theta d\theta}_0 \underbrace{\int_0^{2\pi} d\phi}_{2\pi} \Big),$$

where $\hat{x}, \hat{y}, \hat{z}$ are the Cartesian unit vectors in $\mathbb{R}^3$. The integral in V_* above can be evaluated using the integral representation of gamma function given in equation (4.3.8) as given below:

$$\begin{aligned} \int_0^\infty V_*^6 \exp\left(-\frac{\mu_{is} V_*^2}{2k_B T}\right) dV_* &= \frac{1}{2} \Gamma\left(\frac{6+1}{2}\right) \left(\frac{2k_B T}{\mu_{is}}\right)^{\frac{6+1}{2}} \\ &= \frac{1}{2} \Gamma\left(\frac{7}{2}\right) \left(\frac{2k_B T}{\mu_{is}}\right)^{\frac{7}{2}} \\ &= \frac{1}{2} \frac{15\sqrt{\pi}}{8} \left(\frac{2k_B T}{\mu_{is}}\right)^{\frac{7}{2}} \\ &= \frac{15\sqrt{\pi}}{16} \left(\frac{2k_B T}{\mu_{is}}\right)^{\frac{7}{2}}. \end{aligned}$$

Therefore,

$$\begin{aligned} \int_{\mathbb{R}^3} \mathbf{V}_* \exp\left(-\frac{\mu_{is} V_*^2}{2k_B T}\right) V_*^3 d\mathbf{V}_* &= \frac{15\sqrt{\pi}}{16} \left(\frac{2k_B T}{\mu_{is}}\right)^{\frac{7}{2}} (\hat{x}(0) + \hat{y}(0) + \hat{z}(0)) \\ &= \frac{15\sqrt{\pi}}{16} \left(\frac{2k_B T}{\mu_{is}}\right)^{\frac{7}{2}} \times \mathbf{0} \\ &= \mathbf{0}. \end{aligned} \tag{B.1.10}$$

Substituting equation (B.1.10) into (B.1.9) gives:

$$\int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \mathbf{V}_* \exp\left(-\frac{M_{is} X_*^2 + \mu_{is} V_*^2}{2k_B T}\right) V_*^3 d\mathbf{X}_* d\mathbf{V}_* = \left(\frac{2\pi k_B T}{M_{is}}\right)^{\frac{3}{2}} \times \mathbf{0} = \mathbf{0}. \tag{B.1.11}$$

Substituting equations (B.1.4), (B.1.7), (B.1.8) and (B.1.11) into the integral $\mathcal{V}$ gives:

$$\begin{aligned} \mathcal{V} &= \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \left(\mathbf{X}_* - \frac{m_s \mathbf{V}_*}{M_{is}}\right) \exp\left(-\frac{M_{is} X_*^2 + \mu_{is} V_*^2}{2k_B T}\right) \\ &\quad \times \left[\mathbf{V}_* \cdot \left(\mathbf{X}_* - \frac{m_s \mathbf{V}_*}{M_{is}}\right)\right] V_* d\mathbf{X}_* d\mathbf{V}_* = 0. \end{aligned} \tag{B.1.12}$$

Next let us evaluate the integral $\mathcal{W}$ given in equation (B.1.2). Expanding it, we obtain:

$$\mathcal{W} = \underbrace{\int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \mathbf{X}_* \exp\left(-\frac{M_{is} X_*^2 + \mu_{is} V_*^2}{2k_B T}\right) V_*^3 d\mathbf{X}_* d\mathbf{V}_*}_{\mathcal{V}_2}$$

$$- \underbrace{\frac{m_s}{M_{is}} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \mathbf{V}_* \exp \left(- \frac{M_{is} X_*^2 + \mu_{is} V_*^2}{2k_B T} \right) V_*^3 d\mathbf{X}_* d\mathbf{V}_*}_{\mathcal{V}_4}.$$

Substituting equations (B.1.7) and (B.1.11) into the previous equation, we obtain:

$$\mathcal{W} = \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \left(\mathbf{X} - \frac{m_s \mathbf{V}_*}{M_{is}} \right) \exp \left(- \frac{M_{is} X_*^2 + \mu_{is} V_*^2}{2k_B T} \right) V_*^3 d\mathbf{X}_* d\mathbf{V}_* = 0. \quad (\text{B.1.13})$$

Finally, substituting equations (B.1.12) and (B.1.13) into the integral (B.1.2), we obtain:

$$\tilde{\mathcal{O}}_i^{(2)} = 0.$$

B.2 Evaluation of the Integral $\tilde{\mathcal{P}}_i^{(2)}$

In this section, the integral $\tilde{\mathcal{P}}_i^{(2)}$ given in equation (5.4.19) will be evaluated. To do this, we substitute equation (B.1.1) with s replaced by j into $\tilde{\mathcal{P}}_i^{(2)}$ and obtain:

$$\begin{aligned} \tilde{\mathcal{P}}_i^{(2)} &= \alpha \beta_{ij} \sigma_{ij}^2 \frac{T_i^\alpha - T_j^\alpha}{k_B T^2} \frac{m_i}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} m_i \mathbf{v}_i M_i^\alpha M_j^\alpha \left(\frac{4\mu_{ij}}{m_i} \cos \theta (\mathbf{v}_j - \mathbf{v}_i) \cdot \mathbf{v}_i \right. \\ &\quad \left. + \frac{4\mu_{ij}^2}{m_i^2} (\|\mathbf{v}_i - \mathbf{v}_j\| \cos \theta)^2 \right) \Theta \left(\langle \epsilon, c_0 \mathbf{v}_i - c_0 \mathbf{v}_j \rangle - \Xi_{ij} \right) \langle \epsilon, \mathbf{v}_i - \mathbf{v}_j \rangle d\epsilon d\mathbf{v}_j d\mathbf{v}_i \\ &= \alpha \beta_{ij} \sigma_{ij}^2 \frac{T_i^\alpha - T_j^\alpha}{k_B T^2} 2\mu_{ij} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} m_i \mathbf{v}_i M_i^\alpha M_j^\alpha \cos \theta ((\mathbf{v}_j - \mathbf{v}_i) \cdot \mathbf{v}_i) \\ &\quad \times \Theta \left(\langle \epsilon, c_0 \mathbf{v}_i - c_0 \mathbf{v}_j \rangle - \Xi_{ij} \right) \langle \epsilon, \mathbf{v}_i - \mathbf{v}_j \rangle d\epsilon d\mathbf{v}_j d\mathbf{v}_i \\ &\quad + \alpha \beta_{ij} \sigma_{ij}^2 \frac{T_i^\alpha - T_j^\alpha}{k_B T^2} 2\mu_{ij}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} \mathbf{v}_i M_i^\alpha M_j^\alpha (\|\mathbf{v}_i - \mathbf{v}_j\| \cos \theta)^2 \\ &\quad \times \Theta \left(\langle \epsilon, c_0 \mathbf{v}_i - c_0 \mathbf{v}_j \rangle - \Xi_{ij} \right) \langle \epsilon, \mathbf{v}_i - \mathbf{v}_j \rangle d\epsilon d\mathbf{v}_j d\mathbf{v}_i. \end{aligned}$$

Observe that

$$\begin{aligned} &\int_{\mathbb{S}_+^2} \cos^2 \theta \Theta \left(\langle \epsilon, c_0 \mathbf{v}_i - c_0 \mathbf{v}_j \rangle - \Xi_{ij} \right) \langle \epsilon, \mathbf{v}_i - \mathbf{v}_j \rangle d\epsilon \\ &= \int_{\mathbb{S}_+^2} \cos^2 \theta \Theta \left(c_0 \|\mathbf{v}_i - \mathbf{v}_j\| \cos \theta - \Xi_{ij} \right) \|\mathbf{v}_i - \mathbf{v}_j\| \cos \theta d\epsilon \\ &= \int_0^{\frac{\pi}{2}} \int_0^{2\pi} \cos^2 \theta \Theta \left(c_0 \|\mathbf{v}_i - \mathbf{v}_j\| \cos \theta - \Xi_{ij} \right) \|\mathbf{v}_i - \mathbf{v}_j\| \cos \theta \sin \theta d\phi d\theta \\ &= 2\pi \int_0^{\frac{\pi}{2}} \Theta \left(c_0 \|\mathbf{v}_i - \mathbf{v}_j\| \cos \theta - \Xi_{ij} \right) \|\mathbf{v}_i - \mathbf{v}_j\| \cos^3 \theta \sin \theta d\theta \\ &= 2\pi \int_0^{\arccos \left(\frac{\Xi_{ij}}{c_0 \|\mathbf{v}_i - \mathbf{v}_j\|} \right)} \Theta \left(\|\mathbf{v}_i - \mathbf{v}_j\| - \frac{\Xi_{ij}}{c_0} \right) \|\mathbf{v}_i - \mathbf{v}_j\| \cos^3 \theta \sin \theta d\theta \end{aligned}$$

$$\begin{aligned}
&= 2\pi\Theta\left(\|\mathbf{v}_i - \mathbf{v}_j\| - \frac{\Xi_{ij}}{c_0}\right)\|\mathbf{v}_i - \mathbf{v}_j\|\int_0^{\arccos\left(\frac{\Xi_{ij}}{c_0\|\mathbf{v}_i - \mathbf{v}_j\|}\right)}\cos^3\theta\sin\theta d\theta \\
&= 2\pi\Theta\left(\|\mathbf{v}_i - \mathbf{v}_j\| - \frac{\Xi_{ij}}{c_0}\right)\|\mathbf{v}_i - \mathbf{v}_j\|\left[-\frac{\cos^4\theta}{4}\right]_0^{\arccos\left(\frac{\Xi_{ij}}{c_0\|\mathbf{v}_i - \mathbf{v}_j\|}\right)} \\
&= -\frac{\pi}{2}\Theta\left(\|\mathbf{v}_i - \mathbf{v}_j\| - \frac{\Xi_{ij}}{c_0}\right)\|\mathbf{v}_i - \mathbf{v}_j\|\left[\left(\frac{\Xi_{ij}}{c_0\|\mathbf{v}_i - \mathbf{v}_j\|}\right)^4 - 1\right] \\
&= \frac{\pi}{2}\Theta\left(\|\mathbf{v}_i - \mathbf{v}_j\| - \frac{\Xi_{ij}}{c_0}\right)\|\mathbf{v}_i - \mathbf{v}_j\|\left[1 - \left(\frac{\Xi_{ij}}{c_0\|\mathbf{v}_i - \mathbf{v}_j\|}\right)^4\right]. \tag{B.2.1}
\end{aligned}$$

Substituting equation (4.4.26) into the first integral on the right-hand side of the last equality of $\tilde{\mathcal{P}}_i^{(2)}$ above and equation (B.2.1) into the second integral gives:

$$\begin{aligned}
\tilde{\mathcal{P}}_i^{(2)} &= \alpha\beta_{ij}\sigma_{ij}^2\frac{T_i^\alpha - T_j^\alpha}{k_B T^2}\frac{4\pi\mu_{ij}}{3}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}m_i\mathbf{v}_iM_i^\alpha M_j^\alpha((\mathbf{v}_j - \mathbf{v}_i) \cdot \mathbf{v}_i) \\
&\quad \times \Theta\left(\|\mathbf{v}_i - \mathbf{v}_j\| - \frac{\Xi_{ij}}{c_0}\right)\|\mathbf{v}_i - \mathbf{v}_j\|\left[1 - \left(\frac{\Xi_{ij}}{c_0\|\mathbf{v}_i - \mathbf{v}_j\|}\right)^3\right]d\mathbf{v}_j d\mathbf{v}_i \\
&+ \alpha\beta_{ij}\sigma_{ij}^2\frac{T_i^\alpha - T_j^\alpha}{k_B T^2}\mu_{ij}^2\pi\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\mathbf{v}_iM_i^\alpha M_j^\alpha\|\mathbf{v}_i - \mathbf{v}_j\|^2\Theta\left(\|\mathbf{v}_i - \mathbf{v}_j\| - \frac{\Xi_{ij}}{c_0}\right) \\
&\quad \times \|\mathbf{v}_i - \mathbf{v}_j\|\left[1 - \left(\frac{\Xi_{ij}}{c_0\|\mathbf{v}_i - \mathbf{v}_j\|}\right)^4\right]d\mathbf{v}_j d\mathbf{v}_i \\
&= \alpha\beta_{ij}\sigma_{ij}^2\frac{T_i^\alpha - T_j^\alpha}{k_B T^2}\frac{4\pi\mu_{ij}}{3}\frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3}c_i^\alpha c_j^\alpha\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}m_i\mathbf{v}_i\exp\left(-\frac{m_i(\mathbf{v}_i)^2 + m_j(\mathbf{v}_j)^2}{2k_B T}\right) \\
&\quad \times ((\mathbf{v}_j - \mathbf{v}_i) \cdot \mathbf{v}_i)\Theta\left(\|\mathbf{v}_i - \mathbf{v}_j\| - \frac{\Xi_{ij}}{c_0}\right)\|\mathbf{v}_i - \mathbf{v}_j\|\left[1 - \left(\frac{\Xi_{ij}}{c_0\|\mathbf{v}_i - \mathbf{v}_j\|}\right)^3\right]d\mathbf{v}_j d\mathbf{v}_i \\
&+ \alpha\beta_{ij}\sigma_{ij}^2\frac{T_i^\alpha - T_j^\alpha}{k_B T^2}\mu_{ij}^2\pi\frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3}c_i^\alpha c_j^\alpha\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\mathbf{v}_i\exp\left(-\frac{m_i(\mathbf{v}_i)^2 + m_j(\mathbf{v}_j)^2}{2k_B T}\right)\|\mathbf{v}_i - \mathbf{v}_j\|^3 \\
&\quad \times \Theta\left(\|\mathbf{v}_i - \mathbf{v}_j\| - \frac{\Xi_{ij}}{c_0}\right)\left[1 - \left(\frac{\Xi_{ij}}{c_0\|\mathbf{v}_i - \mathbf{v}_j\|}\right)^4\right]d\mathbf{v}_j d\mathbf{v}_i.
\end{aligned}$$

It will be convenient to transform the above six fold integrals from $\mathbf{v}_i$ and $\mathbf{v}_j$ to the centre of mass velocity $\mathbf{X}^*$ and relative velocity $\mathbf{V}^*$ defined as given in equations (2.4.6) and (2.4.7), respectively. More precisely, using equations (2.4.7), (2.4.10) and (2.4.12) with $(m_i + m_j) = M$ together with equation (4.3.21) gives:

$$\begin{aligned}
\tilde{\mathcal{P}}_i^{(2)} &= \alpha\beta_{ij}\sigma_{ij}^2\frac{T_i^\alpha - T_j^\alpha}{k_B T^2}\frac{4\pi\mu_{ij}}{3}\frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3}c_i^\alpha c_j^\alpha \\
&\quad \times \int_{\mathbb{R}^3}\int_{\mathbb{R}^3}m_i\left(\mathbf{X}^* - \frac{m_j\mathbf{V}^*}{M}\right)\exp\left(-\frac{MX^{*2} + \mu_{ij}V^{*2}}{2k_B T}\right)
\end{aligned}$$

$$\begin{aligned}
& \times \left[\mathbf{V}^* \cdot \left(\mathbf{X}^* - \frac{m_j \mathbf{V}^*}{M} \right) \right] \Theta \left(V^* - \frac{\Xi_{ij}}{c_0} \right) V^* \left[1 - \left(\frac{\Xi_{ij}}{c_0 V^*} \right)^3 \right] d\mathbf{X}^* d\mathbf{V}^* \\
& + \alpha \beta_{ij} \sigma_{ij}^2 \frac{T_i^\alpha - T_j^\alpha}{k_B T^2} \pi \mu_{ij}^2 \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_j^\alpha \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \left(\mathbf{X}^* - \frac{m_j \mathbf{V}^*}{M} \right) \exp \left(- \frac{M X^{*2} + \mu_{ij} V^{*2}}{2k_B T} \right) \\
& \quad \times V^{*3} \Theta \left(V^* - \frac{\Xi_{ij}}{c_0} \right) \left[1 - \left(\frac{\Xi_{ij}}{c_0 V^*} \right)^4 \right] d\mathbf{X}^* d\mathbf{V}^* \\
& = \alpha \beta_{ij} \sigma_{ij}^2 \frac{T_i^\alpha - T_j^\alpha}{k_B T^2} \frac{4\pi \mu_{ij}}{3} \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_j^\alpha \\
& \quad \times \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} m_i \left(\mathbf{X}^* - \frac{m_j \mathbf{V}^*}{M} \right) \exp \left(- \frac{M X^{*2} + \mu_{ij} V^{*2}}{2k_B T} \right) \\
& \quad \times \left[\mathbf{V}^* \cdot \left(\mathbf{X}^* - \frac{m_j \mathbf{V}^*}{M} \right) \right] \Theta \left(V^* - \frac{\Xi_{ij}}{c_0} \right) V^* d\mathbf{X}^* d\mathbf{V}^* \\
& - \alpha \beta_{ij} \sigma_{ij}^2 \frac{T_i^\alpha - T_j^\alpha}{k_B T^2} \frac{4\pi \mu_{ij}}{3} \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_j^\alpha \\
& \quad \times \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} m_i \left(\mathbf{X}^* - \frac{m_j \mathbf{V}^*}{M} \right) \exp \left(- \frac{M X^{*2} + \mu_{ij} V^{*2}}{2k_B T} \right) \\
& \quad \times \left[\mathbf{V}^* \cdot \left(\mathbf{X}^* - \frac{m_j \mathbf{V}^*}{M} \right) \right] \Theta \left(V^* - \frac{\Xi_{ij}}{c_0} \right) V^* \left(\frac{\Xi_{ij}}{c_0 V^*} \right)^3 d\mathbf{X}^* d\mathbf{V}^* \\
& + \alpha \beta_{ij} \sigma_{ij}^2 \frac{T_i^\alpha - T_j^\alpha}{k_B T^2} \pi \mu_{ij}^2 \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_j^\alpha \\
& \quad \times \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \left(\mathbf{X}^* - \frac{m_j \mathbf{V}^*}{M} \right) \exp \left(- \frac{M X^{*2} + \mu_{ij} V^{*2}}{2k_B T} \right) V^{*3} \Theta \left(V^* - \frac{\Xi_{ij}}{c_0} \right) d\mathbf{X}^* d\mathbf{V}^* \\
& - \alpha \beta_{ij} \sigma_{ij}^2 \frac{T_i^\alpha - T_j^\alpha}{k_B T^2} \pi \mu_{ij}^2 \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_j^\alpha \\
& \quad \times \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \left(\mathbf{X}^* - \frac{m_j \mathbf{V}^*}{M} \right) \exp \left(- \frac{M X^{*2} + \mu_{ij} V^{*2}}{2k_B T} \right) \\
& \quad \times V^{*3} \Theta \left(V^* - \frac{\Xi_{ij}}{c_0} \right) \left(\frac{\Xi_{ij}}{c_0 V^*} \right)^4 d\mathbf{X}^* d\mathbf{V}^*,
\end{aligned}$$

where equation (4.4.27) have been used to obtain the previous equation. Observe that

$$\begin{aligned}
& \left(\mathbf{X}^* - \frac{m_j \mathbf{V}^*}{M} \right) \left[\mathbf{V}^* \cdot \left(\mathbf{X}^* - \frac{m_j \mathbf{V}^*}{M} \right) \right] \\
& = \left(\mathbf{X}^* - \frac{m_j \mathbf{V}^*}{M} \right) \left[\mathbf{V}^* \cdot \mathbf{X}^* - \frac{m_j V^{*2}}{M} \right] \\
& = \mathbf{X}^* (\mathbf{V}^* \cdot \mathbf{X}^*) - \mathbf{X}^* \frac{m_j V^{*2}}{M} - \frac{m_j \mathbf{V}^*}{M} (\mathbf{V}^* \cdot \mathbf{X}^*) + \left(\frac{m_j V^*}{M} \right)^2 \mathbf{V}^*.
\end{aligned}$$

Therefore,

$$\begin{aligned}
\tilde{\mathcal{P}}_i^{(2)} = & \alpha\beta_{ij}\sigma_{ij}^2 \frac{T_i^\alpha - T_j^\alpha}{k_B T^2} \frac{4\pi\mu_{ij}}{3} \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_j^\alpha \\
& \times \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} m_i \left[\mathbf{X}^*(\mathbf{V}^* \cdot \mathbf{X}^*) - \mathbf{X}^* \frac{m_j V^{*2}}{M} - \frac{m_j \mathbf{V}^*}{M} (\mathbf{V}^* \cdot \mathbf{X}^*) + \left(\frac{m_j V^*}{M} \right)^2 \mathbf{V}^* \right] \\
& \times \exp \left(- \frac{M X^{*2} + \mu_{ij} V^{*2}}{2k_B T} \right) \Theta \left(V^* - \frac{\Xi_{ij}}{c_0} \right) V^* d\mathbf{X}^* d\mathbf{V}^* \\
& - \alpha\beta_{ij}\sigma_{ij}^2 \frac{T_i^\alpha - T_j^\alpha}{k_B T^2} \frac{4\pi\mu_{ij}}{3} \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_j^\alpha \\
& \times \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} m_i \left[\mathbf{X}^*(\mathbf{V}^* \cdot \mathbf{X}^*) - \mathbf{X}^* \frac{m_j V^{*2}}{M} - \frac{m_j \mathbf{V}^*}{M} (\mathbf{V}^* \cdot \mathbf{X}^*) + \left(\frac{m_j V^*}{M} \right)^2 \mathbf{V}^* \right] \\
& \times \exp \left(- \frac{M X^{*2} + \mu_{ij} V^{*2}}{2k_B T} \right) \Theta \left(V^* - \frac{\Xi_{ij}}{c_0} \right) V^* \left(\frac{\Xi_{ij}}{c_0 V^*} \right)^3 d\mathbf{X}^* d\mathbf{V}^* \\
& + \alpha\beta_{ij}\sigma_{ij}^2 \frac{T_i^\alpha - T_j^\alpha}{k_B T^2} \pi \mu_{ij}^2 \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_j^\alpha \\
& \times \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \left(\mathbf{X}^* - \frac{m_j \mathbf{V}^*}{M} \right) \exp \left(- \frac{M X^{*2} + \mu_{ij} V^{*2}}{2k_B T} \right) V^{*3} \Theta \left(V^* - \frac{\Xi_{ij}}{c_0} \right) d\mathbf{X}^* d\mathbf{V}^* \\
& - \alpha\beta_{ij}\sigma_{ij}^2 \frac{T_i^\alpha - T_j^\alpha}{k_B T^2} \pi \mu_{ij}^2 \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_j^\alpha \\
& \times \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \left(\mathbf{X}^* - \frac{m_j \mathbf{V}^*}{M} \right) \exp \left(- \frac{M X^{*2} + \mu_{ij} V^{*2}}{2k_B T} \right) \\
& \times V^{*3} \Theta \left(V^* - \frac{\Xi_{ij}}{c_0} \right) \left(\frac{\Xi_{ij}}{c_0 V^*} \right)^4 d\mathbf{X}^* d\mathbf{V}^*.
\end{aligned}$$

Expanding gives:

$$\begin{aligned}
\tilde{\mathcal{P}}_i^{(2)} = & \alpha\beta_{ij}\sigma_{ij}^2 \frac{T_i^\alpha - T_j^\alpha}{k_B T^2} \frac{4\pi\mu_{ij}}{3} \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_j^\alpha m_i \\
& \times \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \mathbf{X}^*(\mathbf{V}^* \cdot \mathbf{X}^*) \exp \left(- \frac{M X^{*2} + \mu_{ij} V^{*2}}{2k_B T} \right) \Theta \left(V^* - \frac{\Xi_{ij}}{c_0} \right) V^* d\mathbf{X}^* d\mathbf{V}^* \\
& - \alpha\beta_{ij}\sigma_{ij}^2 \frac{T_i^\alpha - T_j^\alpha}{k_B T^2} \frac{4\pi\mu_{ij}}{3} \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_j^\alpha \mu_{ij} \\
& \times \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \mathbf{X}^* V^{*2} \exp \left(- \frac{M X^{*2} + \mu_{ij} V^{*2}}{2k_B T} \right) \Theta \left(V^* - \frac{\Xi_{ij}}{c_0} \right) V^* d\mathbf{X}^* d\mathbf{V}^* \\
& - \alpha\beta_{ij}\sigma_{ij}^2 \frac{T_i^\alpha - T_j^\alpha}{k_B T^2} \frac{4\pi\mu_{ij}}{3} \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_j^\alpha \mu_{ij} \\
& \times \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \mathbf{V}^*(\mathbf{V}^* \cdot \mathbf{X}^*) \exp \left(- \frac{M X^{*2} + \mu_{ij} V^{*2}}{2k_B T} \right) \Theta \left(V^* - \frac{\Xi_{ij}}{c_0} \right) V^* d\mathbf{X}^* d\mathbf{V}^* \\
& + \alpha\beta_{ij}\sigma_{ij}^2 \frac{T_i^\alpha - T_j^\alpha}{k_B T^2} \frac{4\pi\mu_{ij}}{3} \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_j^\alpha \frac{\mu_{ij} m_j}{M}
\end{aligned}$$

$$\begin{aligned}
& \times \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} V^{*2} \mathbf{V}^* \exp \left(-\frac{MX^{*2} + \mu_{ij} V^{*2}}{2k_B T} \right) \Theta \left(V^* - \frac{\Xi_{ij}}{c_0} \right) V^* d\mathbf{X}^* d\mathbf{V}^* \\
& - \alpha \beta_{ij} \sigma_{ij}^2 \frac{T_i^\alpha - T_j^\alpha}{k_B T^2} \frac{4\pi \mu_{ij}}{3} \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_j^\alpha m_i \\
& \times \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \mathbf{X}^* (\mathbf{V}^* \cdot \mathbf{X}^*) \exp \left(-\frac{MX^{*2} + \mu_{ij} V^{*2}}{2k_B T} \right) \Theta \left(V^* - \frac{\Xi_{ij}}{c_0} \right) V^* \left(\frac{\Xi_{ij}}{c_0 V^*} \right)^3 d\mathbf{X}^* d\mathbf{V}^* \\
& + \alpha \beta_{ij} \sigma_{ij}^2 \frac{T_i^\alpha - T_j^\alpha}{k_B T^2} \frac{4\pi \mu_{ij}}{3} \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_j^\alpha \mu_{ij} \\
& \times \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \mathbf{X}^* V^{*2} \exp \left(-\frac{MX^{*2} + \mu_{ij} V^{*2}}{2k_B T} \right) \Theta \left(V^* - \frac{\Xi_{ij}}{c_0} \right) V^* \left(\frac{\Xi_{ij}}{c_0 V^*} \right)^3 d\mathbf{X}^* d\mathbf{V}^* \\
& + \alpha \beta_{ij} \sigma_{ij}^2 \frac{T_i^\alpha - T_j^\alpha}{k_B T^2} \frac{4\pi \mu_{ij}}{3} \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_j^\alpha \mu_{ij} \\
& \times \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \mathbf{V}^* (\mathbf{V}^* \cdot \mathbf{X}^*) \exp \left(-\frac{MX^{*2} + \mu_{ij} V^{*2}}{2k_B T} \right) \Theta \left(V^* - \frac{\Xi_{ij}}{c_0} \right) V^* \left(\frac{\Xi_{ij}}{c_0 V^*} \right)^3 d\mathbf{X}^* d\mathbf{V}^* \\
& - \alpha \beta_{ij} \sigma_{ij}^2 \frac{T_i^\alpha - T_j^\alpha}{k_B T^2} \frac{4\pi \mu_{ij}}{3} \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_j^\alpha \frac{\mu_{ij} m_j}{M} \\
& \times \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} V^{*2} \mathbf{V}^* \exp \left(-\frac{MX^{*2} + \mu_{ij} V^{*2}}{2k_B T} \right) \Theta \left(V^* - \frac{\Xi_{ij}}{c_0} \right) V^* \left(\frac{\Xi_{ij}}{c_0 V^*} \right)^3 d\mathbf{X}^* d\mathbf{V}^* \\
& + \alpha \beta_{ij} \sigma_{ij}^2 \frac{T_i^\alpha - T_j^\alpha}{k_B T^2} \pi \mu_{ij}^2 \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_j^\alpha \\
& \times \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \mathbf{X}^* \exp \left(-\frac{MX^{*2} + \mu_{ij} V^{*2}}{2k_B T} \right) V^{*3} \Theta \left(V^* - \frac{\Xi_{ij}}{c_0} \right) d\mathbf{X}^* d\mathbf{V}^* \\
& - \alpha \beta_{ij} \sigma_{ij}^2 \frac{T_i^\alpha - T_j^\alpha}{k_B T^2} \pi \mu_{ij}^2 \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_j^\alpha \frac{m_j}{M} \\
& \times \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \mathbf{V}^* \exp \left(-\frac{MX^{*2} + \mu_{ij} V^{*2}}{2k_B T} \right) V^{*3} \Theta \left(V^* - \frac{\Xi_{ij}}{c_0} \right) d\mathbf{X}^* d\mathbf{V}^* \\
& - \alpha \beta_{ij} \sigma_{ij}^2 \frac{T_i^\alpha - T_j^\alpha}{k_B T^2} \pi \mu_{ij}^2 \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_j^\alpha \\
& \times \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \mathbf{X}^* \exp \left(-\frac{MX^{*2} + \mu_{ij} V^{*2}}{2k_B T} \right) V^{*3} \Theta \left(V^* - \frac{\Xi_{ij}}{c_0} \right) \left(\frac{\Xi_{ij}}{c_0 V^*} \right)^4 d\mathbf{X}^* d\mathbf{V}^* \\
& + \alpha \beta_{ij} \sigma_{ij}^2 \frac{T_i^\alpha - T_j^\alpha}{k_B T^2} \pi \mu_{ij}^2 \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_j^\alpha \frac{m_j}{M} \\
& \times \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \mathbf{V}^* \exp \left(-\frac{MX^{*2} + \mu_{ij} V^{*2}}{2k_B T} \right) V^{*3} \Theta \left(V^* - \frac{\Xi_{ij}}{c_0} \right) \left(\frac{\Xi_{ij}}{c_0 V^*} \right)^4 d\mathbf{X}^* d\mathbf{V}^*.
\end{aligned}$$

The above equation can be rewritten as:

$$\begin{aligned}
\tilde{\mathcal{P}}_i^{(2)} = & \alpha\beta_{ij}\sigma_{ij}^2 \frac{T_i^\alpha - T_j^\alpha}{k_B T^2} \frac{4\pi\mu_{ij}}{3} \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_j^\alpha m_i \\
& \times \underbrace{\int_{\mathbb{R}^3} \mathbf{X}^* \exp\left(-\frac{MX^{*2}}{2k_B T}\right) \left[\mathbf{X}^* \cdot \int_{\mathbb{R}^3} \mathbf{V}^* \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) V^* d\mathbf{V}^* \right] d\mathbf{X}^*}_{\mathcal{U}_1} \\
& - \alpha\beta_{ij}\sigma_{ij}^2 \frac{T_i^\alpha - T_j^\alpha}{k_B T^2} \frac{4\pi\mu_{ij}}{3} \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_j^\alpha \mu_{ij} \\
& \times \underbrace{\int_{\mathbb{R}^3} \mathbf{X}^* \exp\left(-\frac{MX^{*2}}{2k_B T}\right) d\mathbf{X}^* \int_{\mathbb{R}^3} V^{*3} \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) d\mathbf{V}^*}_{\mathcal{U}_2} \\
& - \alpha\beta_{ij}\sigma_{ij}^2 \frac{T_i^\alpha - T_j^\alpha}{k_B T^2} \frac{4\pi\mu_{ij}}{3} \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_j^\alpha \mu_{ij} \\
& \times \underbrace{\int_{\mathbb{R}^3} \mathbf{V}^* \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) V^* \left[\mathbf{V}^* \cdot \int_{\mathbb{R}^3} \mathbf{X}^* \exp\left(-\frac{MX^{*2}}{2k_B T}\right) d\mathbf{X}^* \right] d\mathbf{V}^*}_{\mathcal{U}_3} \\
& + \alpha\beta_{ij}\sigma_{ij}^2 \frac{T_i^\alpha - T_j^\alpha}{k_B T^2} \frac{4\pi\mu_{ij}}{3} \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_j^\alpha \frac{\mu_{ij} m_j}{M} \\
& \times \underbrace{\int_{\mathbb{R}^3} \exp\left(-\frac{MX^{*2}}{2k_B T}\right) d\mathbf{X}^* \int_{\mathbb{R}^3} \mathbf{V}^* \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) V^{*3} \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) d\mathbf{V}^*}_{\mathcal{U}_4} \\
& - \alpha\beta_{ij}\sigma_{ij}^2 \frac{T_i^\alpha - T_j^\alpha}{k_B T^2} \frac{4\pi\mu_{ij}}{3} \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_j^\alpha m_i \\
& \times \underbrace{\int_{\mathbb{R}^3} \mathbf{X}^* \exp\left(-\frac{MX^{*2}}{2k_B T}\right) \left[\mathbf{X}^* \cdot \int_{\mathbb{R}^3} \mathbf{V}^* \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) V^* \left(\frac{\Xi_{ij}}{c_0 V^*}\right)^3 d\mathbf{V}^* \right] d\mathbf{X}^*}_{\mathcal{U}_5} \\
& + \alpha\beta_{ij}\sigma_{ij}^2 \frac{T_i^\alpha - T_j^\alpha}{k_B T^2} \frac{4\pi\mu_{ij}}{3} \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_j^\alpha \mu_{ij} \\
& \times \underbrace{\left(\frac{\Xi_{ij}}{c_0}\right)^3 \int_{\mathbb{R}^3} \mathbf{X}^* \exp\left(-\frac{MX^{*2}}{2k_B T}\right) d\mathbf{X}^* \int_{\mathbb{R}^3} \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) d\mathbf{V}^*}_{\mathcal{U}_6} \\
& + \alpha\beta_{ij}\sigma_{ij}^2 \frac{T_i^\alpha - T_j^\alpha}{k_B T^2} \frac{4\pi\mu_{ij}}{3} \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_j^\alpha \mu_{ij} \\
& \times \underbrace{\int_{\mathbb{R}^3} \mathbf{V}^* \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) V^* \left[\mathbf{V}^* \cdot \int_{\mathbb{R}^3} \mathbf{X}^* \exp\left(-\frac{MX^{*2}}{2k_B T}\right) d\mathbf{X}^* \right] \left(\frac{\Xi_{ij}}{c_0 V^*}\right)^3 d\mathbf{V}^*}_{\mathcal{U}_7} \\
& - \alpha\beta_{ij}\sigma_{ij}^2 \frac{T_i^\alpha - T_j^\alpha}{k_B T^2} \frac{4\pi\mu_{ij}}{3} \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_j^\alpha \frac{\mu_{ij} m_j}{M}
\end{aligned}$$

$$\begin{aligned}
& \times \left(\frac{\Xi_{ij}}{c_0} \right)^3 \int_{\mathbb{R}^3} \exp \left(-\frac{MX^{*2}}{2k_B T} \right) d\mathbf{X}^* \underbrace{\int_{\mathbb{R}^3} \mathbf{V}^* \exp \left(-\frac{\mu_{ij} V^{*2}}{2k_B T} \right) \Theta \left(V^* - \frac{\Xi_{ij}}{c_0} \right) d\mathbf{V}^*}_{\mathcal{U}_8} \\
& + \alpha \beta_{ij} \sigma_{ij}^2 \frac{T_i^\alpha - T_j^\alpha}{k_B T^2} \pi \mu_{ij}^2 \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_j^\alpha \\
& \times \int_{\mathbb{R}^3} \mathbf{X}^* \exp \left(-\frac{MX^{*2}}{2k_B T} \right) d\mathbf{X}^* \underbrace{\int_{\mathbb{R}^3} V^{*3} \exp \left(-\frac{\mu_{ij} V^{*2}}{2k_B T} \right) \Theta \left(V^* - \frac{\Xi_{ij}}{c_0} \right) d\mathbf{V}^*}_{\mathcal{U}_2} \\
& - \alpha \beta_{ij} \sigma_{ij}^2 \frac{T_i^\alpha - T_j^\alpha}{k_B T^2} \pi \mu_{ij}^2 \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_j^\alpha \frac{m_j}{M} \\
& \times \int_{\mathbb{R}^3} \exp \left(-\frac{MX^{*2}}{2k_B T} \right) d\mathbf{X}^* \underbrace{\int_{\mathbb{R}^3} \mathbf{V}^* \exp \left(-\frac{\mu_{ij} V^{*2}}{2k_B T} \right) V^{*3} \Theta \left(V^* - \frac{\Xi_{ij}}{c_0} \right) d\mathbf{V}^*}_{\mathcal{U}_4} \\
& - \alpha \beta_{ij} \sigma_{ij}^2 \frac{T_i^\alpha - T_j^\alpha}{k_B T^2} \pi \mu_{ij}^2 \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_j^\alpha \\
& \times \int_{\mathbb{R}^3} \mathbf{X}^* \exp \left(-\frac{MX^{*2}}{2k_B T} \right) d\mathbf{X}^* \underbrace{\int_{\mathbb{R}^3} V^{*3} \exp \left(-\frac{\mu_{ij} V^{*2}}{2k_B T} \right) \Theta \left(V^* - \frac{\Xi_{ij}}{c_0} \right) \left(\frac{\Xi_{ij}}{c_0 V^*} \right)^4 d\mathbf{V}^*}_{\mathcal{U}_9} \\
& + \alpha \beta_{ij} \sigma_{ij}^2 \frac{T_i^\alpha - T_j^\alpha}{k_B T^2} \pi \mu_{ij}^2 \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_j^\alpha \frac{m_j}{M} \\
& \times \int_{\mathbb{R}^3} \exp \left(-\frac{MX^{*2}}{2k_B T} \right) d\mathbf{X}^* \underbrace{\int_{\mathbb{R}^3} \mathbf{V}^* \exp \left(-\frac{\mu_{ij} V^{*2}}{2k_B T} \right) V^{*3} \Theta \left(V^* - \frac{\Xi_{ij}}{c_0} \right) \left(\frac{\Xi_{ij}}{c_0 V^*} \right)^4 d\mathbf{V}^*}_{\mathcal{U}_{10}}.
\end{aligned}$$

The values of the last and second to the last integrals in $\mathbf{X}^*$ in the previous equation are given in equations (4.4.28). Now let us evaluate the integrals in $\mathbf{V}^*$. The value of integral in $\mathbf{V}^*$ given in the integral $\mathcal{U}_1$ is given in equation (4.4.30). Therefore, the integral $\mathcal{U}_1$ reduces to:

$$\begin{aligned}
\mathcal{U}_1 &= \int_{\mathbb{R}^3} \mathbf{X}^* \exp \left(-\frac{MX^{*2}}{2k_B T} \right) (\mathbf{X}^* \cdot \mathbf{0}) d\mathbf{X}^* \\
&= \int_{\mathbb{R}^3} \left[\mathbf{X}^* \exp \left(-\frac{MX^{*2}}{2k_B T} \right) \times 0 \right] d\mathbf{X}^* \\
&= \int_0^\infty \int_0^\pi \int_0^{2\pi} 0 X^{*2} \sin \theta d\phi d\theta dX^* \\
&= \underbrace{\int_0^\infty 0 dX^*}_0 \underbrace{\int_0^\pi \sin \theta d\theta}_2 \underbrace{\int_0^{2\pi} d\phi}_{2\pi} \\
&= 0.
\end{aligned} \tag{B.2.2}$$

The integral $\mathcal{U}_2$ can be written in spherical coordinates and evaluated as given below:

$$\begin{aligned}\mathcal{U}_2 &= \int_0^\infty \int_0^\pi \int_0^{2\pi} V^{*3} \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) V^{*2} \sin\theta \, d\phi \, d\theta \, dV^* \\ &= \int_{V^* \geq \frac{\Xi_{ij}}{c_0}}^\infty V^{*5} \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) dV^* \underbrace{\int_0^\pi \sin\theta \, d\theta}_2 \underbrace{\int_0^{2\pi} d\phi}_{2\pi}.\end{aligned}$$

The value of the integral in V^* in the last equality of the previous equation is given in equation (4.4.33). Therefore,

$$\mathcal{U}_2 = \int_{\mathbb{R}^3} V^{*3} \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) d\mathbf{V}^* = 2\pi \left(\frac{2k_B T}{\mu_{ij}}\right)^3 \Gamma(3, z_i^*). \quad (\text{B.2.3})$$

Next let us evaluate the integral $\mathcal{U}_3$. To do this, we use equation (4.4.28)₂ to obtain:

$$\begin{aligned}\mathcal{U}_3 &= \int_{\mathbb{R}^3} \mathbf{V}^* \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) V^* \left[\mathbf{V}^* \cdot \int_{\mathbb{R}^3} \mathbf{X}^* \exp\left(-\frac{M X^{*2}}{2k_B T}\right) d\mathbf{X}^* \right] d\mathbf{V}^* \\ &= \int_{\mathbb{R}^3} \left[\left(\mathbf{V}^* \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) V^* \right) (\mathbf{V}^* \cdot \mathbf{0}) \right] d\mathbf{V}^* \\ &= \int_{\mathbb{R}^3} \left[\left(\mathbf{V}^* \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) V^* \right) \times 0 \right] d\mathbf{V}^* \\ &= \int_0^\infty \int_0^\pi \int_0^{2\pi} 0 V^{*2} \sin\theta \, d\phi \, d\theta \, dV^* \\ &= \underbrace{\int_0^\infty 0 \, dV^*}_0 \underbrace{\int_0^\pi \sin\theta \, d\theta}_2 \underbrace{\int_0^{2\pi} d\phi}_{2\pi} \\ &= 0.\end{aligned} \quad (\text{B.2.4})$$

Next let us evaluate the integral $\mathcal{U}_4$. To do this, we use the fact that any vector $\mathbf{V}^*$ can be written in terms of a unit vector as $\mathbf{V}^* = V^* \vec{v}$, with $V^* = \|\mathbf{V}^*\|$, $\vec{v}$ a unit vector, and obtain:

$$\int_{\mathbb{R}^3} \mathbf{V}^* \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) V^{*3} \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) d\mathbf{V}^* = \int_{\mathbb{R}^3} V^* \vec{v} \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) V^{*3} \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) d\mathbf{V}^*.$$

Writing the integral on the right-hand side of the previous equation in spherical coordinates and integrating gives:

$$\begin{aligned}&\int_{\mathbb{R}^3} V^* \vec{v} \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) V^{*3} \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) d\mathbf{V}^* \\ &= \int_0^\infty \int_0^\pi \int_0^{2\pi} V^* (\hat{x} \sin\theta \cos\phi + \hat{y} \sin\theta \sin\phi + \hat{z} \cos\theta) \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) V^{*3} \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) d\phi \, d\theta \, dV^*\end{aligned}$$

$$\begin{aligned}
& \times \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) V^{*2} \sin \theta d\phi d\theta dV^* \\
& = \int_{V^* \geq \frac{\Xi_{ij}}{c_0}}^\infty V^{*6} \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) dV^* \left(\underbrace{\hat{\mathbf{x}} \int_0^\pi \sin^2 \theta d\theta}_{\frac{\pi}{2}} \underbrace{\int_0^{2\pi} \cos \phi d\phi}_0 \right. \\
& \quad \left. + \underbrace{\hat{\mathbf{y}} \int_0^\pi \sin^2 \theta d\theta}_{\frac{\pi}{2}} \underbrace{\int_0^{2\pi} \sin \phi d\phi}_0 + \underbrace{\hat{\mathbf{z}} \int_0^\pi \sin \theta \cos \theta d\theta}_0 \underbrace{\int_0^{2\pi} d\phi}_{2\pi} \right),
\end{aligned}$$

where $\hat{\mathbf{x}}, \hat{\mathbf{y}}, \hat{\mathbf{z}}$ are the Cartesian unit vectors in $\mathbb{R}^3$. Using the change of variable given in equation (4.3.23) together with equations (4.3.24) and (4.3.25), the integral in V^* above can be rewritten as:

$$\begin{aligned}
\int_{V^* \geq \frac{\Xi_{ij}}{c_0}}^\infty V^{*6} \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) dV^* &= \int_{z_i^*}^\infty z^3 \left(\frac{2k_B T}{\mu_{ij}}\right)^3 \exp(-z) \frac{1}{2z^{\frac{1}{2}}} \left(\frac{2k_B T}{\mu_{ij}}\right)^{\frac{1}{2}} dz \\
&= \frac{1}{2} \left(\frac{2k_B T}{\mu_{ij}}\right)^{\frac{7}{2}} \int_{z_i^*}^\infty z^{\frac{5}{2}} \exp(-z) dz.
\end{aligned}$$

Using the incomplete Euler gamma function defined in equation (4.3.3), with $\eta - 1 = \frac{5}{2}$ i.e $\eta = \frac{7}{2}$, we obtain:

$$\int_{V^* \geq \frac{\Xi_{ij}}{c_0}}^\infty V^{*6} \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) dV^* = \frac{1}{2} \left(\frac{2k_B T}{\mu_{ij}}\right)^{\frac{7}{2}} \Gamma\left(\frac{7}{2}, z_i^*\right).$$

Therefore,

$$\begin{aligned}
\int_{\mathbb{R}^3} \mathbf{V}^* \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) V^{*3} \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) d\mathbf{V}^* &= \frac{1}{2} \left(\frac{2k_B T}{\mu_{ij}}\right)^{\frac{7}{2}} \Gamma\left(\frac{7}{2}, z_i^*\right) \left[\hat{\mathbf{x}}(0) + \hat{\mathbf{y}}(0) + \hat{\mathbf{z}}(0) \right] \\
&= \mathbf{0}.
\end{aligned} \tag{B.2.5}$$

Next let us evaluate the integral $\mathcal{U}_5$. Observe that the value of the integral in $\mathbf{V}^*$ given in the integral $\mathcal{U}_5$ is given in equation (4.4.32). Therefore, the integral $\mathcal{U}_5$ reduces to:

$$\begin{aligned}
\mathcal{U}_5 &= \int_{\mathbb{R}^3} \mathbf{X}^* \exp\left(-\frac{MX^{*2}}{2k_B T}\right) \left[\mathbf{X}^* \cdot \mathbf{0} \right] d\mathbf{X}^* \\
&= \int_{\mathbb{R}^3} \left[\left(\mathbf{X}^* \exp\left(-\frac{MX^{*2}}{2k_B T}\right) \right) \times \mathbf{0} \right] d\mathbf{X}^* \\
&= \int_0^\infty \int_0^\pi \int_0^{2\pi} 0 X^{*2} \sin \theta d\phi d\theta dX^* \\
&= \underbrace{\int_0^\infty 0 dX^*}_0 \underbrace{\int_0^\pi \sin \theta d\theta}_2 \underbrace{\int_0^{2\pi} d\phi}_{2\pi} \\
&= 0.
\end{aligned} \tag{B.2.6}$$

The integral $\mathcal{U}_6$ can be written in spherical coordinates and evaluated as follows:

$$\begin{aligned}\mathcal{U}_6 &= \int_0^\infty \int_0^\pi \int_0^{2\pi} \exp\left(-\frac{\mu_{ij}V^{*2}}{2k_B T}\right) \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) V^{*2} \sin\theta \, d\phi \, d\theta \, dV^* \\ &= \int_{V^* \geq \frac{\Xi_{ij}}{c_0}}^\infty V^{*2} \exp\left(-\frac{\mu_{ij}V^{*2}}{2k_B T}\right) dV^* \underbrace{\int_0^\pi \sin\theta \, d\theta}_2 \underbrace{\int_0^{2\pi} d\phi}_{2\pi}.\end{aligned}$$

The value of the integral in V^* in the last equality of the previous equation is given in equation (4.4.35).

Therefore,

$$\mathcal{U}_6 = \int_{\mathbb{R}^3} \exp\left(-\frac{\mu_{ij}V^{*2}}{2k_B T}\right) \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) d\mathbf{V}^* = 2\pi \left(\frac{2k_B T}{\mu_{ij}}\right)^{\frac{3}{2}} \Gamma\left(\frac{3}{2}, z_i^*\right). \quad (\text{B.2.7})$$

Now let us evaluate the integral $\mathcal{U}_7$. To do this, observe that the value of the integral in $\mathbf{X}^*$ in the integral $\mathcal{U}_7$ is given in equation (4.4.28)₂. Therefore, the integral $\mathcal{U}_7$ reduces to:

$$\begin{aligned}\mathcal{U}_7 &= \int_{\mathbb{R}^3} \mathbf{V}^* \exp\left(-\frac{\mu_{ij}V^{*2}}{2k_B T}\right) \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) V^* \left(\frac{\Xi_{ij}}{c_0 V^*}\right)^3 (\mathbf{V}^* \cdot \mathbf{0}) d\mathbf{V}^* \\ &= \int_{\mathbb{R}^3} \left[\left(\mathbf{V}^* \exp\left(-\frac{\mu_{ij}V^{*2}}{2k_B T}\right) \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) V^* \left(\frac{\Xi_{ij}}{c_0 V^*}\right)^3 \right) \times 0 \right] d\mathbf{V}^* \\ &= \int_0^\infty \int_0^\pi \int_0^{2\pi} 0 V^{*2} \sin\theta \, d\phi \, d\theta \, dV^* \\ &= \underbrace{\int_0^\infty 0 \, dV}_0 \underbrace{\int_0^\pi \sin\theta \, d\theta}_2 \underbrace{\int_0^{2\pi} d\phi}_{2\pi} \\ &= 0.\end{aligned} \quad (\text{B.2.8})$$

Next let us evaluate integral $\mathcal{U}_8$. Using the fact that any vector $\mathbf{V}^*$ can be written in terms of a unit vector as $\mathbf{V}^* = V^* \vec{v}$, with $V^* = \|\mathbf{V}^*\|$ and $\vec{v}$ a unit vector, we obtain:

$$\int_{\mathbb{R}^3} \mathbf{V}^* \exp\left(-\frac{\mu_{ij}V^{*2}}{2k_B T}\right) \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) d\mathbf{V}^* = \int_{\mathbb{R}^3} V^* \vec{v} \exp\left(-\frac{\mu_{ij}V^{*2}}{2k_B T}\right) \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) d\mathbf{V}^*$$

Writing the integral on the right-hand side of the previous equation in spherical coordinates and integrating gives:

$$\begin{aligned}\mathcal{U}_8 &= \int_0^\infty \int_0^\pi \int_0^{2\pi} V^* (\hat{x} \sin\theta \cos\phi + \hat{y} \sin\theta \sin\phi + \hat{z} \cos\theta) \\ &\quad \times \exp\left(-\frac{\mu_{ij}V^{*2}}{2k_B T}\right) \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) V^{*2} \sin\theta \, d\phi \, d\theta \, dV^* \\ &= \int_{V^* \geq \frac{\Xi_{ij}}{c_0}}^\infty V^{*3} \exp\left(-\frac{\mu_{ij}V^{*2}}{2k_B T}\right) dV^* \underbrace{\left(\hat{x} \int_0^\pi \sin^2\theta \, d\theta \right)}_{\frac{\pi}{2}} \underbrace{\left(\int_0^{2\pi} \cos\phi \, d\phi \right)}_0\end{aligned}$$

$$+ \hat{\mathbf{y}} \underbrace{\int_0^\pi \sin^2 \theta d\theta}_{\frac{\pi}{2}} \underbrace{\int_0^{2\pi} \sin \phi d\phi}_0 + \hat{\mathbf{z}} \underbrace{\int_0^\pi \sin \theta \cos \theta d\theta}_0 \underbrace{\int_0^{2\pi} d\phi}_{2\pi} \Big),$$

where $\hat{\mathbf{x}}, \hat{\mathbf{y}}, \hat{\mathbf{z}}$ are the Cartesian unit vectors in $\mathbb{R}^3$. Using the change of variable given in equation (4.3.23) together with equations (4.3.24) and (4.3.25), we have that the integral in V^* in the last equality of the previous equation can be rewritten as:

$$\begin{aligned} \int_{V^* \geq \frac{\Xi_{ij}}{c_0}}^\infty V^{*3} \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) dV^* &= \int_{z_i^*}^\infty z^{\frac{3}{2}} \left(\frac{2k_B T}{\mu_{ij}}\right)^{\frac{3}{2}} \exp(-z) \frac{1}{2z^{\frac{1}{2}}} \left(\frac{2k_B T}{\mu_{ij}}\right)^{\frac{1}{2}} dz \\ &= \frac{1}{2} \left(\frac{2k_B T}{\mu_{ij}}\right)^2 \int_{z_i^*}^\infty z \exp(-z) dz. \end{aligned}$$

Using the incomplete Euler gamma function given in equation (4.3.3) with $\eta - 1 = 1$ i.e $\eta = 2$, we obtain:

$$\int_{V^* \geq \frac{\Xi_{ij}}{c_0}}^\infty V^{*3} \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) dV^* = \frac{1}{2} \left(\frac{2k_B T}{\mu_{ij}}\right)^2 \Gamma(2, z_i^*). \quad (\text{B.2.9})$$

Therefore,

$$\begin{aligned} \int_{\mathbb{R}^3} \mathbf{V}^* \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) d\mathbf{V}^* &= \frac{1}{2} \left(\frac{2k_B T}{\mu_{ij}}\right)^2 \Gamma(2, z_i^*) \left[\hat{\mathbf{x}}(0) + \hat{\mathbf{y}}(0) + \hat{\mathbf{z}}(0)\right] \\ &= \mathbf{0}. \end{aligned} \quad (\text{B.2.10})$$

The integral $\mathcal{U}_9$ can be written in spherical coordinates and integrated as follows:

$$\begin{aligned} &\int_{\mathbb{R}^3} V^{*3} \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) \left(\frac{\Xi_{ij}}{c_0 V^*}\right)^4 d\mathbf{V}^* \\ &= \int_0^\infty \int_0^\pi \int_0^{2\pi} V^{*3} \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) \left(\frac{\Xi_{ij}}{c_0 V^*}\right)^4 V^{*2} \sin \theta d\phi d\theta dV^* \\ &= \left(\frac{\Xi_{ij}}{c_0}\right)^4 \int_{V^* \geq \frac{\Xi_{ij}}{c_0}}^\infty V^* \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) dV^* \underbrace{\int_0^\pi \sin \theta d\theta}_2 \underbrace{\int_0^{2\pi} d\phi}_{2\pi}. \end{aligned}$$

The value of the integral in V^* in the last equality of the previous equation is given in equation (4.4.31).

Therefore,

$$\begin{aligned} \int_{\mathbb{R}^3} V^{*3} \exp\left(-\frac{\mu_{ij} V^{*2}}{2k_B T}\right) \Theta\left(V^* - \frac{\Xi_{ij}}{c_0}\right) \left(\frac{\Xi_{ij}}{c_0 V^*}\right)^4 d\mathbf{V}^* \\ = 2\pi \left(\frac{\Xi_{ij}}{c_0}\right)^4 \left(\frac{2k_B T}{\mu_{ij}}\right) \Gamma(1, z_i^*). \end{aligned} \quad (\text{B.2.11})$$

Finally, using the fact that any vector $\mathbf{V}^*$ can be written in terms of a unit vector as $\mathbf{V}^* = V^* \vec{\mathbf{v}}$, with $V^* = \|\mathbf{V}^*\|$ and $\vec{\mathbf{v}}$ a unit vector, one can write the integral $\mathcal{U}_{10}$ as follows:

$$\begin{aligned}
& \int_{\mathbb{R}^3} \mathbf{V}^* \exp \left(-\frac{\mu_{ij} V^{*2}}{2k_B T} \right) V^{*3} \Theta \left(V^* - \frac{\Xi_{ij}}{c_0} \right) \left(\frac{\Xi_{ij}}{c_0 V^*} \right)^4 d\mathbf{V}^* \\
&= \int_{\mathbb{R}^3} V^* \vec{\mathbf{v}} \exp \left(-\frac{\mu_{ij} V^{*2}}{2k_B T} \right) V^{*3} \Theta \left(V^* - \frac{\Xi_{ij}}{c_0} \right) \left(\frac{\Xi_{ij}}{c_0 V^*} \right)^4 d\mathbf{V}^*.
\end{aligned}$$

Writing the integral on the right-hand side of the previous equation in spherical coordinates and integrating gives:

$$\begin{aligned}
& \int_{\mathbb{R}^3} V^* \vec{\mathbf{v}} \exp \left(-\frac{\mu_{ij} V^{*2}}{2k_B T} \right) V^{*3} \Theta \left(V^* - \frac{\Xi_{ij}}{c_0} \right) \left(\frac{\Xi_{ij}}{c_0 V^*} \right)^4 d\mathbf{V}^* \\
&= \int_0^\infty \int_0^\pi \int_0^{2\pi} V^* (\hat{\mathbf{x}} \sin \theta \cos \phi + \hat{\mathbf{y}} \sin \theta \sin \phi + \hat{\mathbf{z}} \cos \theta) \exp \left(-\frac{\mu_{ij} V^{*2}}{2k_B T} \right) V^{*3} \\
&\quad \times \Theta \left(V^* - \frac{\Xi_{ij}}{c_0} \right) \left(\frac{\Xi_{ij}}{c_0 V^*} \right)^4 V^{*2} \sin \theta d\phi d\theta dV^* \\
&= \left(\frac{\Xi_{ij}}{c_0} \right)^4 \int_{V^* \geq \frac{\Xi_{ij}}{c_0}}^\infty V^{*2} \exp \left(-\frac{\mu_{ij} V^{*2}}{2k_B T} \right) dV^* \left(\hat{\mathbf{x}} \underbrace{\int_0^\pi \sin^2 \theta d\theta}_{\frac{\pi}{2}} \underbrace{\int_0^{2\pi} \cos \phi d\phi}_0 \right. \\
&\quad \left. + \hat{\mathbf{y}} \underbrace{\int_0^\pi \sin^2 \theta d\theta}_{\frac{\pi}{2}} \underbrace{\int_0^{2\pi} \sin \phi d\phi}_0 + \hat{\mathbf{z}} \underbrace{\int_0^\pi \sin \theta \cos \theta d\theta}_0 \underbrace{\int_0^{2\pi} d\phi}_{2\pi} \right).
\end{aligned}$$

The value of the integral in V^* in the last equality of the previous equation is given in equation (4.4.35). Therefore,

$$\begin{aligned}
& \int_{\mathbb{R}^3} \mathbf{V}^* \exp \left(-\frac{\mu_{ij} V^{*2}}{2k_B T} \right) V^{*3} \Theta \left(V^* - \frac{\Xi_{ij}}{c_0} \right) \left(\frac{\Xi_{ij}}{c_0 V^*} \right)^4 d\mathbf{V}^* \\
&= \left(\frac{\Xi_{ij}}{c_0} \right)^4 \frac{1}{2} \left(\frac{2k_B T}{\mu_{ij}} \right)^{\frac{3}{2}} \Gamma \left(\frac{3}{2}, z_i^* \right) \left[\hat{\mathbf{x}}(0) + \hat{\mathbf{y}}(0) + \hat{\mathbf{z}}(0) \right] \\
&= \mathbf{0}.
\end{aligned} \tag{B.2.12}$$

Substituting equations (4.4.28), (B.2.2), (B.2.3), (B.2.4), (B.2.5), (B.2.6), (B.2.7), (B.2.8), (B.2.10), (B.2.11), and (B.2.12) into $\tilde{\mathcal{P}}_i^{(2)}$, we obtain

$$\tilde{\mathcal{P}}_i^{(2)} = 0.$$

B.3 Evaluation of the Integral $\tilde{\mathcal{Q}}_i^{(1)}$

To evaluate the integral $\tilde{\mathcal{Q}}_i^{(1)}$ given in equation (5.4.28), we substitute equation (4.3.19) into $\tilde{\mathcal{Q}}_i^{(1)}$ and obtain:

$$\tilde{\mathcal{Q}}_i^{(1)} = \beta_{ij} \sigma_{ij}^2 \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} \left[\left(\frac{\mu_{ij}}{\mu_{kl}} \right)^{\frac{1}{2}} c_k^\alpha c_l^\alpha \exp \left(\frac{Q_R}{k_B T} \right) - c_i^\alpha c_j^\alpha \right] m_i$$

$$\times \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} \mathbf{v}_i \exp\left(-\frac{m_i(\mathbf{v}_i)^2 + m_j(\mathbf{v}_j)^2}{2k_B T}\right) \Theta(\langle \boldsymbol{\epsilon}, c_0 \mathbf{v}_i - c_0 \mathbf{v}_j \rangle - \Xi_{ij}) \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_j \rangle d\boldsymbol{\epsilon} d\mathbf{v}_j d\mathbf{v}_i.$$

The above integral is similar to the two integrals on the right-hand side of $\bar{\mathcal{E}}$ given in equation (A.1.2). Therefore, following the same steps as those used in the computation of the integrals given in equation (A.1.2), one obtains:

$$\tilde{\mathcal{Q}}_i^{(1)} = 0.$$

B.4 Evaluation of the Integral $\tilde{\mathcal{Q}}_i^{(3)}$

In this section, the integral $\tilde{\mathcal{Q}}_i^{(3)}$ given in equation (5.4.28) will be evaluated. To do this, we expand to obtain:

$$\begin{aligned} \tilde{\mathcal{Q}}_i^{(3)} &= \alpha \beta_{ij} \sigma_{ij}^2 (b_k + b_l) m_i \\ &\times \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} \mathbf{v}_i \left(\frac{\mu_{ij}}{\mu_{kl}} \right)^2 M_k^{\alpha\circ} M_l^{\alpha\circ} \Theta(\langle \boldsymbol{\epsilon}, c_0 \mathbf{v}_i - c_0 \mathbf{v}_j \rangle - \Xi_{ij}) \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_j \rangle d\boldsymbol{\epsilon} d\mathbf{v}_j d\mathbf{v}_i \\ &- \alpha \beta_{ij} \sigma_{ij}^2 (b_i + b_j) m_i \\ &\times \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} \mathbf{v}_i M_i^\alpha M_j^\alpha \Theta(\langle \boldsymbol{\epsilon}, c_0 \mathbf{v}_i - c_0 \mathbf{v}_j \rangle - \Xi_{ij}) \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_j \rangle d\boldsymbol{\epsilon} d\mathbf{v}_j d\mathbf{v}_i \\ &= \alpha \beta_{ij} \sigma_{ij}^2 (b_k + b_l) \frac{(m_k m_l)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_k^\alpha c_l^\alpha m_i \left(\frac{\mu_{ij}}{\mu_{kl}} \right)^2 \\ &\times \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} \mathbf{v}_i \exp\left(-\frac{m_k(\mathbf{v}_k^\circ)^2 + m_l(\mathbf{v}_l^\circ)^2}{2k_B T}\right) \Theta(\langle \boldsymbol{\epsilon}, c_0 \mathbf{v}_i - c_0 \mathbf{v}_j \rangle - \Xi_{ij}) \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_j \rangle d\boldsymbol{\epsilon} d\mathbf{v}_j d\mathbf{v}_i \\ &- \alpha \beta_{ij} \sigma_{ij}^2 (b_i + b_j) \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_j^\alpha m_i \\ &\times \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} \mathbf{v}_i \exp\left(-\frac{m_i(\mathbf{v}_i)^2 + m_j(\mathbf{v}_j)^2}{2k_B T}\right) \Theta(\langle \boldsymbol{\epsilon}, c_0 \mathbf{v}_i - c_0 \mathbf{v}_j \rangle - \Xi_{ij}) \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_j \rangle d\boldsymbol{\epsilon} d\mathbf{v}_j d\mathbf{v}_i. \end{aligned}$$

Using the conservation of total energy given in equation (2.3.12), one has that

$$\frac{1}{2} m_k (\mathbf{v}_k^\circ)^2 + \frac{1}{2} m_l (\mathbf{v}_l^\circ)^2 = \frac{1}{2} m_i (\mathbf{v}_i)^2 + \frac{1}{2} m_j (\mathbf{v}_j)^2 + \underbrace{E_i + E_j - E_k - E_l}_{-Q_R}. \quad (\text{B.4.1})$$

Using equation (B.4.1) in the first integral in the last equality of $\tilde{\mathcal{Q}}_i^{(3)}$ above, we obtain:

$$\begin{aligned} \tilde{\mathcal{Q}}_i^{(3)} &= \alpha \beta_{ij} \sigma_{ij}^2 (b_k + b_l) \frac{(m_k m_l)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_k^\alpha c_l^\alpha m_i \left(\frac{\mu_{ij}}{\mu_{kl}} \right)^2 \exp\left(\frac{Q_R}{k_B T}\right) \\ &\times \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} \mathbf{v}_i \exp\left(-\frac{m_i(\mathbf{v}_i)^2 + m_j(\mathbf{v}_j)^2}{2k_B T}\right) \Theta(\langle \boldsymbol{\epsilon}, c_0 \mathbf{v}_i - c_0 \mathbf{v}_j \rangle - \Xi_{ij}) \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_j \rangle d\boldsymbol{\epsilon} d\mathbf{v}_j d\mathbf{v}_i \\ &- \alpha \beta_{ij} \sigma_{ij}^2 (b_i + b_j) \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_j^\alpha m_i \end{aligned}$$

$$\times \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} \mathbf{v}_i \exp \left(-\frac{m_i(\mathbf{v}_i)^2 + m_j(\mathbf{v}_j)^2}{2k_B T} \right) \Theta(\langle \boldsymbol{\epsilon}, c_0 \mathbf{v}_i - c_0 \mathbf{v}_j \rangle - \Xi_{ij}) \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_j \rangle d\boldsymbol{\epsilon} d\mathbf{v}_j d\mathbf{v}_i.$$

The above integrals are similar to the integrals on the right-hand side of $\bar{\mathcal{E}}$ given in equation (A.1.2) which vanish upon evaluation. Therefore, following the same steps as those used in the computation of the integrals given in equation (A.1.2), one has that

$$\tilde{\mathcal{Q}}_i^{(3)} = 0.$$

B.5 Evaluation of the Integral $\tilde{\mathcal{Q}}_i^{(4)}$

In this section, the integral $\tilde{\mathcal{Q}}_i^{(4)}$ given in equation (5.4.28) will be evaluated. Expanding the integral $\tilde{\mathcal{Q}}_i^{(4)}$ gives:

$$\begin{aligned} \tilde{\mathcal{Q}}_i^{(4)} &= -\alpha \beta_{ij} \sigma_{ij}^2 \frac{3}{2T} (T_k^\alpha + T_l^\alpha) m_i \\ &\quad \times \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} \mathbf{v}_i \left(\frac{\mu_{ij}}{\mu_{kl}} \right)^2 M_k^{\alpha\circ} M_l^{\alpha\circ} \Theta(\langle \boldsymbol{\epsilon}, c_0 \mathbf{v}_i - c_0 \mathbf{v}_j \rangle - \Xi_{ij}) \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_j \rangle d\boldsymbol{\epsilon} d\mathbf{v}_j d\mathbf{v}_i \\ &+ \alpha \beta_{ij} \sigma_{ij}^2 \frac{3}{2T} (T_i^\alpha + T_j^\alpha) m_i \\ &\quad \times \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} \mathbf{v}_i M_i^\alpha M_j^\alpha \Theta(\langle \boldsymbol{\epsilon}, c_0 \mathbf{v}_i - c_0 \mathbf{v}_j \rangle - \Xi_{ij}) \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_j \rangle d\boldsymbol{\epsilon} d\mathbf{v}_j d\mathbf{v}_i \\ &= -\alpha \beta_{ij} \sigma_{ij}^2 \frac{3}{2T} (T_k^\alpha + T_l^\alpha) m_i \left(\frac{\mu_{ij}}{\mu_{kl}} \right)^2 \frac{(m_k m_l)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_k^\alpha c_l^\alpha \\ &\quad \times \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} \mathbf{v}_i \exp \left(-\frac{m_k(\mathbf{v}_k^\circ)^2 + m_l(\mathbf{v}_l^\circ)^2}{2k_B T} \right) \Theta(\langle \boldsymbol{\epsilon}, c_0 \mathbf{v}_i - c_0 \mathbf{v}_j \rangle - \Xi_{ij}) \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_j \rangle d\boldsymbol{\epsilon} d\mathbf{v}_j d\mathbf{v}_i \\ &+ \alpha \beta_{ij} \sigma_{ij}^2 \frac{3}{2T} (T_i^\alpha + T_j^\alpha) m_i \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_j^\alpha \\ &\quad \times \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} \mathbf{v}_i \exp \left(-\frac{m_i(\mathbf{v}_i)^2 + m_j(\mathbf{v}_j)^2}{2k_B T} \right) \Theta(\langle \boldsymbol{\epsilon}, c_0 \mathbf{v}_i - c_0 \mathbf{v}_j \rangle - \Xi_{ij}) \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_j \rangle d\boldsymbol{\epsilon} d\mathbf{v}_j d\mathbf{v}_i. \end{aligned}$$

Using equation (B.4.1) in the first integral of last equality of $\tilde{\mathcal{Q}}_i^{(4)}$ above, we obtain:

$$\begin{aligned} \tilde{\mathcal{Q}}_i^{(4)} &= -\alpha \beta_{ij} \sigma_{ij}^2 \frac{3}{2T} (T_k^\alpha + T_l^\alpha) m_i \left(\frac{\mu_{ij}}{\mu_{kl}} \right)^2 \frac{(m_k m_l)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_k^\alpha c_l^\alpha \exp \left(\frac{Q_R}{k_B T} \right) \\ &\quad \times \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} \mathbf{v}_i \exp \left(-\frac{m_i(\mathbf{v}_i)^2 + m_j(\mathbf{v}_j)^2}{2k_B T} \right) \Theta(\langle \boldsymbol{\epsilon}, c_0 \mathbf{v}_i - c_0 \mathbf{v}_j \rangle - \Xi_{ij}) \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_j \rangle d\boldsymbol{\epsilon} d\mathbf{v}_j d\mathbf{v}_i \\ &+ \alpha \beta_{ij} \sigma_{ij}^2 \frac{3}{2T} (T_i^\alpha + T_j^\alpha) m_i \frac{(m_i m_j)^{\frac{3}{2}}}{(2\pi k_B T)^3} c_i^\alpha c_j^\alpha \\ &\quad \times \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} \mathbf{v}_i \exp \left(-\frac{m_i(\mathbf{v}_i)^2 + m_j(\mathbf{v}_j)^2}{2k_B T} \right) \Theta(\langle \boldsymbol{\epsilon}, c_0 \mathbf{v}_i - c_0 \mathbf{v}_j \rangle - \Xi_{ij}) \langle \boldsymbol{\epsilon}, \mathbf{v}_i - \mathbf{v}_j \rangle d\boldsymbol{\epsilon} d\mathbf{v}_j d\mathbf{v}_i. \end{aligned}$$

The above integrals are similar to the integrals of $\bar{\mathcal{E}}$ given in equation (A.1.2) which vanish upon evaluation. Therefore, following the same steps as those used in the computation of the integrals given in equation (A.1.2), one obtains that $\tilde{\mathcal{Q}}_i^{(4)}$ vanishes, that is,

$$\tilde{\mathcal{Q}}_i^{(4)} = 0.$$

Appendix C

Evaluation of the Second and Third Terms of Equation (6.3.50)

C.1 Evaluation of the Second Term of Eq. (6.3.50)

In this section, we show that the second term on the right-hand side of equation (6.3.50) vanishes, that is

$$\sum_{\substack{j=1 \\ j \neq i}}^4 \frac{m_j}{m_i + m_j} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_0^{+\infty} \int_0^{+\infty} \int_0^1 \int_0^1 \int_{\mathbb{S}^2} (\mathbf{a}_{ij} \cdot \boldsymbol{\sigma}) \mathbf{v} \sqrt{\frac{2R\mathcal{E}}{\mu_{ij}}} M_i^\varepsilon M_j^\varepsilon \widehat{V}^{*\gamma-1} \\ \times 2 \Phi_{ij}(I, I_j, R, r) b_{ij}(\cos \theta) \cos \theta (1 - R) d\boldsymbol{\sigma} dr dR dI_j dI d\mathbf{v}_j d\mathbf{v} = 0.$$

To do this, it is enough to show that

$$\int_{\mathbb{S}^2} \boldsymbol{\sigma} b_{ij}(\cos \theta) \cos \theta d\boldsymbol{\sigma} = 0. \quad (\text{C.1.1})$$

Observe that

$$\begin{aligned} & \int_{\mathbb{S}^2} \boldsymbol{\sigma} b_{ij}(\cos \theta) \cos \theta d\boldsymbol{\sigma} \\ &= \int_0^\pi \int_0^{2\pi} (\hat{\mathbf{x}} \sin \theta \cos \phi + \hat{\mathbf{y}} \sin \theta \sin \phi + \hat{\mathbf{z}} \cos \theta) b_{ij}(\cos \theta) \cos \theta \sin \theta d\phi d\theta \\ &= \hat{\mathbf{x}} \int_0^\pi b_{ij}(\cos \theta) \sin^2 \theta \cos \theta d\theta \underbrace{\int_0^{2\pi} \cos \phi d\phi}_0 + \hat{\mathbf{y}} \int_0^\pi b_{ij}(\cos \theta) \sin^2 \theta \cos \theta d\theta \quad (\text{C.1.2}) \\ & \quad \times \underbrace{\int_0^{2\pi} \sin \phi d\phi}_0 + \hat{\mathbf{z}} \int_0^\pi b_{ij}(\cos \theta) \sin \theta \cos^2 \theta d\theta \underbrace{\int_0^{2\pi} d\phi}_{2\pi}. \end{aligned}$$

The integral

$$\int_0^\pi b_{ij}(\cos \theta) \sin \theta \cos^2 \theta d\theta = 0$$

since by our assumption $b_{ij}(\cos \theta)$ is an odd function of $\cos \theta$. Therefore, substituting the previous equation into equation (C.1.2) gives equation (C.1.1)

C.2 Evaluation of the Third Term of Eq. (6.3.50)

In this section, we show that the third term on the right-hand side of (6.3.50) vanishes, that is

$$\begin{aligned} & \sum_{\substack{j=1 \\ j \neq i}}^4 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_0^{+\infty} \int_0^{+\infty} \int_0^1 \int_0^1 \int_{\mathbb{S}^2} \mathbf{v} \left(\frac{T_i^\varepsilon}{k_B T^2} - \frac{T_j^\varepsilon}{k_B T^2} \right) \\ & \quad \times \left(\frac{m_i(\mathbf{v}_i')^2}{2} - \frac{m_i(\mathbf{v})^2}{2} + I_i' - I \right) M_i^\varepsilon M_j^\varepsilon \widehat{V}^{*\gamma-1} \Phi_{ij}(I, I_j, R, r) \\ & \quad \times 2 b_{ij}(\cos \theta) \cos \theta (1 - R) d\boldsymbol{\sigma} dr dR dI_j dI d\mathbf{v}_j d\mathbf{v} = 0. \quad (\text{C.2.1}) \end{aligned}$$

Using equation (6.3.3)₁, observe that:

$$\begin{aligned} (\mathbf{v}_i')^2 &= \left(\frac{m_i \mathbf{v} + m_j \mathbf{v}_j}{m_i + m_j} + \frac{m_j}{m_i + m_j} \sqrt{\frac{2R\mathcal{E}}{\mu_{ij}}} \boldsymbol{\sigma} \right)^2 \\ &= \left(\frac{1}{m_i + m_j} \right)^2 \left(m_i \mathbf{v} + m_j \mathbf{v}_j + m_j \sqrt{\frac{2R\mathcal{E}}{\mu_{ij}}} \boldsymbol{\sigma} \right) \left(m_i \mathbf{v} + m_j \mathbf{v}_j + m_j \sqrt{\frac{2R\mathcal{E}}{\mu_{ij}}} \boldsymbol{\sigma} \right) \\ &= \left(\frac{1}{m_i + m_j} \right)^2 \left[m_i \mathbf{v} \left(m_i \mathbf{v} + m_j \mathbf{v}_j + m_j \sqrt{\frac{2R\mathcal{E}}{\mu_{ij}}} \boldsymbol{\sigma} \right) + m_j \mathbf{v}_j \left(m_i \mathbf{v} + m_j \mathbf{v}_j + m_j \sqrt{\frac{2R\mathcal{E}}{\mu_{ij}}} \boldsymbol{\sigma} \right) \right. \\ & \quad \left. + m_j \sqrt{\frac{2R\mathcal{E}}{\mu_{ij}}} \boldsymbol{\sigma} \left(m_i \mathbf{v} + m_j \mathbf{v}_j + m_j \sqrt{\frac{2R\mathcal{E}}{\mu_{ij}}} \boldsymbol{\sigma} \right) \right] \\ &= \left(\frac{1}{m_i + m_j} \right)^2 \left((m_i \mathbf{v})^2 + m_i m_j (\mathbf{v} \cdot \mathbf{v}_j) + m_i m_j \sqrt{\frac{2R\mathcal{E}}{\mu_{ij}}} (\mathbf{v} \cdot \boldsymbol{\sigma}) + m_i m_j (\mathbf{v} \cdot \mathbf{v}_j) + (m_j \mathbf{v}_j)^2 \right. \\ & \quad \left. + m_j^2 \sqrt{\frac{2R\mathcal{E}}{\mu_{ij}}} (\mathbf{v}_j \cdot \boldsymbol{\sigma}) + m_i m_j \sqrt{\frac{2R\mathcal{E}}{\mu_{ij}}} (\mathbf{v} \cdot \boldsymbol{\sigma}) + m_j^2 \sqrt{\frac{2R\mathcal{E}}{\mu_{ij}}} (\mathbf{v}_j \cdot \boldsymbol{\sigma}) + m_j^2 \frac{2R\mathcal{E}}{\mu_{ij}} \right) \\ &= \left(\frac{1}{m_i + m_j} \right)^2 \left((m_i \mathbf{v})^2 + 2m_i m_j (\mathbf{v} \cdot \mathbf{v}_j) + 2m_i m_j \sqrt{\frac{2R\mathcal{E}}{\mu_{ij}}} (\mathbf{v} \cdot \boldsymbol{\sigma}) + (m_j \mathbf{v}_j)^2 \right. \\ & \quad \left. + 2m_j^2 \sqrt{\frac{2R\mathcal{E}}{\mu_{ij}}} (\mathbf{v}_j \cdot \boldsymbol{\sigma}) + m_j^2 \frac{2R\mathcal{E}}{\mu_{ij}} \right), \end{aligned}$$

where the fact that $\boldsymbol{\sigma} \cdot \boldsymbol{\sigma} = 1$ have been used.

Therefore,

$$\frac{m_i(\mathbf{v}_i')^2}{2} - \frac{m_i(\mathbf{v})^2}{2} + I_i' - I$$

$$\begin{aligned}
&= \frac{m_i}{2} \left(\frac{1}{m_i + m_j} \right)^2 \left((m_i \mathbf{v})^2 + 2m_i m_j (\mathbf{v} \cdot \mathbf{v}_j) + 2m_i m_j \sqrt{\frac{2R\mathcal{E}}{\mu_{ij}}} (\mathbf{v} \cdot \boldsymbol{\sigma}) + (m_j \mathbf{v}_j)^2 \right. \\
&\quad \left. + 2m_j^2 \sqrt{\frac{2R\mathcal{E}}{\mu_{ij}}} (\mathbf{v}_j \cdot \boldsymbol{\sigma}) + m_j^2 \frac{2R\mathcal{E}}{\mu_{ij}} \right) - \frac{m_i (\mathbf{v})^2}{2} + I'_i - I \\
&= \frac{m_i^3 (\mathbf{v})^2}{2(m_i + m_j)^2} + \frac{m_i \mu_{ij} (\mathbf{v} \cdot \mathbf{v}_j)}{m_i + m_j} + \frac{m_i \mu_{ij}}{m_i + m_j} \sqrt{\frac{2R\mathcal{E}}{\mu_{ij}}} (\mathbf{v} \cdot \boldsymbol{\sigma}) + \frac{m_j \mu_{ij} (\mathbf{v}_j)^2}{2(m_i + m_j)} \\
&\quad + \frac{m_j \mu_{ij}}{m_i + m_j} \sqrt{\frac{2R\mathcal{E}}{\mu_{ij}}} (\mathbf{v}_j \cdot \boldsymbol{\sigma}) + \frac{m_j R\mathcal{E}}{m_i + m_j} - \frac{m_i (\mathbf{v})^2}{2} + I'_i - I \\
&= \left(\frac{m_i^3}{2(m_i + m_j)^2} - \frac{m_i}{2} \right) (\mathbf{v})^2 + \frac{m_j \mu_{ij} (\mathbf{v}_j)^2}{2(m_i + m_j)} + \frac{m_i \mu_{ij} (\mathbf{v} \cdot \mathbf{v}_j)}{m_i + m_j} \\
&\quad + \frac{m_i \mu_{ij} (\mathbf{v} \cdot \boldsymbol{\sigma}) (2R\mathcal{E})^{\frac{1}{2}}}{m_i + m_j} + \frac{m_j \mu_{ij} (\mathbf{v}_j \cdot \boldsymbol{\sigma}) (2R\mathcal{E})^{\frac{1}{2}}}{m_i + m_j} + \frac{m_j R\mathcal{E}}{m_i + m_j} + I'_i - I.
\end{aligned}$$

Substituting the last equality of the previous equation into equation (C.2.1) and then expand the resulting equation to obtain:

$$\begin{aligned}
&\sum_{\substack{j=1 \\ j \neq i}}^4 \frac{T_i^\varepsilon - T_j^\varepsilon}{k_B T^2} \left(\frac{m_i^3}{2(m_i + m_j)^2} - \frac{m_i}{2} \right) \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_0^{+\infty} \int_0^{+\infty} \int_0^1 \int_0^1 \int_{\mathbb{S}^2} \mathbf{v} (\mathbf{v})^2 M_i^\varepsilon M_j^\varepsilon \widehat{V}^{*\gamma-1} \\
&\quad \times 2 \Phi_{ij}(I, I_j, R, r) b_{ij}(\cos \theta) \cos \theta (1 - R) d\boldsymbol{\sigma} dr dR dI_j dI d\mathbf{v}_j d\mathbf{v} \\
&+ \sum_{\substack{j=1 \\ j \neq i}}^4 \frac{T_i^\varepsilon - T_j^\varepsilon}{k_B T^2} \frac{m_j \mu_{ij}}{2(m_i + m_j)} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_0^{+\infty} \int_0^{+\infty} \int_0^1 \int_0^1 \int_{\mathbb{S}^2} \mathbf{v} (\mathbf{v}_j)^2 M_i^\varepsilon M_j^\varepsilon \widehat{V}^{*\gamma-1} \\
&\quad \times 2 \Phi_{ij}(I, I_j, R, r) b_{ij}(\cos \theta) \cos \theta (1 - R) d\boldsymbol{\sigma} dr dR dI_j dI d\mathbf{v}_j d\mathbf{v} \\
&+ \sum_{\substack{j=1 \\ j \neq i}}^4 \frac{T_i^\varepsilon - T_j^\varepsilon}{k_B T^2} \frac{m_i \mu_{ij}}{m_i + m_j} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_0^{+\infty} \int_0^{+\infty} \int_0^1 \int_0^1 \int_{\mathbb{S}^2} \mathbf{v} (\mathbf{v} \cdot \mathbf{v}_j) M_i^\varepsilon M_j^\varepsilon \widehat{V}^{*\gamma-1} \\
&\quad \times 2 \Phi_{ij}(I, I_j, R, r) b_{ij}(\cos \theta) \cos \theta (1 - R) d\boldsymbol{\sigma} dr dR dI_j dI d\mathbf{v}_j d\mathbf{v} \\
&+ \sum_{\substack{j=1 \\ j \neq i}}^4 \frac{T_i^\varepsilon - T_j^\varepsilon}{k_B T^2} \frac{m_i \mu_{ij}}{m_i + m_j} \left(\frac{2R\mathcal{E}}{\mu_{ij}} \right)^{\frac{1}{2}} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_0^{+\infty} \int_0^{+\infty} \int_0^1 \int_0^1 \int_{\mathbb{S}^2} \mathbf{v} (\mathbf{v} \cdot \boldsymbol{\sigma}) M_i^\varepsilon M_j^\varepsilon \widehat{V}^{*\gamma-1} \\
&\quad \times 2 \Phi_{ij}(I, I_j, R, r) b_{ij}(\cos \theta) \cos \theta (1 - R) d\boldsymbol{\sigma} dr dR dI_j dI d\mathbf{v}_j d\mathbf{v} \\
&+ \sum_{\substack{j=1 \\ j \neq i}}^4 \frac{T_i^\varepsilon - T_j^\varepsilon}{k_B T^2} \frac{m_j \mu_{ij}}{m_i + m_j} \left(\frac{2R\mathcal{E}}{\mu_{ij}} \right)^{\frac{1}{2}} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_0^{+\infty} \int_0^{+\infty} \int_0^1 \int_0^1 \int_{\mathbb{S}^2} \mathbf{v} (\mathbf{v}_j \cdot \boldsymbol{\sigma}) M_i^\varepsilon M_j^\varepsilon \widehat{V}^{*\gamma-1} \\
&\quad \times 2 \Phi_{ij}(I, I_j, R, r) b_{ij}(\cos \theta) \cos \theta (1 - R) d\boldsymbol{\sigma} dr dR dI_j dI d\mathbf{v}_j d\mathbf{v} \\
&+ \sum_{\substack{j=1 \\ j \neq i}}^4 \frac{T_i^\varepsilon - T_j^\varepsilon}{k_B T^2} \frac{m_j R\mathcal{E}}{m_i + m_j} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_0^{+\infty} \int_0^{+\infty} \int_0^1 \int_0^1 \int_{\mathbb{S}^2} \mathbf{v} M_i^\varepsilon M_j^\varepsilon \widehat{V}^{*\gamma-1} \\
&\quad \times 2 \Phi_{ij}(I, I_j, R, r) b_{ij}(\cos \theta) \cos \theta (1 - R) d\boldsymbol{\sigma} dr dR dI_j dI d\mathbf{v}_j d\mathbf{v}
\end{aligned}$$

$$\begin{aligned}
& + \sum_{\substack{j=1 \\ j \neq i}}^4 \frac{T_i^\varepsilon - T_j^\varepsilon}{k_B T^2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_0^{+\infty} \int_0^{+\infty} \int_0^1 \int_0^1 \int_{\mathbb{S}^2} \mathbf{v} I_i' M_i^\varepsilon M_j^\varepsilon \widehat{V}^{*\gamma-1} \\
& \quad \times 2 \Phi_{ij}(I, I_j, R, r) b_{ij}(\cos \theta) \cos \theta (1 - R) d\boldsymbol{\sigma} dr dR dI_j dI d\mathbf{v}_j d\mathbf{v} \\
& - \sum_{\substack{j=1 \\ j \neq i}}^4 \frac{T_i^\varepsilon - T_j^\varepsilon}{k_B T^2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_0^{+\infty} \int_0^{+\infty} \int_0^1 \int_0^1 \int_{\mathbb{S}^2} \mathbf{v} I M_i^\varepsilon M_j^\varepsilon \widehat{V}^{*\gamma-1} \\
& \quad \times 2 \Phi_{ij}(I, I_j, R, r) b_{ij}(\cos \theta) \cos \theta (1 - R) d\boldsymbol{\sigma} dr dR dI_j dI d\mathbf{v}_j d\mathbf{v}.
\end{aligned}$$

Transforming the integrals in $(\mathbf{v}, \mathbf{v}_j)$ above to the centre of mass velocity and relative velocity, and then evaluate the resulting integrals using the same strategy as those used in the computation of the integral given in equation (6.3.64), one obtains that the six fold integrals in $\mathbf{v}$ and $\mathbf{v}_j$ vanish in the first, second, third, sixth, seventh and eighth terms of the previous equation. Furthermore, using equation (C.1.1), the fourth and fifth terms of the previous equation also vanish.

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