ON THE MAXWELL-STEFAN DIFFUSION LIMIT FOR A REACTIVE MIXTURE OF POLYATOMIC GASES IN NON-ISOTHERMAL SETTING

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(Communicated by Alexander V. Bobylev)

Abstract. In this article we deduce a mathematical model of Maxwell-Stefan type for a reactive mixture of polyatomic gases with a continuous structure of internal energy. The equations of the model are derived in the diffusive limit of a kinetic system of Boltzmann equations for the considered mixture, in the general non-isothermal setting. The asymptotic analysis of the kinetic system is performed under a reactive-diffusive scaling for which mechanical collisions are dominant with respect to chemical reactions. The resulting system couples the Maxwell-Stefan equations for the diffusive fluxes with the evolution equations for the number densities of the chemical species and the evolution equation for the temperature of the mixture. The production terms due to the chemical reaction and the Maxwell-Stefan diffusion coefficients are moreover obtained in terms of general collision kernels and parameters of the kinetic model.

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 behavior of the species is well described by the equations

2010 Mathematics Subject Classification. Primary: 82C40, 35K57, 76R50; Secondary: 76P05, 80A30.

Key words and phrases. Maxwell-Stefan system, reaction-diffusion equations, kinetic theory, Boltzmann equation, polyatomic gas mixtures, chemical reactions, diffusive limit.

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introduced by Maxwell and Stefan in [30, 37], which provide a more general and appropriate framework than the standard Fickian approach [19, 20].

Despite the popularity of Maxwell-Stefan model and its irreplaceability for many applications in chemical engineering [29, 38], the mathematical properties of the Maxwell-Stefan 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 [22] and the references therein). Subsequently, the well-posedness and the long-time behavior of the solutions of the Maxwell-Stefan system (or some variants) have been studied in [10, 13, 16, 24, 27, 28], the numerical simulation of the Maxwell-Stefan system has been the subject of [8, 13, 21, 31], and the relationships between Fickian diffusion and the Maxwell-Stefan model have been analyzed in [11, 36]. 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 Boltzmann equation [2, 3] – several articles have carried out the formal derivation of isothermal multicomponent Maxwell-Stefan type diffusion equations starting from the Boltzmann system for monatomic non-reactive gaseous mixtures [11, 12, 14, 26]. The diffusive limit in a reactive mixture described by the simple reacting sphere kinetic model (SRS), 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 [1].

However, if we consider 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 behavior 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 the present article.

Our approach consists in obtaining the macroscopic equations starting from a kinetic system of equations defined in the phase-space, under a reactive-diffusive scaling. We treat the effects of the binary interactions between particles as a simple scattering event involving, at the microscopic scale, only some fundamental laws (in particular, the conservation of momentum and of the 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 [7, 15, 17], whereas various kinetic models for polyatomic reactive mixtures have been derived in [5, 6, 18, 23].

The polyatomic structure of particles may be modeled 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 [22], while the state of art of kinetic and Extended Thermodynamics approaches with a continuous energy have been summarized in [35].
In this article we consider, as starting point, the kinetic system proposed in [18], based on the Borgnakke-Larsen procedure [9], because of its main features and advantages detailed in [18]. The model introduced in [18] describes indeed a mixture of reactive polyatomic gases by adding to the usual independent variables of the phase-space of the system (time \(t\), position \(x\) and velocity \(v\)) 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 \(\varphi(I)dI\), 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 our article, for the sake of clarity, we limit our study to a quaternary mixture of polyatomic gases in the presence of a reversible chemical reaction of bimolecular type. This framework allows us to work in the general non-isothermal setting. Furthermore, we consider some assumptions at the kinetic level that allow us to derive the non-isothermal reaction-diffusion system of Maxwell-Stefan type as limit equations of the considered kinetic model. More specifically, we 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 centered 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 Maxwell-Stefan equations for the diffusive fluxes and the evolution equation for the temperature of the mixture. Of course, generalizations to more complicated mixtures with different type of chemical reactions are possible by considering appropriate kinetic models and introducing suitable modifications in the computations of chemical production rates. With respect to the standard isothermal non-reactive Maxwell-Stefan system, the equations obtained in this article 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 \(E\). We need moreover to take into account the energy balance due to the effects of the chemical reactions.

We highlight that the target equations derived in this article are, up to the best of our 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 the article is the following. After introducing, in Section 2, the model governing the reactive mixture of polyatomic gases proposed in [18] and its main properties (conservation laws, equilibrium states, chemical rates and H-theorem), we consider in Section 3 the scaled system in the reactive-diffusive regime and the assumptions needed in our derivation. Finally, the limiting diffusive equations for the reactive mixture are deduced in Section 4. The conclusion, in Section 5, which summarizes our results, is followed by an appendix which gathers some technical computations that are necessary for deducing the results of Section 4.
2. The model for a reactive mixture of polyatomic gases. In this section we briefly present the kinetic model proposed in [18] for a quaternary reactive mixture of polyatomic gases with a continuous structure of internal energy. We restrict our presentation to the kinetic equations, the central aspects of the collisional dynamics, conservation laws, equilibrium states and $\mathcal{H}$-theorem.

Following [18], we consider a quaternary mixture of species $A_1, A_2, A_3$ and $A_4$, participating in the reversible chemical reaction of type

$$A_1 + A_2 \rightleftharpoons A_3 + A_4. \quad (1)$$

For each species $A_i$, with $i = 1, 2, 3, 4$, we introduce its distribution function $f_i$ which depends on time $t \in \mathbb{R}^+$, position $x \in \mathbb{R}^3$, velocity $v \in \mathbb{R}^3$ and on the internal energy variable $I \in [0, +\infty[$. For sake of simplicity, in many cases we omit the dependence of each $f_i$ on $t$ and $x$, and write $f_i(v, I)$. Sometimes we simply write $f_i$.

We denote the molecular mass of each species by $m_i$ and the chemical binding energy by $E_i$. Furthermore, we introduce a weight $\varphi_i(I)$, which aims at obtaining the energy law of polyatomic gases and the mass action law of chemical kinetics. With reference to the chemical reaction (1), the conservation of mass requires that

$$m_1 + m_2 = m_3 + m_4 = M, \quad (2)$$

and the balance of binding energies is specified by the reaction heat

$$E = E_3 + E_4 - E_1 - E_2, \quad (3)$$

such that $E > 0$ means that the forward reaction $A_1 + A_2 \to A_3 + A_4$ is endothermic whereas $E < 0$ indicates that it is exothermic.

An important aspect of the present description is that the moments of the distribution function $f_i(t, x, v, I)$ are defined in $L^1(\varphi_i(I) dI dv)$. In particular, the number density $n_i$, mass density $\varrho_i$, mean velocity $u_i$ and temperature $T_i$ of each species are respectively given by

$$n_i(t, x) = \int_{\mathbb{R}^3} \int_0^{+\infty} f_i(t, x, v, I) \varphi_i(I) \, dI \, dv, \quad (4)$$

$$\varrho_i(t, x) = m_i n_i(t, x), \quad (5)$$

$$u_i(t, x) = \frac{1}{n_i(t, x)} \int_{\mathbb{R}^3} \int_0^{+\infty} v f_i(t, x, v, I) \varphi_i(I) \, dI \, dv, \quad (6)$$

$$T_i(t, x) = \frac{1}{3 k_B n_i(t, x)} \int_{\mathbb{R}^3} \int_0^{+\infty} m_i |v - u_i(t, x)|^2 f_i(t, x, v, I) \varphi_i(I) \, dI \, dv. \quad (7)$$

2.1. Collisions and Borgnakke-Larsen procedure. The particles of the mixture undergo binary collisions, either of elastic or reactive type. Elastic collisions can occur among particles of the same constituent (mono-species elastic collisions) as well as among particles of different constituents (bi-species elastic collisions). The mono-species and bi-species elastic collisions result in changes in velocities and internal energies 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 particles before the collision by $v_i$, $v_j$ and $I_i$, $I_j$ respectively, and their corresponding post-collisional values by $v_i'$, $v_j'$ and $I_i'$, $I_j'$, the conservation laws of momentum and total energy for elastic collisions are given by

$$m_i v_i + m_j v_j = m_i v_i' + m_j v_j', \quad (8)$$

$$E_i + E_j = E_i' + E_j'. \quad (9)$$
\[ \frac{1}{2} m_i |v_i|^2 + I_i + \frac{1}{2} m_j |v_j|^2 + I_j = \frac{1}{2} m_i |v_i'|^2 + I'_i + \frac{1}{2} m_j |v_j'|^2 + I'_j. \]  

(9)

In particular, \( i \neq j \) for bi-species collisions and \( i = j \) for mono-species collisions. In the latter case, we use the indices \( i \) and \( i_* \) to distinguish the velocities and internal energies of the two colliding particles.

On the other hand, reactive collisions occur among particles of constituents \( A_1, A_2 \) or \( A_3, A_4 \) and follow the reaction law (1). These reactive collisions result not just in changes in velocities and internal energies but also result in a 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 chemical reactions respectively, the conservation laws of momentum and total energy (kinetic and internal energies as well as chemical binding energy) for reactive collisions are given by

\[ m_i v_i + m_j v_j = m_k v_k' + m_l v_l'. \]  

(10)

\[ \frac{1}{2} m_i |v_i|^2 + I_i + E_i + \frac{1}{2} m_j |v_j|^2 + I_j + E_j = \frac{1}{2} m_k |v_k'|^2 + I'_k + E_k + \frac{1}{2} m_l |v_l'|^2 + I'_l + E_l. \]  

(11)

Equation (11) can be written in an equivalent form as

\[ \frac{1}{2} m_i |v_i|^2 + I_i + \frac{1}{2} m_j |v_j|^2 + I_j - \frac{E}{2} = \frac{1}{2} m_k |v_k'|^2 + I'_k + \frac{1}{2} m_l |v_l'|^2 + I'_l + \frac{E}{2}, \]  

(11a)

where \( E \) has been defined in (3).

As usual in kinetic theory, the post-collisional velocities can be expressed in terms of pre-collisional velocities and the corresponding expressions for both elastic and reactive post-collisional velocities are derived from the conservation laws (8),(9) and (10),(11) respectively. In order to give these expressions for the post-collisional velocities, we start by describing the Borngakke-Larsen procedure [9]. Such procedure is based on the repartition of the total energy of the colliding pair into kinetic and internal energies, when the collisions are of elastic type, or into kinetic, internal and chemical binding energies, when the collisions are of reactive type. Let us consider first elastic collisions and compute the total energy \( E \) of the colliding pair. In the centre of mass reference frame, due to the conservation laws (8) and (9), we have that

\[ E = \frac{1}{2} \mu_{ij} |v_i - v_j|^2 + I_i + I_j = \frac{1}{2} \mu_{ij} |v_i' - v_j'|^2 + I'_i + I'_j, \]  

(12)

where \( \mu_{ij} = m_i m_j / (m_i + m_j) \) is the reduced mass of the colliding pair, \( v_i - v_j \) and \( v_i' - v_j' \) are the relative velocities before and after the collision. 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, that is

\[ \frac{1}{2} \mu_{ij} |v_i' - v_j'|^2 = R \mathcal{E} \quad \text{and} \quad I'_i + I'_j = (1 - R) \mathcal{E}. \]  

(13)
The first equation of (13) can be parametrized by a unit vector \( \omega \in S^2 \) to obtain

\[
v'_i - v'_j = \sqrt{\frac{2R E}{\mu_{ij}}} T_\omega \left[ \frac{v_i - v_j}{|v_i - v_j|} \right],
\]

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

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

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

As a consequence of the Borgnakke-Larsen procedure [18], using the conservation law (8) together with (14), we can express the elastic post-collisional velocities in terms of pre-collisional velocities as given below

\[
v'_i = \frac{m_i v_i + m_j v_j}{m_i + m_j} + \frac{m_j}{m_i + m_j} \sqrt{\frac{2R E}{\mu_{ij}}} T_\omega \left[ \frac{v_i - v_j}{|v_i - v_j|} \right],
\]

\[
v'_j = \frac{m_i v_i + m_j v_j}{m_i + m_j} - \frac{m_i}{m_i + m_j} \sqrt{\frac{2R E}{\mu_{ij}}} T_\omega \left[ \frac{v_i - v_j}{|v_i - v_j|} \right].
\]

In the particular case of mono-species elastic collisions, the post-collisional velocities are given by

\[
v'_i = \frac{v_i + v_{i*}}{2} + \sqrt{\frac{R E}{m_i}} T_\omega \left[ \frac{v_i - v_{i*}}{|v_i - v_{i*}|} \right],
\]

\[
v'_i^* = \frac{v_i + v_{i*}}{2} - \sqrt{\frac{R E}{m_i}} T_\omega \left[ \frac{v_i - v_{i*}}{|v_i - v_{i*}|} \right].
\]

Concerning now reactive collisions associated to the forward chemical reaction, we denote by \( E^* \) the total energy of the colliding pair. In the centre of mass reference frame, due to the conservation laws (10) and (11a), we have that

\[
E^* = \frac{1}{2} \mu_{12} |v_1 - v_2|^2 + I_1 + I_2 - \frac{E}{2} = \frac{1}{2} \mu_{34} |v'_3 - v'_4|^2 + I'_3 + I'_4 + \frac{E}{2},
\]

Introducing the parameters \( R, r \in [0,1] \) and assuming the following repartition of the total energy into kinetic and internal energies of the outgoing particles, namely

\[
\frac{1}{2} \mu_{34} |v'_3 - v'_4|^2 = RE^* - \frac{E}{6}, \quad I'_3 + I'_4 = (1-R)E^* - \frac{E}{3},
\]

with

\[
I'_3 = r(1-R)E^* - \frac{E}{6}, \quad I'_4 = (1-r)(1-R)E^* - \frac{E}{6}
\]

we obtain that the first equation of (19) can be parameterized by a unit vector \( \omega \in S^2 \) as given below

\[
v'_5 - v'_4 = \sqrt{\frac{2}{\mu_{34}}} \left( RE^* - \frac{E}{6} \right)^{1/2} T_\omega \left[ \frac{v_1 - v_2}{|v_1 - v_2|} \right].
\]
Using (21) together with the conservation law (10), we can express the reactive post-collisional velocities for the forward reaction in terms of pre-collisional velocities as given below

\[ v_3' = \frac{m_1 v_1 + m_2 v_2}{m_1 + m_2} + \frac{m_4}{m_3 + m_4} \sqrt{\frac{2}{\mu_{34}}} \left( R \mathcal{E}^* - \frac{E}{6} \right)^{1/2} T_\omega \left[ \frac{v_1 - v_2}{|v_1 - v_2|} \right], \]

\[ v_4' = \frac{m_1 v_1 + m_2 v_2}{m_1 + m_2} - \frac{m_3}{m_3 + m_4} \sqrt{\frac{2}{\mu_{34}}} \left( R \mathcal{E}^* - \frac{E}{6} \right)^{1/2} T_\omega \left[ \frac{v_1 - v_2}{|v_1 - v_2|} \right]. \]  

(22)

Analogously, for reactive collisions associated to the backward chemical reaction, we write the conservation law of total energy in the centre of mass reference frame in the form

\[ \mathcal{E}^* = \frac{1}{2} \mu_{34} |v_3 - v_4|^2 + I_3 + I_4 + \frac{E}{2} = \frac{1}{2} \mu_{12} |v_1 - v_2|^2 + I'_1 + I'_2 - \frac{E}{2}, \]  

(23)

Then, as before, we assume the following repartition of the total energy into kinetic and internal energies of the outgoing particles, namely

\[ \frac{1}{2} \mu_{12} |v_1' - v_2'|^2 = R \mathcal{E}^* + \frac{E}{6}, \quad I'_1 + I'_2 = (1 - R) \mathcal{E}^* + \frac{E}{3}, \]  

(24)

with

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

(25)

The first equation of (24) can be parameterized by a unit vector \( \omega \in \mathbb{S}^2 \) as given below

\[ v_1' - v_2' = \sqrt{\frac{2}{\mu_{12}}} \left( R \mathcal{E}^* + \frac{E}{6} \right)^{1/2} T_\omega \left[ \frac{v_3 - v_4}{|v_3 - v_4|} \right]. \]  

(26)

Using (26) together with the conservation law (10), we can express the reactive post-collisional velocities for the backward reaction in terms of pre-collisional velocities as given below

\[ v_1' = \frac{m_3 v_3 + m_4 v_4}{m_3 + m_4} + \frac{m_2}{m_1 + m_2} \sqrt{\frac{2}{\mu_{12}}} \left( R \mathcal{E}^* + \frac{E}{6} \right)^{1/2} T_\omega \left[ \frac{v_3 - v_4}{|v_3 - v_4|} \right], \]

\[ v_2' = \frac{m_3 v_3 + m_4 v_4}{m_3 + m_4} - \frac{m_1}{m_1 + m_2} \sqrt{\frac{2}{\mu_{12}}} \left( R \mathcal{E}^* + \frac{E}{6} \right)^{1/2} T_\omega \left[ \frac{v_3 - v_4}{|v_3 - v_4|} \right]. \]  

(27)

For other details on the collisional dynamics, the reader is referred to \cite{18}.

### 2.2. Kinetic equations.

The time-space evolution of the distribution functions \( f_i(v, I) \), with \( i = 1, \ldots, 4 \), is specified by the system of kinetic equations

\[ \frac{\partial f_i}{\partial t} + v \cdot \nabla_x f_i = \sum_{j=1}^{4} Q_{ij}^e(f_i, f_j) + Q_{ij}^{\text{react}}, \quad i = 1, \ldots, 4. \]  

(28)

Above, when \( i \neq j \), the notation \( Q_{ij}^e \) represents the bi-species elastic collisional operator associated to collisions between one particle of constituent \( i \) and another one of constituent \( j \), whereas when \( i = j \), it reduces to the mono-species elastic collisional operator \( Q_{ii}^e \). Moreover, \( Q_{ij}^{\text{react}} \) represents the reactive collisional operator. The operators \( Q_{ij}^e \) and \( Q_{ij}^{\text{react}} \) are defined as follows. For bi-species non-reactive interactions (i.e. \( i \neq j \)), the operators take the form

\[ Q_{ij}^e(f_i, f_j) = \int_{\mathbb{R}^3} \int_{0}^{+\infty} \int_{0}^{1} \int_{\mathbb{S}^2} [f_i(v'_i, I'_i) f_j(v'_j, I'_j) - f_i(v, I) f_j(v, I)] \]  

(29)
and let $B_{ij}$ are suitable cross sections and $\nu'_i$, $\nu'_j$, $I'_i$ and $I'_j$ are given by

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

In the case of mono-species elastic collisions, the operators have the following structure

$$
Q^*_{ii}(f_i, f_i) = \int_{\mathbb{R}^3} \int_0^{+\infty} \int_{0}^{1} \int_{S^2} \int_{0}^{1} \int_{\mathbb{R}^3} \left[ f_i(v'_i, I'_i) f_i(v'_{i^*}, I'_{i^*}) - f_i(v, I) f_i(v_{i^*}, I_{i^*}) \right] \\
\times B_{ii}(v, v_{i^*}, I, I_{i^*}, R, r, \omega)(1 - R) |v - v_{i^*}|^{-1} \\
\times \varphi_i(I)^{-1} d\omega dr dR dI_{i^*} dv_{i^*},
$$

where $B_{ii}$ are suitable cross sections and $\nu'_i$, $\nu'_{i^*}$, $I'_i$ and $I'_{i^*}$ are given by

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

The reactive collisional operators are defined in a more involved way. Consider for some suitable sets $F_i$ the Heaviside-like function

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

and let $B^{\text{react}} : \mathbb{R}^3 \times \mathbb{R}^3 \times \mathbb{R}^+ \times \mathbb{R}^+ \times [0, 1]^2 \times S^2 \to \mathbb{R}^+$ be a suitable cross-section. We first treat the case of the forward reaction. To do this, we define the total energy

$$
E^*_1 = \frac{1}{2} \mu_{12} |v - v_2|^2 + I + I_2 - \frac{E}{2},
$$
the reactive post-collisional velocities and internal energies

\[
v_3' = \frac{m_1 v + m_2 v_2}{m_1 + m_2} + \frac{m_4}{m_3 + m_4} \sqrt{\frac{2}{\mu_{34}}} \left( R\varepsilon_1^* - \frac{E}{6} \right)^{1/2} T_\omega \left[ \frac{v - v_2}{|v - v_2|} \right],
\]

\[
v_4' = \frac{m_1 v + m_2 v_2}{m_1 + m_2} - \frac{m_3}{m_3 + m_4} \sqrt{\frac{2}{\mu_{34}}} \left( R\varepsilon_1^* - \frac{E}{6} \right)^{1/2} T_\omega \left[ \frac{v - v_2}{|v - v_2|} \right],
\]

\[
I_3' = r(1 - R)\varepsilon_1^* - \frac{E}{6},
\]

\[
I_4' = (1 - r)(1 - R)\varepsilon_1^* - \frac{E}{6},
\]
as well as the admissible set

\[
F_1 = \left\{ (I, I_2, r, R, v, v_2) : I \geq \frac{E}{6}, I_2 \geq \frac{E}{6}, R\varepsilon_1^* \geq \frac{E}{6}, \frac{\mu_{12}}{2} |v - v_2|^2 \geq \frac{E}{6}, (1 - R)r\varepsilon_1^* \geq \frac{E}{6}, (1 - R)(1 - r)\varepsilon_1^* \geq \frac{E}{6} \right\}.
\]

The first collisional integral describing the forward chemical reaction is hence

\[
Q_1^{\text{react}}(v, I) = \int_{R^3} \int_0^{\infty} \int_0^1 \int_0^1 \int_{S^2} \left( \frac{m_1 m_2}{m_3 m_4} \right)^3 f_3(v_3', I_3') f_4(v_4', I_4')
\]

\[
- f_1(v, I) f_2(v_2, I_2) H_1(I, I_2, r, R, v, v_2) B^{\text{react}}(v, v_2, I, I_2, R, r, \omega)
\]

\[
\times (m_1 m_2)^{-2} |v - v_2|^{-1} (1 - R)\varphi_1(I)^{-1} d\omega dr dR dI_2 dv_2.
\]

The structure of \( Q_2^{\text{react}} \) is similar. We define the total energy

\[
\varepsilon_2^* = \frac{1}{2} \mu_{12} |v - v_1|^2 + I + I_1 - \frac{E}{2},
\]

the reactive post-collisional velocities and internal energies

\[
v_3' = \frac{m_1 v_1 + m_2 v}{m_1 + m_2} + \frac{m_4}{m_3 + m_4} \sqrt{\frac{2}{\mu_{34}}} \left( R\varepsilon_2^* - \frac{E}{6} \right)^{1/2} T_\omega \left[ \frac{v_1 - v}{|v_1 - v|} \right],
\]

\[
v_4' = \frac{m_1 v_1 + m_2 v}{m_1 + m_2} - \frac{m_3}{m_3 + m_4} \sqrt{\frac{2}{\mu_{34}}} \left( R\varepsilon_2^* - \frac{E}{6} \right)^{1/2} T_\omega \left[ \frac{v_1 - v}{|v_1 - v|} \right],
\]

\[
I_3' = r(1 - R)\varepsilon_2^* - \frac{E}{6},
\]

\[
I_4' = (1 - r)(1 - R)\varepsilon_2^* - \frac{E}{6},
\]
as well as the admissible set

\[
F_2 = \left\{ (I, I_1, r, R, v, v_1) : I \geq \frac{E}{6}, I_1 \geq \frac{E}{6}, R\varepsilon_2^* \geq \frac{E}{6}, \frac{\mu_{12}}{2} |v - v_1|^2 \geq \frac{E}{6}, (1 - R)r\varepsilon_2^* \geq \frac{E}{6}, (1 - R)(1 - r)\varepsilon_2^* \geq \frac{E}{6} \right\}.
\]
The admissible set 

\[ F \]

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

\[ \text{The collisional integral} \quad Q^\text{react}_2(\bm{v}, I) = \int_{\mathbb{R}^3} \int_0^{+\infty} \int_0^1 \int_{S^2} \\left[ \left( \frac{m_1 m_2}{m_3 m_4} \right)^3 f_3(v_3', I_3') f_4(v_4', I_4') - f_2(\bm{v}, I) f_1(v_1, I_1) \right] H_2(I, I_1, r, R, \bm{v}, \bm{v}_1) B^\text{react}(\bm{v}, \bm{v}_1, I, I_1, R, r, \omega) (32) \]

\[ \times (m_1 m_2)^{-2} |\bm{v} - \bm{v}_1|^{-1} (1 - R) \varphi_2(I)^{-1} \, d\omega \, dr \, dR \, dI_1 \, dv_1. \]

In the case of the backward reaction, we have to treat two cases. Let

\[ \mathcal{E}_3^* = \frac{1}{2} \mu_{34} |\bm{v} - \bm{v}_4|^2 + I + I_4 + \frac{E}{2} \]

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

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

The admissible set \( F_3 \) is

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

and hence the reactive collisional integral \( Q^\text{react}_3(\bm{v}, I) \) describing the backward reaction is defined by

\[ Q^\text{react}_3(\bm{v}, I) = \int_{\mathbb{R}^3} \int_0^{+\infty} \int_0^1 \int_{S^2} \left[ \left( \frac{m_3 m_4}{m_1 m_2} \right)^3 f_3(v_3', I_3') f_4(v_4', I_4') - f_1(\bm{v}, I) f_2(v_1, I_1) \right] H_3(I_4, r, R, \bm{v}_4) B^\text{react}(\bm{v}, \bm{v}_4, I, I_4, R, r, \omega) (33) \]

\[ \times (m_3 m_4)^{-2} |\bm{v} - \bm{v}_4|^{-1} (1 - R) \varphi_3(I)^{-1} \, d\omega \, dr \, dR \, dI_4 \, dv_4. \]

We conclude the description of the reactive collisional operators by defining \( Q^\text{react}_4 \).

Let

\[ \mathcal{E}_4^* = \frac{1}{2} \mu_{34} |\bm{v} - \bm{v}_3|^2 + I + I_3 + \frac{E}{2} \]
be the total energy. Then, as before, we write the reactive post collisional velocities and internal energies, respectively as given below

\[ v'_1 = \frac{m_3 v_3 + m_4 v}{m_3 + m_4} + \frac{m_2}{m_1 + m_2} \sqrt{\frac{2}{\mu_{12}} \left( R E_4^* + \frac{E}{6} \right)^{1/2}} T_\omega \frac{v_3 - v}{|v_3 - v|}, \]

\[ v'_2 = \frac{m_3 v_3 + m_4 v}{m_3 + m_4} - \frac{m_1}{m_1 + m_2} \sqrt{\frac{2}{\mu_{12}} \left( R E_4^* + \frac{E}{6} \right)^{1/2}} T_\omega \frac{v_3 - v}{|v_3 - v|}. \]

\[ I'_1 = r(1 - R) E_4^* + \frac{E}{6}, \]

\[ I'_2 = (1 - r)(1 - R) E_4^* + \frac{E}{6}. \]

The admissible set \( F_1 \) is

\[ F_1 = \{ (I_3, r, R, v_3) : I_3 \geq 0, \ v_3 \in \mathbb{R}^3, \ r, R \in [0, 1] \}, \]

and hence the reactive collisional integral \( Q^\text{react}_4 \) describing the backward reaction is defined by

\[
Q_4^\text{react}(v, I) = \int_{\mathbb{R}^3} \int_0^{+\infty} \int_{0}^{1} \int_{0}^{1} \int_{\mathbb{R}} \left[ \left( \frac{m_3 m_4}{m_1 m_2} \right)^3 f_i(v'_1, I'_1) f_2(v'_2, I'_2) - f_2(v, I) f_3(v_3, I_3) H_4(I_3, r, R, v_3) B^\text{react}(v, v_3, I, I_3, R, r, \omega) \right] d\omega dr dR dI_3 dv_3.
\]

(34)

2.3. Properties of the collisional operators. Here we review some properties of the collisional operators given in [18] that will be used in the derivation of the limit equations.

**Lemma 2.1.** (See Lemma 2, page 223 of [18]) Let \( \psi : \mathbb{R}^3 \times [0, +\infty) \rightarrow \mathbb{R} \) be a function such that the weak formulation

\[ \int_{\mathbb{R}^3} \int_0^{+\infty} Q_i^r \psi(v, I) \varphi_i(I) dIdv \]

makes sense. Then

\[
\int_{\mathbb{R}^3} \int_0^{+\infty} Q_i^r \psi(v, I) \varphi_i(I) dIdv
= -\frac{1}{4} \int_{\mathbb{R}^3} \int_0^{+\infty} \int_0^{+\infty} \int_0^{+\infty} \int_{\mathbb{R}} \left[ f_i(v'_i, I'_i) f_i(v'_i, I'_i) - f_i(v, I) f_i(v_i, I_i) \right]
\]

\[
\times \left[ \psi(v'_i, I'_i) + \psi(v'_i, I'_i) - \psi(v, I) - \psi(v_i, I_i) \right]
\]

\[
\times B_i(v, v_i, I, I_i, R, r, \omega) (1 - R) |v - v_i|^1 d\omega dr dR dI_i dI_i dv_i dv.
\]

**Lemma 2.2.** (See Lemma 3, page 224 of [18]) Let \( j \neq i \) and \( \psi : \mathbb{R}^3 \times [0, +\infty) \rightarrow \mathbb{R} \) be a function such that the formulas

\[ \int_{\mathbb{R}^3} \int_0^{+\infty} Q^r_{ij} \psi(v, I) \varphi_i(I) dIdv \quad \text{and} \quad \int_{\mathbb{R}^3} \int_0^{+\infty} Q^r_{ij} \psi(v_j, I_j) \varphi_j(I_j) dI_j dv_j \]
Lemma 2.3. 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

$$\int_{\mathbb{R}^3} \int_0^{+\infty} Q_i^{r,e\text{act}}(v, I) \varphi_i(I) dI dv$$

makes sense. Additionally, if $B^{r,e\text{act}}(v_i, v_j, I, I_j, R, r, \omega)$ for $(i, j, k, l) \in \{(1, 2, 3, 4), (2, 1, 4, 3)\}$ is equal to $B^{r,e\text{act}}(v_i, v_j, I, I_j, R, r, \omega)$ for $(i, j, k, l) \in \{(3, 4, 1, 2), (4, 3, 2, 1)\}$, then

$$\sum_{i=1}^{4} \int_{\mathbb{R}^3} \int_0^{+\infty} Q_i^{r,e\text{act}}(v, I) \varphi_i(I) dI dv$$

$$= -\int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_0^{+\infty} \int_0^{+\infty} \int_0^{1} \int_{\mathbb{R}^2} \left[ \frac{f_k(v'_i, I'_k) f_l(v'_j, I'_l)}{(m_k m_l)^3} - \frac{f_l(v_i, I_l) f_k(v_j, I_j)}{(m_i m_j)^3} \right] H_i$$

$$\times \left[ \psi(v'_i, I'_i) + \psi(v'_j, I'_j) - \psi(v_i, I_i) - \psi(v_j, I_j) \right]$$

$$\times B^{r,e\text{act}}(v_i, v_j, I, I_j, R, r, \omega) m_i m_j (1 - R) |v_i - v_j|^{-1} d\omega dr dR dI_j dI_i dv_j dv_i.$$

2.4 Conservation laws and chemical rates. The conservation laws of the model are obtained from the properties stated in Lemmas 2.1, 2.2 and 2.3 of Subsection 2.3.

Lemma 2.4. Consider the functions $\Psi(v, I) = (\psi_1, \psi_2, \psi_3, \psi_4)$, with $\psi_1 = m_i v_x$, $\psi_2 = m_i v_y$, $\psi_3 = m_i v_z$, and $\psi_4 = \frac{1}{2} m_i v^2 + I + E_i$. Then,

$$\sum_{i=1}^{4} \int_{\mathbb{R}^3} \int_0^{+\infty} \left( \sum_{j=1}^{4} Q_{ij} + Q_{i}^{r,e\text{act}} \right) \psi_i(v, I) \varphi_i(I) dI dv = 0.$$
Property (39) indicates that elastic and reactive collisional operators are consistent with 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 2.5.** The reactive collisional operators are such that

\[
\int_{\mathbb{R}^3}^\infty Q_1^{\text{react}} \varphi_1(I_1) \, dI_1 \, dv_1 = \int_{\mathbb{R}^3}^\infty Q_2^{\text{react}} \varphi_2(I_2) \, dI_2 \, dv_2
\]

\[
= - \int_{\mathbb{R}^3}^\infty Q_3^{\text{react}} \varphi_3(I_3) \, dI_3 \, dv_3
\]

\[
= - \int_{\mathbb{R}^3}^\infty Q_4^{\text{react}} \varphi_4(I_4) \, dI_4 \, dv_4. \tag{40}
\]

Properties (40) indicate that reactive collision terms assure the correct chemical exchange rates for the considered chemical reaction (1).

2.5. **Equilibrium state and H-theorem.** In paper [18], the equilibrium solutions of the kinetic equations (28) were studied in two steps, namely by considering first the mechanical equilibrium associated to elastic collision operators and then the chemical equilibrium associated to the reactive collisional operator.

The mechanical equilibrium is defined by distribution functions $f_i(v, I)$, $i = 1, \ldots, 4$, such that

\[
Q_{j}^{\text{e}}(f_i, f_j) = 0, \quad i, j = 1, \ldots, 4. \tag{41}
\]

Assuming that the mechanical equilibrium is reached, the chemical equilibrium is then defined in paper [18] by distribution functions satisfying, besides conditions (41), the further condition

\[
Q_{i}^{\text{react}} = 0, \quad i = 1, \ldots, 4. \tag{42}
\]

The following proposition summarizes the $\mathcal{H}$-theorems stated in paper [18] and characterizes the equilibrium states of the model.

**Proposition 1.** (See Propositions 1 and 2, pages 231–233 of [18]) Let $B_{i,j}(v, v, I, I, R, r, \omega)$ and $B_{i}^{\text{react}}(v, v, I, I, R, r, \omega)$ be strictly positive almost everywhere and let the distribution functions $f_i$ be non-negative for all $i = 1, \ldots, 4$ and such that the collisional operators $Q_{ij}^{\text{e}}$ and $Q_{i}^{\text{react}}$ are well defined.

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

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

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

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

   \[
   M(n_i, u, T) = \frac{n_i(t, x)}{q_i(T(t, x))} \left( \frac{m_i}{2\pi k_B T(t, x)} \right)^{3/2} \exp \left( -\frac{m_i |v - u(t, x)|^2}{2k_B T(t, x)} - \frac{I}{k_B T(t, x)} \right) \tag{43}
   \]
and
\[
q_i(T(t, x)) = \int_{0}^{+\infty} \varphi_i(I) \exp \left( -\frac{I}{k_B T(t, x)} \right) dI,
\]
\[\text{(44)}\]

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 \((43)\), the following three properties related to chemical equilibrium are equivalent

\(a\) \(Q_{\text{react}}^i = 0\) for all \(i = 1, \ldots, 4\), \(v \in \mathbb{R}^3\), \(I \in \mathbb{R}^+\);

\(b\) \[
\sum_{i=1}^{4} \int_{\mathbb{R}^3} \int_{0}^{+\infty} Q_{\text{react}}^i \log \left( \frac{f_i(v, I)}{m_i^3} \right) \varphi_i(I) dI dv = 0;
\]

\(c\) The following mass action law holds
\[
\frac{n_1 n_2}{n_3 n_4} = \left( \frac{m_1 m_2}{m_3 m_4} \right)^{3/2} \frac{q_1(T) q_2(T)}{q_3(T) q_4(T)} \exp \left( \frac{E}{k_B T} \right).
\]
\[\text{(45)}\]

3. Scaled equations and assumptions. In this section we define the scaling regime for the kinetic equations and introduce the assumptions to be considered at the kinetic level, in order to derive the non-isothermal reaction-diffusion system of Maxwell-Stefan 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.

3.1. Scaling regime. Let \(\varepsilon\) be a scaling parameter representing the mean free path or, equivalently, the Knudsen number, with \(0 < \varepsilon \ll 1\). We scale the time and space variables as \((t, x) \mapsto (\varepsilon^2 t, \varepsilon x)\) and the distribution functions in the transformed variables are denoted by \(f_i^{\varepsilon}\).

We consider a diffusive scaling regime for which elastic collisions are dominant with respect to reactive collisions. Accordingly, we start our analysis from the following scaled Cauchy problem for the distribution functions \(f_i^{\varepsilon}\),

\[
\varepsilon \frac{\partial f_i^{\varepsilon}}{\partial t} + v \cdot \nabla_x f_i^{\varepsilon} = \frac{1}{\varepsilon} \sum_{j=1}^{4} Q_{ij}^{\varepsilon} (f_i^{\varepsilon}, f_j^{\varepsilon}) + \varepsilon Q_{i}^{\text{react}}, \quad i = 1, \ldots, 4,
\]
\[\text{(46)}\]

for \((t, x, v, I) \in [0, +\infty[ \times \mathbb{R}_3 \times \mathbb{R}_3 \times [0, +\infty[\).

\[
f_i^{\varepsilon}(0, x, v, I) = (f_i^{\text{in}})^{(\varepsilon)}(x, v, I), \quad \text{for} \quad (x, v, I) \in \mathbb{R}^3 \times \mathbb{R}^3 \times [0, +\infty[.
\]
\[\text{(47)}\]

The properties of the collisional operators stated in Section 2, with the obvious adjustments, are still valid for the scaled operators.

3.2. Assumptions. In view of the reaction-diffusion limit to be investigated in this paper, we will consider the following assumptions:

\(a\) 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) velocity of the mixture is small and goes to zero as the parameter \(\varepsilon\) tends to zero.
(c) We assign as initial conditions \((f_i^{(\infty)})^e\) Maxwellian functions centered at the species mass velocity \(\varepsilon u_i^{(\infty)}(x)\) and species temperature \(T^{(\infty)}(x) + \varepsilon T_i^{(\infty)}(x)\):

\[
(f_i^{(\infty)})^e(x, v, I) = M_i^{(\infty)}
\]

\[
= \frac{n_i^{(\infty)}(x)}{q_i(T^{(\infty)}(x) + \varepsilon T_i^{(\infty)}(x))} \left(\frac{m_i}{2\pi k_B(T^{(\infty)}(x) + \varepsilon T_i^{(\infty)}(x))}\right)^{3/2} \times \exp \left[ - \frac{m_i}{2k_B(T^{(\infty)}(x) + \varepsilon T_i^{(\infty)}(x))} \left| v - \varepsilon u_i^{(\infty)}(x) \right|^2 \right]
\]

\[
\times \exp \left[ - \frac{I}{k_B(T^{(\infty)}(x) + \varepsilon T_i^{(\infty)}(x))}\right]
\]

for some \(n_i^{(\infty)}, T^{(\infty)}, T_i^{(\infty)}: \Omega \rightarrow \mathbb{R}^+\) and \(u_i^{(\infty)}: \Omega \rightarrow \mathbb{R}^3\).

(d) We assume that the time evolution of \(f_i^e\) established by equations (46) preserves for any time \(t > 0\) the initial Maxwellian structure of species distributions; more precisely, we consider that the distribution functions \(f_i^e\), at time \(t > 0\), are Maxwellians of the form

\[
f_i^e(v, I) = \frac{n_i^e(t, x)}{q_i(T(t, x) + \varepsilon T_i^e(t, x))} \left(\frac{m_i}{2\pi k_B(T(t, x) + \varepsilon T_i^e(t, x))}\right)^{3/2} \times \exp \left[ - \frac{m_i}{2k_B(T(t, x) + \varepsilon T_i^e(t, x))} \left| v - \varepsilon u_i^e(t, x) \right|^2 \right]
\]

\[
\times \exp \left[ - \frac{I}{k_B(T(t, x) + \varepsilon T_i^e(t, x))}\right]
\]

for some functions \(n_i^e, T_i^e, T: \mathbb{R}^+ \times \Omega \rightarrow \mathbb{R}^+\) and \(u_i^e: \mathbb{R}^+ \times \Omega \rightarrow \mathbb{R}^3\).

Assumptions (c) and (d) are consistent with the fact that the scaled equations (46) provide, as \(\varepsilon \to 0\),

\[
\sum_{j=1}^4 Q_{ij}(f_i^e, f_j^e) = O(\varepsilon).
\]

Hence the distributions \(f_i^e\) should be, as \(\varepsilon \to 0\), \(O(\varepsilon)\) 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

\[
f_i^e(v, I) = M_i \left( n_i(t, x), 0, T(t, x) \right) \left(1 + O(\varepsilon)\right),
\]

where \(M_i\) is an elastic Maxwellian equilibrium state as defined in (43). Hence, up to the order \(O(\varepsilon)\), we can suppose that

\[
f_i^e(v, I) = M_i \left( n_i^e(t, x), \varepsilon u_i^e(t, x), T(t, x) + \varepsilon T_i^e(t, x) \right)
\]

with

\[
\lim_{\varepsilon \to 0} \left( n_i^e(t, x), \varepsilon u_i^e(t, x), T(t, x) + \varepsilon T_i^e(t, x) \right) = \left( n_i(t, x), 0, T(t, x) \right),
\]

(51)
and
\[ u_i^\varepsilon(t, x) = O(1), \quad T_i^\varepsilon(t, x) = O(1). \]

Assumption (49) is one of the simplest options to fulfill the property (50), and it will be sufficient to obtain a system of Maxwell-Stefan type in the asymptotic limit \( \varepsilon \to 0 \).

4. The limiting equations for the reactive mixture. In this section, we derive the macroscopic equations in the hydrodynamic limit of the scaled kinetic equations (46) with initial conditions defined by (47) and (48). As usual in kinetic theory [2, 3, 4, 11, 25, 26], such equations are obtained by taking the appropriate moments of equations (46) with respect to the velocity \( v \) and here also with respect to internal energy parameter \( I \). In the present case, the balance equations obtained in the limit for \( \varepsilon \to 0 \) constitute a non-isothermal reaction-diffusion system of Maxwell-Stefan type for the reactive mixture of polyatomic gases. The system is formed by the number density equations, the momentum equation for each constituent and the balance equation for the mixture temperature. Assumptions (b) and (d) considered in Subsection 3.2 play a crucial role in the passage from the kinetic equations to the Maxwell-Stefan setting.

4.1. Preliminaries. In what follows, instead of the unit vector \( \omega \in S^2 \) parametrization used in (14) and (21) to obtain the elastic and reactive post-collisional velocities, we will use the following unit vector \( \sigma \in S^2 \) parametrization and show how to pass from one to the other.

Proposition 2. Let
\[ \sigma = y - 2(\omega \cdot y)\omega, \quad y = \frac{v - v_*}{|v - v_*|}, \]  
where \( \sigma \) and \( \omega \) are unit vectors in the sphere \( S^2 \) and \( v, v_* \) denote the velocities of the colliding pair of particles. The Jacobian of the transformation from \( \omega \) to \( \sigma \) is given by
\[ J_{\omega \to \sigma} = 4 |\omega \cdot y|, \quad \forall y \in \mathbb{R}^3. \]

Proof. See [32], page 41.

Remark 1.

(i) Using the \( \sigma \)-parametrization given in (52), the post-collisional velocities (16) for a bi-species elastic collision between a particle of species \( i \) with ingoing parameters \( (v, I) \) and a particle of species \( j \) with parameters \( (v_j, I_j) \) can be rewritten as
\[ v'_i = \frac{m_i v + m_j v_j}{m_i + m_j} + \frac{m_j}{m_i + m_j} \sqrt{\frac{2RE}{\mu_{ij}}} \sigma, \quad v'_j = \frac{m_i v + m_j v_j}{m_i + m_j} - \frac{m_i}{m_i + m_j} \sqrt{\frac{2RE}{\mu_{ij}}} \sigma. \]

Therefore,
\[ v'_i - v = \frac{m_j}{m_i + m_j} V + \frac{m_j}{m_i + m_j} \sqrt{\frac{2RE}{\mu_{ij}}} \sigma, \]  
where
\[ V = v_j - v. \]
(ii) As a consequence of Proposition 2, the bi-species elastic and reactive collision kernels can be written as, see [39],
\[ B_{ij}(v, v_j, I, I_j, R, r, \omega) d\omega = 2 |\omega \cdot y| B_{ij}(v, v_j, I, I_j, R, r, \sigma) d\sigma, \]  
(57)
\[ B^{\text{react}}_{ij}(v, v_j, I, I_j, R, r, \omega) d\omega = 2 |\omega \cdot y| B^{\text{react}}_{ij}(v, v_j, I, I_j, R, r, \sigma) d\sigma, \]  
(58)
where \( y = -V / |V| \).

From now on we will sometimes skip for brevity the dependencies of distributions on velocity and internal energy, and we set \( f_i^e = f_i^e(v, I) \), \( f_j^e = f_j^e(v_j, I_j) \), \( f_i^{r'} = f_i^{r'}(v', I') \), \( f_j^{r'} = f_j^{r'}(v', I') \). Analogously, for Maxwellian distributions, we will omit their dependencies on \( n_i^e, 0, T \) and write, for example, \( M_i^e \) instead of \( M_i(n_i^e(t, x), 0, T(t, x)) \).

**Proposition 3.** Using the Taylor expansion with respect to \( \varepsilon \) of the distribution functions (49), one can write

\[ (a) \quad f_i^{e'} f_j^{r'} - f_i^e f_j^r = M_i^e M_j^r [\varepsilon (a_{ij} \cdot (v_i^e - v)) + \varepsilon (T_i^e/k_BT - T_j^r/k_BT)] \times \left( \frac{1}{2} m_i v_i^e \right) - \frac{1}{2} m_i v_i^e I_i + O(\varepsilon^2) \],

(59)

\[ (b) \quad \left( \frac{m_i m_j}{m_k m_l} \right)^3 f_i^{e'} f_j^{r'} - f_i^e f_j^r = \left( \frac{m_i m_j}{m_k m_l} \right)^3 M_k^e M_l^r - M_i^e M_j^r + \left[ \left( \frac{m_i m_j}{m_k m_l} \right)^3 \right] \times M_k^e M_l^r \left( a_{ij} \cdot v_k^e + \frac{m_k T_i^e(v_i^e)^2}{2k_BT^2} - \frac{T_i^e}{k_BT} q_i^r(T) \right) \right] + O(\varepsilon^2), \]

(60)

where

\[ a_{ij} = \frac{m_i (u_i^e - u_j^e)}{k_BT}, \quad a_i = \frac{m_i u_i^e}{k_BT}, \quad a_j = \frac{m_j u_j^e}{k_BT}, \quad a_k = \frac{m_k u_k^e}{k_BT}, \quad a_l = \frac{m_l u_l^e}{k_BT}, \]

(61)

\[ q_i^r(T) = \int_0^\infty \varphi_i(I) \exp \left( -\frac{I}{k_BT} \right) dI, \]

(62)

\[ M_i^e : = \frac{n_i^e}{q_i(T)} \left( \frac{m_i}{2\pi k_BT^3} \right)^{3/2} \exp \left( -\frac{m_i v_i^e^2}{2k_BT} - \frac{I}{k_BT} \right), \]

(63)

and similarly for \( M_j^e, M_k^r, M_l^r \).

**Proof.** See the Appendix, part (A).

Using (a) of Proposition 3 together with (55) and (57), we can write the elastic bi-species collisional operator as

\[ Q^{e}_{ij}(f_i, f_j) = \varepsilon \frac{m_j}{m_i + m_j} \int_{\mathbb{R}^3} \int_0^1 \int_0^1 \int_{S^2} (a_{ij} \cdot V) M_i^e M_j^r \]

...
\[ \times B_{ij}(v, v_j, I, I_j, R, r, \sigma) \frac{2 \cos \theta (1 - R)}{\varphi_i(I)} \, d\sigma \, dr \, dR \, dI_j \, dv_j \]

\[ + \varepsilon \frac{m_j}{m_i + m_j} \mathbf{a}_{ij} \cdot \int_{\mathbb{R}^3} \int_{0}^{+\infty} \int_{0}^{1} \int_{S^2} \frac{2 R^\varepsilon}{\mu_{ij}} \sigma M_i^x M_j^x \]

\[ \times B_{ij}(v, v_j, I, I_j, R, r, \sigma) \frac{2 \cos \theta (1 - R)}{\varphi_i(I)} \, d\sigma \, dr \, dR \, dI_j \, dv_j \]

\[ + \varepsilon \int_{\mathbb{R}^3} \int_{0}^{+\infty} \int_{0}^{1} \int_{S^2} \left( \frac{T_i}{k_B T^2} - \frac{T_j}{k_B T^2} \right) \]

\[ \times \left( \frac{m_i (v_i')^2}{2} - \frac{m_j v_j^2}{2} + I_j^2 - I \right) M_i^x M_j^x \]

\[ \times B_{ij}(v, v_j, I, I_j, R, r, \sigma) \frac{2 \cos \theta (1 - R)}{\varphi_i(I)} \, d\sigma \, dr \, dR \, dI_j \, dv_j \]

\[ + O(\varepsilon^2). \]

Similarly, using (b) of Proposition 3 together with (58), we can write the reactive collisional operator as

\[ Q_i^{react} = \int_{\mathbb{R}^3} \int_{0}^{+\infty} \int_{0}^{1} \int_{S^2} \left[ \left( \frac{m_i m_j}{m_i + m_j} \right)^3 M_i^x M_j^x' - M_i^x M_j^x' \right] \]

\[ \times B_{ij}^{react}(v, v_j, I, I_j, R, r, \sigma) H_i \, 2 \cos \theta (1 - R) V^{-1} \]

\[ \times \varphi_i(I)^{-1} \left( m_i m_j \right)^{-2} \, d\sigma dr dR dI_j dv_j + O(\varepsilon), \]

where \(|\omega \cdot v| = \cos \theta, V = |v - v_j| = ||V||\) and for the forward and backward reactive 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. The notation \(M_i^x, M_j^x, M_i^x'\) and \(M_j^x'\) indicates Maxwellian distributions defined as in (63).

Also, we consider general collision kernels and split both the bi-species and reactive collision kernels into the product of kinetic and angular collision kernels (see [39]) as given below

\[ B_{ij}(v, v_j, I, I_j, R, r, \sigma) = \left[ v - v_j \right]^\gamma \Phi_{ij}(I, I_j, R, r) b_{ij}^{kinetic} \left( \cos \theta \right), \]

\[ B_{ij}^{react}(v, v_j, I, I_j, R, r, \sigma) = \left[ v - v_j \right]^\gamma \Phi_{ij}^{react}(I, I_j, R, r) b_{ij}^{react} \left( \cos \theta \right), \]

where \(\gamma\) is a parameter such that \(\gamma \geq 1\). This decomposition of the collision kernels is enough to obtain appropriate expressions for the integral production terms. Finally, we will use in the sequel the integral representation of both the gamma function and the incomplete gamma function, respectively defined as given below

\[ \int_{0}^{+\infty} x^n e^{-\alpha x^2} \, dx = \frac{1}{2} \Gamma \left( \frac{n + 1}{2} \right) \left( \frac{1}{\alpha} \right)^{\frac{n+1}{2}}, \]

\[ \Gamma(\alpha, x) = \int_{x}^{+\infty} t^{\alpha-1} e^{-t} \, dt. \]
4.2. Moment of order zero. From the scaled equations (46), we first derive the evolution equation for the number density of each constituent. The relevant result is the following.

**Lemma 4.1.** The balance equation for the number density of each constituent in the reactive mixture can be written in the form

$$\frac{\partial n_i}{\partial t} + \nabla \cdot (n_i u_i) = -\lambda_i A, \quad i = 1, 2, 3, 4,$$

(70)

where

$$n_i = \lim_{\varepsilon \to 0} n_i^\varepsilon, \quad u_i = \lim_{\varepsilon \to 0} u_i^\varepsilon,$$

and

$$\lambda_1 = \lambda_2 = 1, \quad \lambda_3 = \lambda_4 = -1$$

(71)

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 $\varepsilon \to 0$ of

$$A^\varepsilon = \frac{\left(\frac{m_3 m_4}{m_1 m_2}\right)^{3/2} n_1^\varepsilon n_2^\varepsilon}{q_1(T) q_2(T)} \exp \left( -\frac{E}{k_B T} - \frac{n_3^\varepsilon n_4^\varepsilon}{q_3(T) q_4(T)} \right)$$

(72)

$$\times \frac{4}{(m_3 m_4)^2} \frac{2 k_B T}{\mu_{34}} \left( \frac{\gamma - 1}{2} \right) \Gamma \left( \frac{\gamma + 2}{2} \right) \int_0^\infty \int_0^{\infty} \int_0^1 \int_0^1 \int_0^1 \exp \left( -\frac{I+I_4}{k_B T} \right)$$

$$\times \Phi_{\text{react}}(I, I_4, R, r) \Phi_{\text{react}}(\cos \theta) \cos \theta (1 - R) d\sigma dr dI_4 + O(\varepsilon).$$

**Proof.** Multiplying equations (46) by $\varphi_i(I)$ and integrating with respect to $v \in \mathbb{R}^3$ and $I \in \mathbb{R}_+$, we obtain

$$\varepsilon \frac{\partial}{\partial t} \left[ \int_{\mathbb{R}^3} \int_0^{+\infty} f_i^\varepsilon \varphi_i(I) dI dv \right] + \nabla \cdot \left( n_i^\varepsilon u_i^\varepsilon \varphi_i(I) dI dv \right)$$

(73)

$$= \frac{1}{\varepsilon} \int_{\mathbb{R}^3} \int_0^{+\infty} Q_i^{\varepsilon} \varphi_i(I) dI dv + \frac{1}{\varepsilon} \sum_{j=1}^4 \int_{\mathbb{R}^3} \int_0^{+\infty} Q_{ij}^{\varepsilon} \varphi_i(I) dI dv$$

$$+ \int_{\mathbb{R}^3} \int_0^{+\infty} Q_i^{\varepsilon} \varphi_i(I) dI dv$$

$$- \lambda_i A^\varepsilon$$

where the term $A^\varepsilon$ is given by (72). Moreover, we have used properties (35) and (36), respectively, with $\psi(v, I) = 1$, for the vanishing of the first two terms on the right hand side of equation (73). To obtain the last term on the right hand side of equation (73), we have used the more convenient form of the reactive operator $Q_i^{\varepsilon}$, given in (65). Then we have used the decomposition of the reactive kernel given in (67) and the conservation of total energy for reactive collisions given by condition (11). See the Appendix, part (B).

Finally, dividing both sides of equation (73) by $\varepsilon$ and taking the limit as $\varepsilon \to 0$, we obtain the evolution equation (70) for the constituent number density. □
4.3. **Moment of order one.** From the scaled equations (46), we then derive the evolution equation for the momentum of each species, as stated in the following result.

**Lemma 4.2.** (i) The balance equation for the momentum of each constituent in the reactive mixture can be written in the form

\[ \nabla_x (n_i k_B T) = m_i \mathbf{B}_i, \quad i = 1, 2, 3, 4, \quad n_i = \lim_{\varepsilon \to 0} n_i^\varepsilon, \quad T = \lim_{\varepsilon \to 0} (T + \varepsilon T_i^\varepsilon), \quad (74) \]

where \( \mathbf{B}_i \) is the production term associated to the momentum balance of the species, namely the formal limit for \( \varepsilon \to 0 \) of

\[
B_i^\varepsilon = \sum_{j=1}^{4} \frac{m_j}{m_i + m_j} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{0}^{+\infty} \int_{0}^{+\infty} \int_{0}^{1} \int_{S^2} (a_{ij} \cdot \mathbf{V}) v M_i^\varepsilon M_j^\varepsilon V^{\gamma - 1} \times 2 \Phi_{ij} (I, I_j, R, r) b_{ij} (\cos \theta) \cos \theta (1 - R) \, d\sigma dr dI dJ d\mathbf{v} d\mathbf{w} \\
+ \sum_{j=1}^{4} \frac{m_j}{m_i} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{0}^{+\infty} \int_{0}^{+\infty} \int_{0}^{1} \int_{S^2} (a_{ij} \cdot \sigma) v \sqrt{2 R E \frac{M_i^\varepsilon M_j^\varepsilon V^{\gamma - 1}}{\mu_{ij}}} \times 2 \Phi_{ij} (I, I_j, R, r) b_{ij} (\cos \theta) \cos \theta (1 - R) \, d\sigma dr dI dJ d\mathbf{v} d\mathbf{w} \\
+ \sum_{j=1}^{4} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{0}^{+\infty} \int_{0}^{+\infty} \int_{0}^{1} \int_{S^2} v \left( \frac{2 T_i^\varepsilon}{k_B T^2} - \frac{1}{k_B T^2} \right) \times \left( \frac{m_i (v_j^0)^2}{2} - \frac{m_j v_j^2}{2} + I_i^0 - I \right) M_j^\varepsilon M_j^\varepsilon V^{\gamma - 1} \Phi_{ij} (I, I_j, R, r) \times 2 b_{ij} (\cos \theta) \cos \theta (1 - R) \, d\sigma dr dI dJ d\mathbf{v} d\mathbf{w} \\
+ O(\varepsilon). \]

(ii) Moreover, if the angular collision kernel of the elastic bi-species kernel is an odd function of \( \cos \theta \), then the production term \( \mathbf{B}_i \) is the formal limit for \( \varepsilon \to 0 \) of

\[
B_i^\varepsilon = \sum_{j=1}^{4} \left( \frac{m_j}{m_i + m_j} \right)^2 \left( \frac{m_i}{2 \pi k_B T} \right)^{3/2} \left( \frac{m_j}{2 \pi k_B T} \right)^{3/2} \frac{n_i^\varepsilon J_j^\varepsilon - n_j^\varepsilon J_i^\varepsilon}{q_i(T) q_j(T)} \times \left( \frac{2 \pi k_B T}{m_i + m_j} \right)^{3/2} \left( \frac{2 \pi k_B T}{m_i} \right)^{3/2} \left( \frac{2 \pi k_B T}{m_j} \right)^{3/2} \frac{\gamma + 4}{\mu_{ij}} \left( \frac{2 k_B T}{\mu_{ij}} \right)^{3/2} \times \int_{0}^{+\infty} \int_{0}^{+\infty} \int_{0}^{1} \int_{S^2} \exp \left( - \frac{I + I_j}{k_B T} \right) \times \Phi_{ij} (I, I_j, R, r) 2 \cos \theta (1 - R) b_{ij} (\cos \theta) \, d\sigma dr dI dJ dI \times \Phi_{ij} (I, I_j, R, r) 2 \cos \theta (1 - R) b_{ij} (\cos \theta) \, d\sigma dr dI dJ dI + O(\varepsilon), \]

where \( J_i^\varepsilon \) denotes the molar diffusive flux of the species given by

\[ J_i^\varepsilon = n_i^\varepsilon (u_i^\varepsilon - \mathbf{u}_i^\varepsilon). \]
Proof. (i) First we multiply equations (46) by $v \phi_i(I)$ and integrate with respect to $v \in \mathbb{R}^3$ and $I \in \mathbb{R}_+$ to obtain

$$
\varepsilon \frac{\partial}{\partial t} \left\{ \int_{\mathbb{R}^3} \int_0^{+\infty} v f_i^l \phi_i(I) dI dv \right\} + \nabla_x \left\{ \int_{\mathbb{R}^3} \int_0^{+\infty} v \otimes v f_i^l \phi_i(I) dI dv \right\} = \varepsilon n_i T_i \mathbf{u}_i^l \left\{ \frac{k_B(T+\frac{T_i^l}{m_i})}{m_i} n_i^l + \varepsilon^2 (u_i^l \otimes u_i^l) \right\}
$$

$$
= \frac{1}{\varepsilon} \int_{\mathbb{R}^3} \int_0^{+\infty} v Q^l_{ii} \phi_i(I) dI dv + \frac{1}{\varepsilon} \sum_{j=1}^{4} \int_{\mathbb{R}^3} \int_0^{+\infty} v Q^l_{ij} \phi_j(I) dI dv
$$

$$
+ \varepsilon \int_{\mathbb{R}^3} \int_0^{+\infty} v Q^{\text{react}}_{i} \phi_i(I) dI dv
$$

where property (35) was used with $\psi(v, I) = v$ to obtain the vanishing of the first term on the right hand side. Moreover, concerning the term $B_i^l$ on the right-hand side of (78) we have used the elastic bi-species operator $Q_{ii}^l$ given in (64) and the decomposition of the elastic bi-species kernel indicated in (66) to obtain the expression for $B_i^l$ given in (75). Upon specifying $\Phi_{ij}(I, I_j, R, r)$, the integrals with respect to $I, I_j, R, r, \sigma$ can be evaluated explicitly and the six fold integrals with respect to $v, v_j$ can be transformed to the center of mass velocity and relative velocity and the resulting integrals can be evaluated using the integral representation of gamma function given in (68).

Then, concerning the term $C_i^l$ on the right-hand side of (78), we have used the form of the reactive operator $Q^{\text{react}}_i$ given in (65) and the decomposition (67) for the reactive kernel $B^{\text{react}}(v, v_j, I, I_j, R, r, \sigma)$ to obtain

$$
C_i^l = \varepsilon \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_0^{+\infty} \int_0^{+\infty} \int_0^1 \int_{S^2} v \left( \frac{m_i m_j}{m_k m_l} \right)^3 M_i^l M_j^r - M_i^r M_j^l \right) \times V^{r-1} \Phi^{\text{react}}(I, I_j, R, r) b^{\text{react}}(\cos \theta) H_i(m_i, m_j)^{-2}
$$

$$
\times \cos \theta (1 - R) d\sigma d\nu dIdv_j dw + O(\varepsilon^2).
$$

Again, upon specifying $\Phi^{\text{react}}(I, I_j, R, r)$, the integrals on the right hand side of equation (79) can be computed. Specifically, the integrals with respect to $I, I_j, R, r, \sigma$ can be evaluated explicitly and the six fold integrals with respect to $v, v_j$ can be transformed to the center of mass velocity and relative velocity and the resulting integrals can either be evaluated using the integral representation of gamma function given in (68) or be represented by the incomplete gamma function given in (69).

Finally we take the limit as $\varepsilon \to 0$ in equation (78) and obtain the balance equation (74) for the momentum of each species, in which the production term $B_i$ is the formal limit for $\varepsilon \to 0$ of the term $B_i^l$ given in (75).

(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 (75) vanishes. See the Appendix, part (C1). Transforming the six fold integral over $v$ and $v_j$ in the first and third terms on the right hand side of (75) to the center of
mass velocity and relative velocity and evaluating the resulting integrals using (68),
we obtain that the third term on the right hand side of (75) vanishes. See the
Appendix, part (C2). Moreover, the six fold integral over \( \mathbf{v} \) and \( \mathbf{v}_j \) in the first term
on the right hand side of the same equation reduces to

\[
\int_{\mathbb{R}^3} \int_{\mathbb{R}^3} (a_{ij} \cdot \mathbf{V}) \nu M_i^\varepsilon M_j^\varepsilon V^{\gamma-1} \nu_j \, d\mathbf{v} \, d\mathbf{v}
\]

Se see the Appendix part (C2). Now, substituting (80) into the first addend in (75),
we obtain the desired result. \( \square \)

**Remark 2.** Observe that the production term \( B_i^T \) given in equation (76) has
the Maxwell-Stefan structure [11, 26]. The remaining integrals involved in equation
(76), when evaluated, will only contribute to the definition of the diffusion
coefficients. \( \square \)

4.4. **Conservation of energy.** From the scaled equations (46), we finally derive
the evolution equation for the energy of the mixture as stated in the following
lemma.

**Lemma 4.3.** The balance equation for the energy of the reactive mixture can be
written in the form

\[
\frac{\partial}{\partial t} \left[ \sum_{i=1}^{4} \left( \frac{3}{2} n_i k_B T + n_i q_i(T) \right) \right] + \nabla \cdot \left[ \sum_{i=1}^{4} \left( \frac{5}{2} n_i k_B T \mathbf{u}_i + n_i q_i(T) \right) \right] = -EA,
\]

where

\[
n_i = \lim_{\varepsilon \to 0} n_i^\varepsilon, \quad \mathbf{u}_i = \lim_{\varepsilon \to 0} \mathbf{u}_i^\varepsilon, \quad T = \lim_{\varepsilon \to 0} (T + \varepsilon T^\gamma),
\]

\( q_i^*(T) \) has been defined in (62), and \( A \) is the production term defined as in Subsection 4.2.

**Proof.** Multiplying Eqs. (46) by \( \left[ m_i v^2 / 2 + I \right] \varphi_i(I) \), integrating with respect to
\( \mathbf{v} \in \mathbb{R}^3 \) and \( I \in \mathbb{R}_+ \), and then summing over the species \( i = 1, 2, 3, 4 \), we obtain

\[
\varepsilon \frac{\partial}{\partial t} \sum_{i=1}^{4} \left\{ \int_{\mathbb{R}^3} \int_{0}^{+\infty} \left[ \frac{m_i v^2}{2} + I \right] \varphi_i(I) \nu_i^\varepsilon \, dI \, d\mathbf{v} \right\} + \nabla \cdot \sum_{i=1}^{4} \left\{ \int_{\mathbb{R}^3} \int_{0}^{+\infty} \left[ \frac{m_i v^2}{2} + I \right] \varphi_i(I) \nu_i^\varepsilon \, dI \, d\mathbf{v} \right\}
\]

\[
= \mathcal{D}^\varepsilon + \mathcal{E}^\varepsilon + \mathcal{F}^\varepsilon,
\]
where $D^\varepsilon$, $E^\varepsilon$, $F^\varepsilon$ are the production terms defined by

\[
D^\varepsilon = \frac{1}{\varepsilon} \sum_{i=1}^{4} \int_{\mathbb{R}^3} \int_0^{+\infty} \left[ \frac{m_i v_i^2}{2} + I \right] \varphi_i(I) Q_i^\varepsilon_d dI dv,
\]

\[
E^\varepsilon = \frac{1}{\varepsilon} \sum_{i=1}^{4} \sum_{j=1}^{4} \int_{\mathbb{R}^3} \int_0^{+\infty} \left[ \frac{m_i v_i^2}{2} + I \right] \varphi_i(I) Q_{ij}^\varepsilon dI dv,
\]

\[
F^\varepsilon = \varepsilon \sum_{i=1}^{4} \int_{\mathbb{R}^3} \int_0^{+\infty} \left[ \frac{m_i v_i^2}{2} + I \right] \varphi_i(I) Q_{i}\text{react} dI dv.
\]

Using properties (35), (37) and (38), with $\psi(v, I) = [m_i v_i^2 / 2 + I]$, for the production terms $D^\varepsilon$, $E^\varepsilon$ and $F^\varepsilon$, respectively, we obtain that

\[
D^\varepsilon = 0, \quad E^\varepsilon = 0 \quad \text{and} \quad F^\varepsilon = -\varepsilon EA^\varepsilon, \tag{83}
\]

with $A^\varepsilon$ being defined by equation (72). Substituting (83) into (82) and dividing both sides by $\varepsilon$, we obtain

\[
\frac{\partial}{\partial t} \left\{ \sum_{i=1}^{4} \left[ \frac{3}{2} n_i^2 k_B (T + \varepsilon T_i^\varepsilon) + \frac{1}{2} \varepsilon^2 m_i n_i^2 (u_i^\varepsilon)^2 + n_i^2 q_i^\varepsilon (T + \varepsilon T_i^\varepsilon) \right] \right\} + \nabla \cdot \left\{ \sum_{i=1}^{4} \left[ \frac{5}{2} n_i^2 k_B (T + \varepsilon T_i^\varepsilon) + \frac{1}{2} \varepsilon^2 m_i n_i^2 (u_i^\varepsilon)^2 \right] u_i^\varepsilon + n_i^2 u_i^\varepsilon q_i^\varepsilon (T + \varepsilon T_i^\varepsilon) \right\}
\]

\[= -\varepsilon EA^\varepsilon. \tag{84}\]

Taking the limit as $\varepsilon \to 0$ in equation (84), we obtain the balance equation for the energy of the mixture in the form of equation (81).

4.5. Limit equations. In this section, we summarize the results of Section 4 and write the limit equations when the angular collision kernels of both the elastic bi-species and the reactive operators are odd functions of $\cos \theta$. By recalling that, due to assumption (b), in the limit as $\varepsilon \to 0$, we have $J_i = n_i u_i$, for all $i = 1, 2, 3, 4$, and putting together the balance equations (70) and (74) for the number densities and momentum of the constituents as well as the balance equation (81) for the total energy of the mixture, we obtain the following macroscopic system of non-isothermal reaction-diffusion equations,

\[
\frac{\partial n_i}{\partial t} + \nabla \cdot J_i = -\lambda_i A, \quad i = 1, 2, 3, 4,
\]

\[
\nabla \cdot \left( n_i k_B T \right) = -\sum_{j=1}^{4} \frac{n_j J_i - n_i J_j}{D_{ij}}, \quad i = 1, 2, 3, 4, \tag{85}
\]

\[
\frac{\partial}{\partial t} \left[ \sum_{i=1}^{4} n_i \left( \frac{3}{2} k_B T + \frac{q_i^\varepsilon(T)}{q_i(T)} \right) \right] + \nabla \cdot \left[ \sum_{i=1}^{4} \left( \frac{5}{2} k_B T + \frac{q_i^\varepsilon(T)}{q_i(T)} \right) J_i \right] = -EA,
\]

where $A$ is the production term derived in Subsection 4.2 as the formal limit for $\varepsilon \to 0$ of the approximate production term $A^\varepsilon$ given in equation (72). Moreover, $D_{ij}$, for $i = 1, 2, 3, 4$, and $i \neq j$, are diffusion coefficients that can be recovered from
the production term $B_i$ obtained in Subsection 4.3 as the formal limit for $\varepsilon \to 0$ of $B^\varepsilon_i$ given in (76). The production term $A$ is given by

$$A = \left( \frac{m_3 m_4}{m_1 m_2} \right)^{3/2} \frac{n_1 n_2}{q_1(T(t, x))q_2(T(t, x))} \exp \left( -\frac{E}{k_B T(t, x)} \right)$$

$$- \frac{n_3 n_4}{q_3(T(t, x))q_4(T(t, x))} \frac{4}{\sqrt{\pi}(m_3 m_4)^2} \Gamma \left( \frac{\gamma + 2}{2} \right) \left( \frac{2k_B T}{\mu_{34}} \right)^{(\gamma - 1)/2}$$

$$\times \int_0^1 \int_0^1 \int_0^1 \exp \left( -\frac{I+I_4}{k_B T(t, x)} \right) \Phi_{\text{react}}(I, I_4, R, r)$$

$$\times b_{\text{react}}(\cos \theta) \cos \theta (1 - R) \, d\sigma dr dI_4 dI,$$

and the diffusion coefficients $D_{ij}$ are defined as

$$\frac{1}{D_{ij}} = \frac{4}{3\sqrt{\pi}} \mu_{ij}^{(3-\gamma)/2}(2k_B T(t, x))^{(\gamma - 1)/2} \frac{1}{q_i(T(t, x))q_j(T(t, x))}$$

$$\times \Gamma \left( \frac{\gamma + 4}{2} \right) \int_0^1 \int_0^1 \int_0^1 \exp \left( -\frac{I+I_j}{k_B T(t, x)} \right) \Phi_{ij}(I, I_j, R, r)$$

$$\times \cos \theta (1 - R) b_{ij}(\cos \theta) \, d\sigma dr dI_j dI.$$

The equations in the second row of (85) are the Maxwell-Stefan equations for the reactive mixture of polyatomic gases considered in this paper. Upon specifying the kinetic and the angular kernels, the integrals appearing in equations (86) and (87) can be evaluated explicitly and detailed expressions for the reactive production terms $A$, $EA$ and diffusion coefficients $D_{ij}$ can be obtained.

5. Conclusion. In this article we have derived a set of non-isothermal reaction diffusion equations of Maxwell-Stefan type for describing 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 gases proposed by Desvillettes, Monaco and Salvarani [18], which has been studied here under a reactive-diffusive scaling.

The form of the limiting equations (85) 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 shows 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.

We highlight 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 (85) vanishes. Therefore they do not constitute a set of independent equations for the fluxes $J_i$. 
The limit equations are compatible with the internal energy law of polyatomic gases and the law of mass action. At the equilibrium, from both the equation (85) and the formulation of the source term (86), the law of mass action reads

$$\frac{n_1 n_2}{n_3 n_4} = \left( \frac{m_1 m_2}{m_3 m_4} \right)^{3/2} \frac{q_1(T(t, x)) q_2(T(t, x))}{q_3(T(t, x)) q_4(T(t, x))} \exp \left( \frac{E}{k_B T(t, x)} \right),$$

which is exactly the same as in [18].

Of course, all the computations heavily depend on the choice of the functional forms of the weights $\varphi_i$ which can be – in principle – freely chosen, provided that they induce a macroscopic behavior consistent with the physical situation under investigation.

In case of polytropic gases, the weights $\varphi_i$ 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 [18, 33]. Thanks to this choice of the weights $\varphi_i$ we can compute

$$q_i(T(t, x)) = \int_0^{+\infty} I^{\alpha_i} e^{-I/(k_B T(t, x))} dI = [k_B T(t, x)]^{\alpha_i + 1}(\alpha_i!),$$

with the convention $0! = 1$, and analogously

$$q_i^*(T(t, x)) = \int_0^{1/\infty} I^{\alpha_i + 1} e^{-I/(k_B T(t, x))} dI = [k_B T(t, x)]^{\alpha_i + 2}(\alpha_i + 1)!.$$  

The model is thus consistent with the energy law of polytropic molecules, which provides a linear dependence on temperature $T(t, x)$. More precisely, the total energy at the equilibrium state becomes

$$\sum_{i=1}^{4} n_i \left( \frac{3}{2} k_B T + \frac{q_i^*(T)}{q_i(T)} \right) = \sum_{i=1}^{4} n_i \left( \frac{3}{2} + \alpha_i + 1 \right) k_B T(t, x).$$

Because of the total conservation of the mass during the chemical reaction (i.e. $\alpha_1 + \alpha_2 = \alpha_3 + \alpha_4$), we can conclude that

$$\frac{q_1(T(t, x)) q_2(T(t, x))}{q_3(T(t, x)) q_4(T(t, x))} = \frac{(\alpha_1!)(\alpha_2!)}{(\alpha_3!)(\alpha_4!)},$$

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 $\varphi_i$ 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 [7].

Acknowledgments. The paper is partially supported by the Portuguese FCT Project UID/MAT/00013/2013, by the PhD grant PD/BD/128188/2016, by the bilateral Pessoa project 7854WM and 406/4/4/2017/S “Derivation of macroscopic PDEs from kinetic theory (mesoscopic scale) and from interacting particle systems (microscopic scale)”, by the ANR project Kimega (ANR-14-ACHN-0030-01), by the French-Italian program Galileo (project G18-296), by the Italian National Research Project PRIN 2017YBKNC, by the Italian Ministry of Education, University and Research (MIUR), Dipartimenti di Eccellenza Program - Dept. of Mathematics “F. Casorati”, University of Pavia, by the University of Parma and by the Italian National Institute of Higher Mathematics INdAM–GNFM.
Appendix. In part (A) of this appendix, we give the central ideas to prove Proposition 3 stated in Subsection 4.1. Then, in parts (B) and (C), we give some details of the computation of the production terms $A^\varepsilon$ and $B_i^\varepsilon$ given in (72) and (76), respectively.

(A) Proof of Proposition 3, Subsection 4.1. By expanding the quadratic term in the first exponential appearing in the Maxwellian (49), one can split it into three exponentials. Taylor expanding with respect to $\varepsilon$ the resulting four exponentials as well as the other two terms in front of the exponentials, we can write $f_i^\varepsilon$ in the form

$$f_i^\varepsilon = \frac{n_i^\varepsilon}{q_i(T)} \left( \frac{m_i}{2\pi k_B T} \right)^{3/2} \exp \left( -\frac{m_i v_i^2}{2 k_B T} + I \right)$$

$$\times \left[ 1 + \varepsilon \frac{m_i v_i \cdot u_i}{k_B T} + \varepsilon \frac{m_i v_i^2 T^\varepsilon}{2 k_B T^2} + \varepsilon \frac{IT^\varepsilon}{k_B T} - \varepsilon \frac{q_i^\varepsilon (T)}{k_B T q_i(T)} T^\varepsilon I - \frac{3 T^\varepsilon}{2 k_B T} + O(\varepsilon^2) \right]$$

where $q_i^\varepsilon (T)$ has been defined in (62), and similar expansions hold for $f_j^\varepsilon$, $f_i^\varepsilon$, $f_j^\varepsilon$ as well as for $f_k^\varepsilon$, $f_l^\varepsilon$.

To prove part (a), we perform the products $f_i^\varepsilon f_j^\varepsilon$, $f_i^\varepsilon f_j^\varepsilon$ and use the conservation of energy for elastic collisions given in (9), to obtain

$$f_i^\varepsilon f_j^\varepsilon - f_i^\varepsilon f_j^\varepsilon = M_i M_j \left\{ \varepsilon \left[ \frac{u_i \cdot m_j (v_i^j - v)}{k_B T} \right. \right.$$

$$+ \left. \frac{u_j \cdot m_j (v_i^j - v)}{k_B T} + \frac{T^\varepsilon}{k_B T^2} \left( \frac{m_i (v_i^j)^2}{2} - \frac{m_i v_i^2}{2} + I - I \right) \right.$$ 

$$- \frac{T^\varepsilon}{k_B T^2} \left( \frac{m_j (v_i^j)^2}{2} - \frac{m_j v_i^2}{2} + I - I \right) \right\} + O(\varepsilon^2).$$

Using the conservation of momentum (8) for the two first addends within the brackets and the conservation of energy (9) for the next two addends, we obtain the result stated in equation (59). Therefore, part (a) of Proposition 3 is proven.

Similarly, to prove part (b), we perform the products $f_i^\varepsilon f_j^\varepsilon$, $f_i^\varepsilon f_j^\varepsilon$ and we obtain

$$\left( \frac{m_i m_j}{m_k m_l} \right)^3 \frac{f_k^\varepsilon f_l^\varepsilon}{f_k^\varepsilon f_l^\varepsilon} = \left( \frac{m_i m_j}{m_k m_l} \right)^3 \frac{n_k n_l (m_k m_l)^{3/2}}{q_k(T) q_l(T) (2\pi k_B T^3)^3} \exp \left( -\frac{m_i (v_i^j)^2}{2 k_B T} - \frac{m_i v_i^2}{2 k_B T} - I^j - I^l \right)$$

$$\times \left[ 1 + \varepsilon \frac{m_i u_i \cdot v_i^j}{k_B T} + \varepsilon \frac{m_i T^\varepsilon (v_i^j)^2}{2 k_B T^2} + \varepsilon \frac{T^\varepsilon I^j I^l}{k_B T^2} + \varepsilon \frac{T^\varepsilon I^j I^l}{k_B T^2} - \varepsilon \frac{T^\varepsilon q_i^\varepsilon (T) q_i^\varepsilon (T)}{k_B T q_i(T) q_l(T)} - \frac{3 T^\varepsilon}{2 k_B T} + O(\varepsilon^2) \right]$$

$$- \frac{n_k n_l}{q_k(T) q_l(T) (2\pi k_B T^3)^3} \exp \left( -\frac{m_i v_i^2}{2 k_B T} - \frac{m_j v_j^2}{2 k_B T} - I - I \right)$$

$$\times \left[ 1 + \varepsilon \frac{m_i u_i \cdot v_i^j}{k_B T} + \varepsilon \frac{m_i T^\varepsilon v_i^2}{2 k_B T^2} + \varepsilon \frac{T^\varepsilon I^j I^l}{k_B T^2} - \varepsilon \frac{T^\varepsilon q_i^\varepsilon (T) q_i^\varepsilon (T)}{k_B T q_i(T) q_l(T)} - \frac{3 T^\varepsilon}{2 k_B T} \right].$$
The production rate corresponding to species \( B \) is given by

\[
A^\varepsilon = \int_{\mathbb{R}^3} \int_{r_0}^{+\infty} Q_3^{\text{react}} \varphi_3(I) dI dv 
\]

\[
= \int_{\mathbb{R}^3} \int_{r_0}^{+\infty} \int_{\mathbb{R}^3} \int_{1}^{1} \int_{\mathbb{R}^2} \left[ \frac{m_3 m_4}{m_1 m_2} \right]^{3/2} \left[ \frac{n_1 n_2}{q_1(T) q_2(T)} \right] \exp \left( -\frac{E}{k_B T} \right) - \frac{n_3 n_4}{q_3(T) q_4(T)} \right] \times \exp \left( -\frac{m_3 v^2 + m_4 (v_4)^2}{2k_B T} \right) - \frac{I + I_4}{k_B T} \right) \times V^{\gamma - 1} \Phi_{\text{react}}(I, I_4, R, r) b^{\text{react}}(\cos \theta) (m_3 m_4)^{-2} \times \cos \theta \left( 1 - R \right) d\sigma dr dI dI dX dV. 
\]

where \( V = \|V\| \) and \( X = \|X\| \). Now, the integral in \( X \) results in

\[
\int_{\mathbb{R}^3} \exp \left( -\frac{M X^2}{2k_B T} \right) dX = \left( \frac{2\pi k_B T}{M} \right)^{3/2} , 
\]

since

\[
\int_{\mathbb{R}^3} \exp \left( -\frac{M X^2}{2k_B T} \right) dX = \int_{0}^{+\infty} \pi \int_{0}^{2\pi} X^2 \exp \left( -\frac{M X^2}{2k_B T} \right) \sin \theta d\phi d\theta dX
\]

\[
= 4\pi \int_{0}^{+\infty} X^2 \exp \left( -\frac{M X^2}{2k_B T} \right) dX. 
\]
Evaluating the previous integral using definition (68) gives the result in (92).

Also, the integral in V results in
\[
\int_{\mathbb{R}^3} V^{\gamma - 1} \exp\left(-\frac{\mu_3 V^2}{2k_B T}\right) dV = 2\pi \left(\frac{2k_B T}{\mu_3}\right)^{(\gamma + 2)/2} \Gamma\left(\frac{\gamma + 2}{2}\right). \tag{93}
\]

Indeed,
\[
\int_{\mathbb{R}^3} V^{\gamma - 1} \exp\left(-\frac{\mu_3 V^2}{2k_B T}\right) dV = \int_0^{+\infty} \int_0^\pi \int_0^{2\pi} V^{\gamma + 1} \exp\left(-\frac{\mu_3 V^2}{2k_B T}\right) \sin \theta d\phi d\theta dV
\]
\[
= 4\pi \int_0^{+\infty} V^{\gamma + 1} \exp\left(-\frac{\mu_3 V^2}{2k_B T}\right) dV.
\]

Evaluating the previous integral using definition (68) gives the result in (93).

Finally, substituting equations (92) and (93) into equation (91), we obtain the desired expression for \( A^\varepsilon \) given in (72).

\((C)\) On the computation of the simple form of the production term \( B^\varepsilon_i \) appearing in equation (76) of Subsection 4.3.

To prove part (C1), i.e. to show that the second term on the right hand side of equation (75) vanishes, it is enough to show that
\[
\int_{S^2} \sigma b_{ij} (\cos \theta) \cos \theta d\sigma = 0. \tag{94}
\]

To see this, observe that
\[
\int_{S^2} \sigma b_{ij} (\cos \theta) \cos \theta d\sigma
\]
\[
= \int_0^\pi \int_0^{2\pi} \left( \hat{x} \sin \theta \cos \phi + \hat{y} \sin \theta \sin \phi + \hat{z} \cos \theta \right) b_{ij} (\cos \theta) \cos \theta \sin \theta d\phi d\theta
\]
\[
= \hat{x} \int_0^\pi b_{ij} (\cos \theta) \sin^2 \theta \cos \theta d\theta \int_0^{2\pi} \cos \phi d\phi
\]
\[
+ \hat{y} \int_0^\pi b_{ij} (\cos \theta) \sin^2 \theta \cos \theta d\theta \int_0^{2\pi} \sin \phi d\phi + \hat{z} \int_0^\pi b_{ij} (\cos \theta) \sin \theta \cos^2 \theta d\theta \int_0^{2\pi} d\phi.
\]

To prove part (C2), i.e. to show how to obtain equation (80), we first transform to the centre of mass velocity and relative velocity and obtain
\[
\int_{\mathbb{R}^3} \int_{\mathbb{R}^3} (a_{ij} \cdot \mathbf{V}) \nu M_i^\varepsilon M_j^\varepsilon V^{\gamma - 1} d\mathbf{v} d\mathbf{v}
\]
\[
= \frac{n_i^\varepsilon n_j^\varepsilon (m_i m_j)^{3/2}}{\bar{q}_i \bar{q}_j (2\pi k_B T)^3} \exp\left(-\frac{I + I_j}{k_B T}\right) \int_{\mathbb{R}^3} (a_{ij} \cdot \mathbf{V}) \left( X - \frac{m_j \mathbf{V}}{m_i + m_j} \right)
\]
\[
\times \exp\left(-\frac{MX^2 + \mu_3 V^2}{2k_B T}\right) V^{\gamma - 1} dV dX
\]
\[
= \frac{n_i^\varepsilon n_j^\varepsilon (m_i m_j)^{3/2}}{\bar{q}_i \bar{q}_j (2\pi k_B T)^3} \exp\left(-\frac{I + I_j}{k_B T}\right) \int_{\mathbb{R}^3} X \exp\left(-\frac{MX^2}{2k_B T}\right) dX
\]
× \int_{R^3} (a_{ij} \cdot V) \exp \left( -\frac{\mu_{ij} V^2}{2k_B T} \right) V^{\gamma - 1} dV - \int_{R^3} \exp \left( -\frac{MX^2}{2k_B T} \right) dX \frac{m_j}{m_i + m_j} \\
× \int_{R^3} V (a_{ij} \cdot V) \exp \left( -\frac{\mu_{ij} V^2}{2k_B T} \right) V^{\gamma - 1} dV \right]. \tag{95}

Next we compute the integrals in X and V on the right hand side of Eq. (95). We use the fact that any vector can be written in terms of a unit vector, i.e., \( V = V \hat{v}, X = X \hat{x}, \) where \( X = \|X\|, V = \|V\|. \) Also, we write the unit vectors \( \hat{v} \) and \( \hat{x} \) in terms of the Cartesian unit vectors \( \hat{x}, \hat{y}, \hat{z} \) in \( R^3. \) Finally, we use the notation \( a_{ij} \cdot V = \|a_{ij}\| \|V\| \cos \theta = a_{ij} V \cos \theta. \)

(a) For the first integral in X appearing in the last equality of (95), we obtain
\[
\int_{R^3} X \exp \left( -\frac{MX^2}{2k_B T} \right) dX = 0, \tag{96}
\]

since
\[
\int_{R^3} X \exp \left( -\frac{MX^2}{2k_B T} \right) dX = \int_{R^3} X \hat{x} \exp \left( -\frac{MX^2}{2k_B T} \right) dX
\]
\[
= \frac{1}{2\pi} \int_0^{2\pi} \int_0^\infty X (\hat{x} \sin \theta \cos \phi + \hat{y} \sin \theta \sin \phi + \hat{z} \cos \theta) \exp \left( -\frac{MX^2}{2k_B T} \right) X^2 \sin \theta \cos \theta \sin \phi d\phi d\theta dX
\]
\[
= \hat{x} \int_0^{\infty} X^3 \exp \left( -\frac{MX^2}{2k_B T} \right) dX \int_0^\pi \sin^2 \theta \cos \theta d\theta \int_0^{2\pi} \cos \phi d\phi
\]
\[
+ \hat{y} \int_0^{\infty} X^3 \exp \left( -\frac{MX^2}{2k_B T} \right) dX \int_0^\pi \sin^2 \theta \sin \phi d\theta \int_0^{2\pi} \sin \phi d\phi
\]
\[
+ \hat{z} \int_0^{\infty} X^3 \exp \left( -\frac{MX^2}{2k_B T} \right) dX \int_0^\pi \sin \theta \cos \theta \cos \phi d\theta \int_0^{2\pi} \sin \phi d\phi = 0.
\]

(b) The second integral in X appearing in the last equality of (95) has been evaluated in part (B) of this Appendix, see Equation (92).

(c) For the first integral in V appearing in the last equality of (95), we obtain
\[
\int_{R^3} (a_{ij} \cdot V) \exp \left( -\frac{\mu_{ij} V^2}{2k_B T} \right) V^{\gamma - 1} dV = 0 \tag{97}
\]

since
\[
\int_{R^3} (a_{ij} \cdot V) \exp \left( -\frac{\mu_{ij} V^2}{2k_B T} \right) V^{\gamma - 1} dV \\
= \int_{R^3} a_{ij} V \cos \theta \exp \left( -\frac{\mu_{ij} V^2}{2k_B T} \right) V^{\gamma - 1} dV \\
= a_{ij} \int_0^{\infty} \int_0^\pi \int_0^{2\pi} V^{\gamma + 2} \exp \left( -\frac{\mu_{ij} V^2}{2k_B T} \right) \sin \theta \cos \theta d\phi d\theta dV
\]
To prove part (C3), i.e. to show that the third term on the right hand side of equation (75) vanishes, observe that using the definition of \( v'_i \) given in (54), we obtain that

\[
\begin{align*}
\frac{m_i(v'_i)^2}{2} - \frac{m_i v^2}{2} + I'_i - I &= \left( \frac{m_i^3}{2(m_i + m_j)} \right) v^2 + \left( \frac{m_j \mu_{ij} v^2}{2(m_i + m_j)} \right) + \frac{m_i \mu_{ij} (v \cdot v_j)}{m_i + m_j} \\
&+ \frac{m_i \mu_{ij} (v \cdot \sigma)}{m_i + m_j} + \frac{2R \varepsilon}{\mu_{ij}} + \frac{m_j \mu_{ij} (v_j \cdot \sigma)}{m_i + m_j} + \frac{2R \varepsilon}{\mu_{ij}} + \frac{m_j \mu_{ij} (v_j \cdot \sigma)}{m_i + m_j} + I'_i - I.
\end{align*}
\]
Substituting the previous expression into the third term on the right hand side of Equation (75) and then expanding, we obtain that such term can be given by

\[
\sum_{j=1}^{4} \frac{T_i^j - T_j^i}{k_B T^2} \left( \frac{m_i^3}{2(m_i + m_j)^2} - \frac{m_j}{2} \right) \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{0}^{+\infty} \int_{0}^{+\infty} \int_{0}^{1} \int_{S^2} v_i^2 M_i^j M_j^i V^{\gamma - 1} \times 2 \Phi_{ij}(I, I, J, R, \theta) \cos \theta (1 - R) d\sigma d\rho dI_d I_d d\nu_d dv
+ \sum_{j=1}^{4} \frac{T_i^j - T_j^i}{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_{S^2} v_i^j M_i^j M_j^i V^{\gamma - 1} \times 2 \Phi_{ij}(I, I, J, R, \theta) \cos \theta (1 - R) d\sigma d\rho dI_d I_d d\nu_d dv
+ \sum_{j=1}^{4} \frac{T_i^j - T_j^i}{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_{S^2} v_i^j M_i^j M_j^i V^{\gamma - 1} \times 2 \Phi_{ij}(I, I, J, R, \theta) \cos \theta (1 - R) d\sigma d\rho dI_d I_d d\nu_d dv
+ \sum_{j=1}^{4} \frac{T_i^j - T_j^i}{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_{S^2} v_i^j M_i^j M_j^i V^{\gamma - 1} \times 2 \Phi_{ij}(I, I, J, R, \theta) \cos \theta (1 - R) d\sigma d\rho dI_d I_d d\nu_d dv
+ \sum_{j=1}^{4} \frac{T_i^j - T_j^i}{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_{S^2} v_i^j M_i^j M_j^i V^{\gamma - 1} \times 2 \Phi_{ij}(I, I, J, R, \theta) \cos \theta (1 - R) d\sigma d\rho dI_d I_d d\nu_d dv
+ \sum_{j=1}^{4} \frac{T_i^j - T_j^i}{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_{S^2} v_i^j M_i^j M_j^i V^{\gamma - 1} \times 2 \Phi_{ij}(I, I, J, R, \theta) \cos \theta (1 - R) d\sigma d\rho dI_d I_d d\nu_d dv
+ \sum_{j=1}^{4} \frac{T_i^j - T_j^i}{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_{S^2} v_i^j M_i^j M_j^i V^{\gamma - 1} \times 2 \Phi_{ij}(I, I, J, R, \theta) \cos \theta (1 - R) d\sigma d\rho dI_d I_d d\nu_d dv
+ \sum_{j=1}^{4} \frac{T_i^j - T_j^i}{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_{S^2} v_i^j M_i^j M_j^i V^{\gamma - 1} \times 2 \Phi_{ij}(I, I, J, R, \theta) \cos \theta (1 - R) d\sigma d\rho dI_d I_d d\nu_d dv
\]

Transforming the above integrals into the center of mass velocity and relative velocity and then evaluating the resulting integrals using the same strategy as in part (C2), we obtain that the six fold integrals in \(v\) and \(v_j\) vanish in the first, second, third, sixth, seventh and eight terms of the above expression (99). Furthermore, using equation (94), we conclude that the fourth and fifth terms of expression (99) also vanish.

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Received February 2019; revised July 2019.

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