On modified simple reacting spheres kinetic model for chemically reactive gases

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Abstract

We consider the modified simple reacting spheres (MSRS) kinetic model that, in addition to the conservation of energy and momentum, also preserves the angular momentum in the collisional processes. In contrast to the line-of-center models or chemical reactive models considered in [1], in the MSRS (SRS) kinetic models, the microscopic reversibility (detailed balance) can be easily shown to be satisfied, and thus all mathematical aspects of the model can be fully justified. In the MSRS model, the molecules behave as if they were single mass points with two internal states. Collisions may alter the internal states of the molecules, and this occurs when the kinetic energy associated with the reactive motion exceeds the activation energy. Reactive and non-reactive collision events are considered to be hard spheres-like. We consider a four component mixture A, B, A^*, B^*, in which the chemical reactions are of the type $A + B \rightleftharpoons A^* + B^*$, with A^* and B^* being distinct species from A and B. We provide fundamental physical and mathematical properties of the MSRS model, concerning the consistency of the model, the entropy inequality for the reactive system, the characterization of the equilibrium solutions, the macroscopic setting of the model and the spatially homogeneous evolution. Moreover, we show that the MSRS kinetic model reduces to the previously considered SRS model (e.g., [2], [3]) if the reduced masses of the reacting pairs are the same before and after collisions, and state in the Appendix the more important properties of the SRS system.

Keywords: kinetic theory of gas mixtures, chemical reactions, hard-sphere systems.

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1 Introduction

The investigation of chemically reactive mixtures is fundamental in several practical applications, such as combustion engineering, chemical reactors and many other industrial processes. This has motivated a wide range of research works concerning theoretical and formal studies as well as physical applications and numerical simulations. In particular, in the frame of the kinetic theory of chemically reacting gases, several contributions have been advanced, after the pioneering papers by Prigogine and collaborators [4], [5], and further works by Present [6], Ross and Mazur [7], Shizgal and Karplus [8], and many others. Besides theoretical and formal studies which in particular deal with existence theory [9], [10], [11], there exists a rather vast bibliography oriented to other connected relevant topics, such as the modeling of multicomponent reactive flows [1], [12], [13], [14], analysis of transport properties [15], [16], investigation of the non-equilibrium effects induced by the chemical reactions [17], [18], construction of generalized BGK theories [15], [19], [20], as well as applications to combustion [21], just to cite a few of them.

In this work, we are interested in the simple reacting spheres (SRS) model of the kinetic theory for chemically reacting gases, that has been developed by N. Xystris, J. S. Dahler [2] and further advanced by J. S. Dahler and L. Qin in [3], [22]. Mathematical aspects of SRS, including global existence in a dilute regime, were studied in [10] and [11]. In [23] the SRS model was compared to a model of chemical reacting gases proposed in [1]. The authors in [11], [24], and [25] studied linearized versions of SRS, including kernel representations of the linear SRS and its compactness.

In the SRS kinetic theory, both elastic and reactive collisions are of hard-sphere type and reactions do not modify the diameters of the molecules. As a consequence, the micro-reversibility principle reduces to a simple condition, when compared to other kinetic theories available in literature for chemically reactive mixtures (see, for example, [1], [12], [13], [14], [16] and references cited therein). Moreover, the SRS theory incorporates other important aspects that renders the SRS kinetic model quite interesting. For example, reactive and elastic collisions are treated in equal pair, contrary to other models that treat the reactive terms as a small perturbation of the elastic ones (see, for example, [4], [5] and [8]). Therefore, the SRS kinetic theory results to be appropriate to deal with processes in which chemical reactions play an important role. Additionally, the SRS kinetic theory, if considered in its general formulation, referes to moderately dense gas systems, and when the chemical reactions are neglected, the model reduces to the revised Enskog theory.

Having all these aspects in mind, our main motivation in the present work is to extend the SRS kinetic theory to other physically relevant situations. In particular, starting from the ideas suggested in [3], we consider the modified SRS (MSRS) model, that adds the additional conservation of angular momentum into the collisional process. The SRS model includes conservation of both the total energy and the linear momentum, but does not include conservation of the angular momentum. For all the above mentioned aspects, the MSRS model turns out to be a bone fide kinetic model for reactive mixtures with all mathematical properties built in the model. Finally, we want to point out that both MSRS (SRS) kinetic models are derived directly from the pseudo-Liouville equations for the corresponding hard-sphere reactive dynamics [22].

In this work, we provide fundamental physical and mathematical properties of the dilute gas regime MSRS model that will be needed in our subsequent work. As a forthcoming work, we plan to investigate different problems associated to the MSRS model, namely existence of renormalized solutions, properties of the linearized kinetic system and kernel representation of the collisional operators, as well as the transport properties (i.e., computations of transport coefficients), and non-equilibrium effects induced by the chemical reaction.

This article is organized as follows. In Section 2 we derive the MSRS kinetic model, and study in detail the collisional dynamics. In Section 3, we consider the dilute regime of the MSRS model and state a fundamental property that will be used in the following sections to prove the mathematical and physical consistency of the model. Section 4 is devoted to the derivation of the conservation laws of the MSRS system, and Section 5 deals with the connection of the MSRS model to the macroscopic framework in terms of hydrodynamic balance equations. In Section 6 we provide the entropy identity, characterize equilibrium solutions and study the tendency of the mixture to approach the equilibrium. In Section 7 we deal with the spatially homogeneous evolution of the mixture in terms of the macroscopic equations and prove the uniqueness of the equilibrium state. Finally, in Section 8, we include an Appendix, where we state the important properties of the SRS system as a particular case of the MSRS model.

2 The MSRS kinetic model

In the MSRS model, the molecules behave as if they were single mass points with two internal states. Collisions may alter the internal states: this occurs when the kinetic energy associated with the reactive motion exceeds the activation energy. Reactive and non-reactive collision events are considered to be hard spheres-like. In a four component mixture A, B, A^*, B^*, the chemical reactions are of the type

$$A + B \rightleftharpoons A^* + B^*. \tag{1}$$

Here, A^* and B^* are distinct species from A and B. We use the indices 1, 2, 3, and 4 for the particles A, B, A^*, and B^*, respectively. Furthermore, if m_i and d_i denote the mass and the diameter of the i-th particle, $i = 1, \ldots, 4$, the reactions take place when the reactive particles are separated by a distance $\sigma_{12} = \frac{1}{2}(d_1 + d_2)$ or $\sigma_{34} = \frac{1}{2}(d_3 + d_4)$. The conservation of mass has the form

$$m_1 + m_2 = m_3 + m_4 = M, \tag{2}$$

2.1 Elastic encounters

In the case of elastic collisions between a pair of particles from species i and s, the initial velocities v, w take post–collisional values

$$v' = v - 2\frac{\mu_{is}}{m_i}\epsilon\langle\epsilon, v - w\rangle, \quad w' = w + 2\frac{\mu_{is}}{m_s}\epsilon\langle\epsilon, v - w\rangle. \tag{3}$$

Here, $\langle\cdot,\cdot\rangle$ is the inner product in $\mathbb{R}^3$, ϵ is a vector along the line passing through the centers of the spheres at the moment of impact, i.e.,

$$\epsilon \in \mathbb{S}^2_+ = \{\tilde{\epsilon} \in \mathbb{R}^3 : |\tilde{\epsilon}| = 1, \langle\tilde{\epsilon}, v - w\rangle \geq 0\}, \tag{4}$$

and

$$\mu_{is} = \frac{m_i m_s}{m_i + m_s} \tag{5}$$

is the reduced mass of the colliding pair.

2.2 Reactive encounters

For the reactive collision between particles of species i and s to occur $(i, s = 1, \ldots, 4)$, the kinetic energy associated with the relative motion along the line of centers must exceed the activation energy γ_i,

$$(1/2)\mu_{is}\big(\langle \epsilon, v - w\rangle\big)^2 \geq \gamma_i. \tag{6}$$

In order to derive the post reactive expressions for velocities v and w, we follow the arguments given in [3] for SRS model (see also the Appendix) with one difference that, in addition to assuming the conservations of momentum and total energy

$$\begin{aligned} m_1 v + m_2 w &= m_3 v^{\ddagger} + m_4 w^{\ddagger} \\ m_1 v^2 + m_2 w^2 &= m_3 v^{\ddagger 2} + m_4 w^{\ddagger 2} + 2E_{abs}, \end{aligned} \tag{7}$$

we also want to incorporate conservation of the angular momentum:

$$\mu_{12}\left[\epsilon \times (v - w)\right] = \mu_{34}\left[\epsilon \times (v^{\ddagger} - w^{\ddagger})\right]. \tag{8}$$

Thus, we replace (122) in the Appendix by

$$\sqrt{\frac{\mu_{34}}{2}}(v^{\ddagger} - w^{\ddagger}) = \sqrt{\frac{\mu_{12}}{\mu_{34}}}\sqrt{\frac{\mu_{12}}{2}}(v - w) + \Lambda'\epsilon, \tag{9}$$

where

$$\Lambda' = -\sqrt{\frac{\mu_{12}}{\mu_{34}}}\left\langle \sqrt{\frac{\mu_{12}}{2}}(v-w), \epsilon \right\rangle + \sqrt{\frac{\mu_{12}}{\mu_{34}}\left\langle \sqrt{\frac{\mu_{12}}{2}}(v-w), \epsilon \right\rangle^2 - \left[E_{abs} + \left(\frac{\mu_{12}}{\mu_{34}} - 1\right)\left(\sqrt{\frac{\mu_{12}}{2}}(v-w)\right)^2\right]}. \tag{10}$$

And finally, in the case of the reaction $A + B \to A^* + B^*$, the post-reactive values of velocities v, w are:

$$v^{\ddagger} = \frac{1}{M}\left[m_1 v + m_2 w + m_4 \frac{\mu_{12}}{\mu_{34}}\Big\{(v-w) - \epsilon\langle \epsilon, v-w\rangle\Big\} + m_4 \epsilon \sqrt{\frac{\mu_{12}}{\mu_{34}}}\alpha^-\right], \tag{11}$$

$$w^{\ddagger} = \frac{1}{M}\left[m_1 v + m_2 w - m_3 \frac{\mu_{12}}{\mu_{34}}\Big\{(v-w) - \epsilon\langle \epsilon, v-w\rangle\Big\} - m_3 \epsilon \sqrt{\frac{\mu_{12}}{\mu_{34}}}\alpha^-\right], \tag{12}$$

with

$$\alpha^- = \sqrt{\frac{\mu_{12}}{\mu_{34}}\big(\langle \epsilon, v-w\rangle\big)^2 - \frac{2E_{abs}}{\mu_{12}} - \left(\frac{\mu_{12}}{\mu_{34}} - 1\right)(v-w)^2}\,, \tag{13}$$

and E_{abs} the energy absorbed by the internal degrees of freedom. The absorbed energy E_{abs} has the property $E_{abs} = E_3 + E_4 - E_1 - E_2 > 0$, where $E_i > 0$, $i = 1, \ldots 4$, is the energy of i-th particle associated with its internal degrees of freedom. The activation energies γ_1, γ_2 for A and B are chosen to satisfy $\gamma_1 \geq E_{abs} > 0$, and by symmetry, $\gamma_2 = \gamma_1$. Also $\gamma_3 = \gamma_1 - E_{abs}$ and $\gamma_4 = \gamma_3$.

From (11)-(12), one obtains

$$\frac{1}{2}\mu_{34}(\langle \epsilon, v^{\ddagger} - w^{\ddagger}\rangle)^2 - \gamma_3 = \left(\frac{\mu_{12}}{\mu_{34}}\right)\left[\frac{1}{2}\mu_{12}\big(\langle \epsilon, v-w\rangle\big)^2 - \gamma_1\right] - \left(\frac{\mu_{12}}{\mu_{34}} - 1\right)\left[\frac{1}{2}\mu_{12}(v-w)^2 - \gamma_1\right]. \tag{14}$$

If $\frac{1}{2}\mu_{12}\big(\langle \epsilon, v-w\rangle\big)^2 - \gamma_1 \geq 0$ then (14) implies that $\frac{1}{2}\mu_{34}(\langle \epsilon, v^\ddagger - w^\ddagger\rangle)^2 - \gamma_3 \geq 0$ if $\frac{\mu_{12}}{\mu_{34}} \leq 1$. If however, $\frac{\mu_{12}}{\mu_{34}} > 1$, then $\frac{1}{2}\mu_{34}(\langle \epsilon, v^\ddagger - w^\ddagger\rangle)^2 - \gamma_3 \geq 0$ if and only if

$$\frac{1}{2}\mu_{12}\big(\langle \epsilon, v-w\rangle\big)^2 \geq \gamma_1 + \left(1 - \frac{\mu_{34}}{\mu_{12}}\right)\left[\frac{1}{2}\mu_{12}(v-w)^2 - \gamma_1\right]. \tag{15}$$

Thus, (15) implies that the reaction $A + B \to A^* + B^*$ takes place when

$$\frac{1}{2}\mu_{12}\big(\langle \epsilon, v-w\rangle\big)^2 \geq \max\left\{\gamma_1, \gamma_1 + \left(1 - \frac{\mu_{34}}{\mu_{12}}\right)\left[\frac{1}{2}\mu_{12}(v-w)^2 - \gamma_1\right]\right\}. \tag{16}$$

Additionally, for $\frac{1}{2}\mu_{12}\big(\langle \epsilon, v-w\rangle\big)^2$ satisfying inequality (16), α^- in (13) is well defined since

$$\mu_{12}\left[\frac{\mu_{12}}{\mu_{34}}\big(\langle \epsilon, v-w\rangle\big)^2 - \frac{2E_{abs}}{\mu_{12}} - \left(\frac{\mu_{12}}{\mu_{34}} - 1\right)(v-w)^2\right] = \mu_{34}(\langle \epsilon, v^\ddagger - w^\ddagger\rangle)^2. \tag{17}$$

For the inverse reaction $A^* + B^* \to A + B$, we proceed in a similar way and obtain the following expressions for $v^\dagger$ and $w^\dagger$

$$v^\dagger = \frac{1}{M}\left[m_3 v + m_4 w + m_2 \frac{\mu_{34}}{\mu_{12}}\Big\{(v-w) - \epsilon\langle \epsilon, v-w\rangle\Big\} + m_2 \epsilon \sqrt{\frac{\mu_{34}}{\mu_{12}}}\alpha^+\right], \tag{18}$$

$$w^\dagger = \frac{1}{M}\left[m_3 v + m_4 w - m_1 \frac{\mu_{34}}{\mu_{12}}\Big\{(v-w) - \epsilon\langle \epsilon, v-w\rangle\Big\} - m_1 \epsilon \sqrt{\frac{\mu_{34}}{\mu_{12}}}\alpha^+\right], \tag{19}$$

with

$$\alpha^+ = \sqrt{\frac{\mu_{34}}{\mu_{12}}\big(\langle \epsilon, v-w\rangle\big)^2 + \frac{2E_{abs}}{\mu_{34}} - \left(\frac{\mu_{34}}{\mu_{12}} - 1\right)(v-w)^2}. \tag{20}$$

From (18)-(19), one obtains

$$\frac{1}{2}\mu_{12}(\langle \epsilon, v^\dagger - w^\dagger\rangle)^2 - \gamma_1 = \left(\frac{\mu_{34}}{\mu_{12}}\right)\left[\frac{1}{2}\mu_{34}\big(\langle \epsilon, v-w\rangle\big)^2 - \gamma_3\right] - \left(\frac{\mu_{34}}{\mu_{12}} - 1\right)\left[\frac{1}{2}\mu_{34}(v-w)^2 - \gamma_3\right]. \tag{21}$$

Now, if $\frac{1}{2}\mu_{34}\big(\langle \epsilon, v-w\rangle\big)^2 - \gamma_3 \geq 0$ then (21) implies that $\frac{1}{2}\mu_{12}(\langle \epsilon, v^\dagger - w^\dagger\rangle)^2 - \gamma_1 \geq 0$ if $\frac{\mu_{34}}{\mu_{12}} \leq 1$. If however, $\frac{\mu_{34}}{\mu_{12}} > 1$ then $\frac{1}{2}\mu_{12}(\langle \epsilon, v^\dagger - w^\dagger\rangle)^2 - \gamma_1 \geq 0$ if and only if

$$\frac{1}{2}\mu_{34}\big(\langle \epsilon, v-w\rangle\big)^2 \geq \gamma_3 + \left(1 - \frac{\mu_{12}}{\mu_{34}}\right)\left[\frac{1}{2}\mu_{34}(v-w)^2 - \gamma_3\right]. \tag{22}$$

Thus, (22) implies that the reaction $A^* + B^* \to A + B$ takes place when

$$\frac{1}{2}\mu_{34}\big(\langle \epsilon, v-w\rangle\big)^2 \geq \max\left\{\gamma_3, \gamma_3 + \left(1 - \frac{\mu_{12}}{\mu_{34}}\right)\left[\frac{1}{2}\mu_{34}(v-w)^2 - \gamma_3\right]\right\}. \tag{23}$$

Additionally, for $\frac{1}{2}\mu_{34}\big(\langle \epsilon, v-w\rangle\big)^2$ satisfying inequality (23), α^+ is well defined since

$$\mu_{34}\left[\frac{\mu_{34}}{\mu_{12}}\big(\langle \epsilon, v-w\rangle\big)^2 + \frac{2E_{abs}}{\mu_{34}} - \left(\frac{\mu_{34}}{\mu_{12}} - 1\right)(v-w)^2\right] = \mu_{12}(\langle \epsilon, v^\dagger - w^\dagger\rangle)^2. \tag{24}$$

Post- and pre-collisional velocities of the reactive pairs satisfy conservation of the momentum

$$m_1 v + m_2 w = m_3 v^{\ddagger} + m_4 w^{\ddagger}, \qquad m_3 v + m_4 w = m_1 v^{\dagger} + m_2 w^{\dagger}. \tag{25}$$

A part of kinetic energy is exchanged with the energy absorbed by the internal states. The following equalities hold:

$$\begin{aligned} m_1 v^2 + m_2 w^2 &= m_3 v^{\ddagger 2} + m_4 w^{\ddagger 2} + 2E_{abs}, \\ m_3 v^2 + m_4 w^2 &= m_1 v^{\dagger 2} + m_2 w^{\dagger 2} - 2E_{abs}. \end{aligned} \tag{26}$$

Finally, using expressions (11)-(12) for the post-reactive velocities, we obtain

$$v^{\ddagger} - w^{\ddagger} = \frac{\mu_{12}}{\mu_{34}} \left[v - w - \epsilon \langle \epsilon, v - w \rangle \right] + \epsilon \sqrt{\frac{\mu_{12}}{\mu_{34}}} \alpha^{-}, \tag{27}$$

and thus the angular momentum (8) is conserved during the reactive collisional process.

An analogical formula relationship holds between $v^{\dagger}$, $w^{\dagger}$, v, and w: $\mu_{34} \left[\epsilon \times (v - w) \right] = \mu_{12} \left[\epsilon \times (v^{\dagger} - w^{\dagger}) \right]$.

We recall that in the SRS kinetic model (see the Appendix) the post-reactive velocities were given by

$$v^{\ddagger} = \frac{1}{M} \left[m_1 v + m_2 w + m_4 \sqrt{\frac{\mu_{12}}{\mu_{34}}} \left\{ (v - w) - \epsilon \langle \epsilon, v - w \rangle + \epsilon \alpha^{-}_{SRS} \right\} \right], \tag{28}$$

$$w^{\ddagger} = \frac{1}{M} \left[m_1 v + m_2 w - m_3 \sqrt{\frac{\mu_{12}}{\mu_{34}}} \left\{ (v - w) - \epsilon \langle \epsilon, v - w \rangle + \epsilon \alpha^{-}_{SRS} \right\} \right], \tag{29}$$

with $\alpha^{-}_{SRS} = \sqrt{\left(\langle \epsilon, v - w \rangle \right)^2 - 2E_{abs}/\mu_{12}}$. The corresponding expression for the relative velocities is

$$v^{\ddagger} - w^{\ddagger} = \sqrt{\frac{\mu_{12}}{\mu_{34}}} \left\{ v - w - \epsilon \left[\langle \epsilon, v - w \rangle - \alpha^{-}_{SRS} \right] \right\}, \tag{30}$$

which shows that in the SRS kinetic model, the angular momentum is not conserved during the reactive collisional process, unless $\mu_{12} = \mu_{34}$.

Furthermore, we observe that MSRS kinetic model reduces to the SRS model when $\mu_{12} = \mu_{34}$.

2.3 The system of equations

For $i = 1, 2, 3, 4$, $f_i(t, x, v)$ denotes the one-particle distribution function of the ith component of the reactive mixture, where $(t, x, v) \in \mathbb{R}^+_0 \times \Omega \times \mathbb{R}^3$, with $\Omega \subseteq \mathbb{R}^3$ being the spatial domain of the gas mixture. Functions $f_i(t, x, v)$, which change in time due to free streaming and collisions (elastic and reactive), represent, at time t, the number densities of particles of species i at point x with velocity v.

The MSRS kinetic system has the form

$$\frac{\partial f_i}{\partial t} + v \frac{\partial f_i}{\partial x} = J^E_i + J^R_i, \quad i = 1, 2, 3, 4, \tag{31}$$

where J^E_i is the non-reactive (hard-sphere) collision operator

$$\begin{aligned} J^E_i = \sum_{s=1}^{4} \Bigg\{ \sigma^2_{is} \iint\limits_{\mathbb{R}^3 \times \mathbb{S}^2_+} \left[f^{(2)}_{is}(t, x, v', x - \sigma_{is}\epsilon, w') - f^{(2)}_{is}(t, x, v, x + \sigma_{is}\epsilon, w) \right] \langle \epsilon, v - w \rangle \, d\epsilon dw \Bigg\} \\ - \beta_{ij} \sigma^2_{ij} \iint\limits_{\mathbb{R}^3 \times \mathbb{S}^2_+} \left[f^{(2)}_{ij}(t, x, v', x - \sigma_{ij}\epsilon, w') - f^{(2)}_{ij}(t, x, v, x + \sigma_{ij}\epsilon, w) \right] \Theta(\langle \epsilon, v - w \rangle - \Gamma_{ij}) \langle \epsilon, v - w \rangle d\epsilon dw, \end{aligned} \tag{32}$$

with $\mathbb{S}^2_+ = \{\tilde{\epsilon} \in \mathbb{R}^3 : |\tilde{\epsilon}| = 1, \langle \tilde{\epsilon}, v - w \rangle \geq 0\}$, and $f^{(2)}_{is}(t, x_1, v_1, x_2, v_2)$ approximates the density of pairs of particles in collisional configurations. The second term in (32), with β_{ij} in front of it, singles out those pre-collisional states that are energetic enough to result in the reaction, and thus preventing double counting of the events in the collisional integrals. In the case when $\beta_{ij} = 0$, for $i, j = 1, \dots, 4$, (31)-(32) reduces to the first BBGKY-hierarchy system for 4-species inert mixtures.

For $i = 1, 2, 3, 4$, the reactive terms are

$$J^R_i = \beta_{ij}\sigma^2_{ij} \iiint\limits_{\mathbb{R}^3\times\mathbb{S}^2_+} \left[\left(\frac{\mu_{ij}}{\mu_{kl}}\right)^3 f^{(2)}_{kl}(t, x, v^{\odot}_{ij}, x-\sigma_{ij}\epsilon, w^{\odot}_{ij}) - f^{(2)}_{ij}(t, x, v, x+\sigma_{ij}\epsilon, w) \right] \Theta\left(\langle \epsilon, v - w\rangle - \Gamma_{ij}\right) \langle \epsilon, v-w\rangle d\epsilon dw. \tag{33}$$

Here, $0 \leq \beta_{ij} \leq 1$ are the steric factors, $\Gamma_{ij} = \sqrt{\max\left\{2\gamma_i/\mu_{ij}, 2\gamma_i/\mu_{ij} + \left(1 - \frac{\mu_{kl}}{\mu_{ij}}\right)[(v-w)^2 - 2\gamma_i/\mu_{ij}]\right\}}$ and Θ is the Heaviside step function. The pairs of post-reactive velocities are $(v^{\odot}_{ij}, w^{\odot}_{ij}) = (v^{\ddagger}, w^{\ddagger})$ for $i, j = 1, 2$, given in (11)-(12), and $(v^{\odot}_{ij}, w^{\odot}_{ij}) = (v^{\dagger}, w^{\dagger})$ for $i, j = 3, 4$, given in (18)-(19). Pairs of indices (i, j) and (k, l) are from the set of quadruples (i, j, k, l):

$$\{(1, 2, 3, 4),\ (2, 1, 4, 3),\ (3, 4, 1, 2),\ (4, 3, 2, 1)\}. \tag{34}$$

Finally, we observe that in view of (15)-(16) and (22)-(23), the Heaviside functions $\Theta(\langle\epsilon, v-w\rangle - \Gamma_{ij})$ appearing in (32)-(33) can be replaced by the product of the symmetric pair of Heaviside functions:

$$\Theta\left(\langle \epsilon, v - w\rangle - \Gamma^*_{ij}\right) \Theta\left(\langle \epsilon, v^{\odot}_{ij} - w^{\odot}_{ij}\rangle - \Gamma^*_{kl}\right), \tag{35}$$

with $\Gamma^*_{ij} = \sqrt{2\gamma_i/\mu_{ij}}$ and the pairs of indices (i, j) and (k, l) are from the set of quadruples given in (34). Therefore, (32) becomes

$$\begin{aligned} J^E_i =& \sum_{s=1}^{4} \left\{ \sigma^2_{is} \iiint\limits_{\mathbb{R}^3\times\mathbb{S}^2_+} \left[f^{(2)}_{is}(t, x, v', x - \sigma_{is}\epsilon, w') - f^{(2)}_{is}(t, x, v, x + \sigma_{is}\epsilon, w) \right] \langle \epsilon, v - w\rangle\, d\epsilon dw \right\} \\ & - \beta_{ij}\sigma^2_{ij} \iiint\limits_{\mathbb{R}^3\times\mathbb{S}^2_+} \left[f^{(2)}_{ij}(t, x, v', x - \sigma_{ij}\epsilon, w') - f^{(2)}_{ij}(t, x, v, x + \sigma_{ij}\epsilon, w) \right] \times \\ & \Theta\left(\langle \epsilon, v - w\rangle - \Gamma^*_{ij}\right) \Theta\left(\langle \epsilon, v^{\odot}_{ij} - w^{\odot}_{ij}\rangle - \Gamma^*_{kl}\right) \langle \epsilon, v - w\rangle d\epsilon dw, \end{aligned} \tag{36}$$

and (33) becomes

$$\begin{aligned} J^R_i =& \beta_{ij}\sigma^2_{ij} \iiint\limits_{\mathbb{R}^3\times\mathbb{S}^2_+} \left[\left(\frac{\mu_{ij}}{\mu_{kl}}\right)^3 f^{(2)}_{kl}(t, x, v^{\odot}_{ij}, x-\sigma_{ij}\epsilon, w^{\odot}_{ij}) - f^{(2)}_{ij}(t, x, v, x+\sigma_{ij}\epsilon, w) \right] \times \\ & \Theta\left(\langle \epsilon, v - w\rangle - \Gamma^*_{ij}\right) \Theta\left(\langle \epsilon, v^{\odot}_{ij} - w^{\odot}_{ij}\rangle - \Gamma^*_{kl}\right) \langle \epsilon, v - w\rangle d\epsilon dw. \end{aligned} \tag{37}$$

Lemma 2.1.

(1) *For $i, s = 1, 2, 3, 4$, the inverse velocities to v', w' are given by*

$$v = v' - 2\frac{\mu_{is}}{m_i}\epsilon\langle \epsilon, v' - w'\rangle, \quad w = w' + 2\frac{\mu_{is}}{m_s}\epsilon\langle \epsilon, v' - w'\rangle. \tag{38}$$

For fixed ϵ, the Jacobian of the transformation $(v, w) \mapsto (v', w')$ is equal to -1. Furthermore, $\langle \epsilon, v' - w'\rangle = -\langle \epsilon, v - w\rangle$,

(2) *The inverse velocities to* $v^\ddagger$, $w^\ddagger$ *are given by*

$$v = \frac{1}{M}\left[m_3 v^\ddagger + m_4 w^\ddagger + m_2 \frac{\mu_{34}}{\mu_{12}}\left\{(v^\ddagger - w^\ddagger) - \epsilon\langle\epsilon, v^\ddagger - w^\ddagger\rangle\right\} + m_2\epsilon\sqrt{\frac{\mu_{34}}{\mu_{12}}}\alpha^+\right], \tag{39}$$

$$w = \frac{1}{M}\left[m_3 v^\ddagger + m_4 w^\ddagger - m_1 \frac{\mu_{34}}{\mu_{12}}\left\{(v^\ddagger - w^\ddagger) - \epsilon\langle\epsilon, v^\ddagger - w^\ddagger\rangle\right\} - m_1\epsilon\sqrt{\frac{\mu_{34}}{\mu_{12}}}\alpha^+\right], \tag{40}$$

and the inverse velocities to $v^\dagger$, $w^\dagger$ *are given by*

$$v = \frac{1}{M}\left[m_1 v^\dagger + m_2 w^\dagger + m_4 \frac{\mu_{12}}{\mu_{34}}\left\{(v^\dagger - w^\dagger) - \epsilon\langle\epsilon, v^\dagger - w^\dagger\rangle\right\} + m_4\epsilon\sqrt{\frac{\mu_{12}}{\mu_{34}}}\alpha^-\right], \tag{41}$$

$$w = \frac{1}{M}\left[m_1 v^\dagger + m_2 w^\dagger - m_3 \frac{\mu_{12}}{\mu_{34}}\left\{(v^\dagger - w^\dagger) - \epsilon\langle\epsilon, v^\dagger - w^\dagger\rangle\right\} - m_3\epsilon\sqrt{\frac{\mu_{12}}{\mu_{34}}}\alpha^-\right]. \tag{42}$$

(3) *For fixed* ϵ, *the Jacobians of the transformations* $(v, w) \mapsto (v^\dagger, w^\dagger)$ *and* $(v, w) \mapsto (v^\ddagger, w^\ddagger)$ *are given by*

$$\left(\frac{\mu_{34}}{\mu_{12}}\right)^{5/2} \frac{\langle\epsilon, v - w\rangle}{\alpha^+} \quad \textit{and} \quad \left(\frac{\mu_{12}}{\mu_{34}}\right)^{5/2} \frac{\langle\epsilon, v - w\rangle}{\alpha^-}, \tag{43}$$

respectively.

(4) Furthermore, $\langle\epsilon, v^\dagger - w^\dagger\rangle = \left(\frac{\mu_{34}}{\mu_{12}}\right)^{1/2}\alpha^+$, $\langle\epsilon, v^\ddagger - w^\ddagger\rangle = \left(\frac{\mu_{12}}{\mu_{34}}\right)^{1/2}\alpha^-$.

Proof of Lemma 2.1. The proof of item (1) of Lemma 2.1 is almost the same as in the case of a single specie Boltzmann equation and will not be given here. The identities in (39)-(42) can be checked by easy inspection.

For the proof of item (3) of Lemma 2.1, consider the Jacobians $J(v^\dagger, w^\dagger; G_{12}^+, V^\dagger)$, $J(G_{12}^\dagger, V^\dagger; G_{34}, V)$, and $J(G_{34}, V; v, w)$ of the transformations $(G_{12}^+, V^\dagger) \mapsto (v^\dagger, w^\dagger)$, $(G_{34}, V) \mapsto (G_{12}^\dagger, V^\dagger)$, and $(v, w) \mapsto (G_{34}, V)$, respectively, where

$$\begin{aligned}
G_{34}(v, w) &= m_3 v + m_4 w, && \text{(the momentum of the colliding pair before reaction)}\\
V(v, w) &= v - w, && \text{(the relative velocity of the colliding pair before reaction)}\\
G_{12}^\dagger(v^\dagger, w^\dagger) &= m_1 v^\dagger + m_2 w^\dagger, && \text{(the momentum of the colliding pair after reaction)}\\
V^\dagger(v^\dagger, w^\dagger) &= v^\dagger - w^\dagger. && \text{(the relative velocity of the colliding pair after reaction)}
\end{aligned} \tag{44}$$

The following equality holds:

$$J(v^\dagger, w^\dagger; v, w) = J(v^\dagger, w^\dagger; G_{12}^\dagger, V^\dagger) \cdot J(G_{12}^\dagger, V^\dagger; G_{34}, V) \cdot J(G_{34}, V; v, w). \tag{45}$$

Now, both $(G_{12}^+, V^\dagger) \mapsto (v^\dagger, w^\dagger)$ and $(v, w) \mapsto (G_{34}, V)$ are linear transformations with the corresponding matrices

$$\begin{bmatrix}
\frac{1}{m_1+m_2} & 0 & 0 & \frac{m_2}{m_1+m_2} & 0 & 0\\
0 & \frac{1}{m_1+m_2} & 0 & 0 & \frac{m_2}{m_1+m_2} & 0\\
0 & 0 & \frac{1}{m_1+m_2} & 0 & 0 & \frac{m_2}{m_1+m_2}\\
\frac{1}{m_1+m_2} & 0 & 0 & -\frac{m_1}{m_1+m_2} & 0 & 0\\
0 & \frac{1}{m_1+m_2} & 0 & 0 & -\frac{m_1}{m_1+m_2} & 0\\
0 & 0 & \frac{1}{m_1+m_2} & 0 & 0 & -\frac{m_1}{m_1+m_2}
\end{bmatrix} \quad \text{and} \quad \begin{bmatrix}
m_3 & 0 & 0 & m_4 & 0 & 0\\
0 & m_3 & 0 & 0 & m_4 & 0\\
0 & 0 & m_3 & 0 & 0 & m_4\\
1 & 0 & 0 & -1 & 0 & 0\\
0 & 1 & 0 & 0 & -1 & 0\\
0 & 0 & 1 & 0 & 0 & -1
\end{bmatrix}, \tag{46}$$

respectively. The determinants of the matrices in (46) are $-1/(m_1+m_2)^3$ and $-(m_3+m_4)^3$, respectively. Therefore, the conservation of mass before and after reaction, $m_1+m_2=m_3+m_4$, yields the identity $J(v^\dagger,w^\dagger;G_{12}^\dagger,V^\dagger)\cdot J(G_{34},V;v,w)=1$.

The conservation of momentum before and after reaction implies that $G_{12}^\dagger=G_{34}$ (see, (25)), and thus,

$$J(G_{12}^\dagger,V^\dagger;G_{34},V)=\begin{bmatrix}\frac{\partial G_1^\dagger}{\partial G_1} & \frac{\partial G_1^\dagger}{\partial G_2} & \frac{\partial G_1^\dagger}{\partial G_3} & \frac{\partial G_1^\dagger}{\partial V_1} & \frac{\partial G_1^\dagger}{\partial V_2} & \frac{\partial G_1^\dagger}{\partial V_3}\\ \frac{\partial G_2^\dagger}{\partial G_1} & \frac{\partial G_2^\dagger}{\partial G_2} & \frac{\partial G_2^\dagger}{\partial G_3} & \frac{\partial G_2^\dagger}{\partial V_1} & \frac{\partial G_2^\dagger}{\partial V_2} & \frac{\partial G_2^\dagger}{\partial V_3}\\ \frac{\partial G_3^\dagger}{\partial G_1} & \frac{\partial G_3^\dagger}{\partial G_2} & \frac{\partial G_3^\dagger}{\partial G_3} & \frac{\partial G_3^\dagger}{\partial V_1} & \frac{\partial G_3^\dagger}{\partial V_2} & \frac{\partial G_3^\dagger}{\partial V_3}\\ \frac{\partial V_1^\dagger}{\partial G_1} & \frac{\partial V_1^\dagger}{\partial G_2} & \frac{\partial V_1^\dagger}{\partial G_3} & \frac{\partial V_1^\dagger}{\partial V_1} & \frac{\partial V_1^\dagger}{\partial V_2} & \frac{\partial V_1^\dagger}{\partial V_3}\\ \frac{\partial V_2^\dagger}{\partial G_1} & \frac{\partial V_2^\dagger}{\partial G_2} & \frac{\partial V_2^\dagger}{\partial G_3} & \frac{\partial V_2^\dagger}{\partial V_1} & \frac{\partial V_2^\dagger}{\partial V_2} & \frac{\partial V_2^\dagger}{\partial V_3}\\ \frac{\partial V_3^\dagger}{\partial G_1} & \frac{\partial V_3^\dagger}{\partial G_2} & \frac{\partial V_3^\dagger}{\partial G_3} & \frac{\partial V_3^\dagger}{\partial V_1} & \frac{\partial V_3^\dagger}{\partial V_2} & \frac{\partial V_3^\dagger}{\partial V_3}\end{bmatrix}=\begin{bmatrix}1&0&0&0&0&0\\0&1&0&0&0&0\\0&0&1&0&0&0\\ \frac{\partial V_1^\dagger}{\partial G_1} & \frac{\partial V_1^\dagger}{\partial G_2} & \frac{\partial V_1^\dagger}{\partial G_3} & \frac{\partial V_1^\dagger}{\partial V_1} & \frac{\partial V_1^\dagger}{\partial V_2} & \frac{\partial V_1^\dagger}{\partial V_3}\\ \frac{\partial V_2^\dagger}{\partial G_1} & \frac{\partial V_2^\dagger}{\partial G_2} & \frac{\partial V_2^\dagger}{\partial G_3} & \frac{\partial V_2^\dagger}{\partial V_1} & \frac{\partial V_2^\dagger}{\partial V_2} & \frac{\partial V_2^\dagger}{\partial V_3}\\ \frac{\partial V_3^\dagger}{\partial G_1} & \frac{\partial V_3^\dagger}{\partial G_2} & \frac{\partial V_3^\dagger}{\partial G_3} & \frac{\partial V_3^\dagger}{\partial V_1} & \frac{\partial V_3^\dagger}{\partial V_2} & \frac{\partial V_3^\dagger}{\partial V_3}\end{bmatrix}=J(V^\dagger,V), \tag{47}$$

where we used vector notations $G_{12}^\dagger=(G_1^\dagger,G_2^\dagger,G_3^\dagger)$, $G_{34}=(G_1,G_2,G_3)$, $V^\dagger=(V_1^\dagger,V_2^\dagger,V_3^\dagger)$, $V=(V_1,V_2,V_3)$, and with $J(V^\dagger,V)$ being the Jacobian of the transformation $V\mapsto V^\dagger$:

$$V^\dagger=\frac{\mu_{34}}{\mu_{12}}\left[V-\epsilon\langle\epsilon,V\rangle\right]+\epsilon\sqrt{\frac{\mu_{34}}{\mu_{12}}}\sqrt{\frac{\mu_{34}}{\mu_{12}}\left(\langle\epsilon,V\rangle\right)^2+\frac{2E_{abs}}{\mu_{34}}-\left(\frac{\mu_{34}}{\mu_{12}}-1\right)V^2}. \tag{48}$$

Finally, by inspection, it is easy to check that

$$J(V^\dagger,V)=\left(\frac{\mu_{34}}{\mu_{12}}\right)^{5/2}\frac{\langle\epsilon,V\rangle}{\sqrt{\frac{\mu_{34}}{\mu_{12}}\left(\langle\epsilon,V\rangle\right)^2+\frac{2E_{abs}}{\mu_{34}}-\left(\frac{\mu_{34}}{\mu_{12}}-1\right)V^2}}. \tag{49}$$

This shows that $J(v^\dagger,w^\dagger;v,w)=\left(\frac{\mu_{34}}{\mu_{12}}\right)^{5/2}\frac{\langle\epsilon,v-w\rangle}{\alpha^+}$.

The proof that $J(v^\ddagger,w^\ddagger;v,w)=\left(\frac{\mu_{12}}{\mu_{34}}\right)^{5/2}\frac{\langle\epsilon,v-w\rangle}{\alpha^-}$ follows the same arguments as above.

The two identities in item (4) of Lemma 2.1 follow from the definitions of $v^\ddagger$, $w^\ddagger$ and $v^\dagger$, $w^\dagger$ given in (11)-(12) and (18)-(19), respectively. □

3 The dilute MSRS kinetic system

The system of equations (31)-(33) (or, equivalently, (31) with (36)-(37)) requires a closure relation for $f_{is}^{(2)}$. In the case of moderately dense gases, the two-particle distribution function $f_{is}^{(2)}$ is usually approximated by

$$f_{is}^{(2)}(t,x_1,v_1,x_2,v_2)=g_{is}^{(2)}\left(x_1,x_2\,|\,\{n_i(t,\cdot)\}\right)f_i(t,x_1,v_1)f_s(t,x_2,v_2), \tag{50}$$

where $n_i(t,x)=\int_{\mathbb{R}^3}f_i(t,x,v)dv$ is the local number density of the component i and $g_{ij}^{(2)}$ is the known pair correlation function for a **non-uniform** hard-sphere system at equilibrium with the local densities $n_i(t,x)$. The notation $g_{ij}^{(2)}(x_1,x_2\,|\,\{n_i(t,\cdot)\})$ indicates that $g_{ij}^{(2)}$ is a functional of the local densities n_i. The closure relation (50) is employed in [3] and [22]. Additionally, in the case of non-reactive mixtures

($\beta_{ij} = 0$, for $i = 1, \dots 4$), the corresponding system of equations (31)-(32) becomes the revised Enskog system for the mixtures [26].

In this work, we will consider only a dilute gas regime with the corresponding closure relation given by:

$$f_{is}^{(2)}(t, x_1, v_1, x_2, v_2) = f_i(t, x_1, v_1) f_s(t, x_2, v_2). \tag{51}$$

The moderately dense case of MSRS model, with the closure relation (50) will be considered in our forthcoming work.

In the dilute gas regime, the system of equations (31) with (36)-(37) takes the form:

$$\frac{\partial f_i}{\partial t} + v \frac{\partial f_i}{\partial x} = J_i^E + J_i^R, \quad f_i(0, x, v) = f_{i0}(x, v), \quad i = 1, \dots, 4, \quad (x, v) \in \Omega \times \mathbb{R}^3, \tag{52}$$

with

$$\begin{aligned} J_i^E =& \sum_{s=1}^{4} \left\{ \sigma_{is}^2 \iint_{\mathbb{R}^3 \times \mathbb{S}_+^2} \Big[f_i(t, x, v') f_s(t, x, w') - f_i(t, x, v) f_s(t, x, w) \Big] \langle \epsilon, v - w \rangle \, d\epsilon dw \right\} \\ & - \beta_{ij} \sigma_{ij}^2 \iint_{\mathbb{R}^3 \times \mathbb{S}_+^2} \Big[f_i(t, x, v') f_j(t, x, w') - f_i(t, x, v) f_j(t, x, w) \Big] \times \\ & \Theta \left(\langle \epsilon, v - w \rangle - \Gamma_{ij}^* \right) \Theta \left(\langle \epsilon, v_{ij}^{\odot} - w_{ij}^{\odot} \rangle - \Gamma_{kl}^* \right) \langle \epsilon, v - w \rangle d\epsilon dw, \end{aligned} \tag{53}$$

and

$$\begin{aligned} J_i^R =& \beta_{ij} \sigma_{ij}^2 \iint_{\mathbb{R}^3 \times \mathbb{S}_+^2} \left[\left(\frac{\mu_{ij}}{\mu_{kl}} \right)^3 f_k(t, x, v_{ij}^{\odot}) f_l(t, x, w_{ij}^{\odot}) - f_i(t, x, v) f_j(t, x, w) \right] \times \\ & \Theta \left(\langle \epsilon, v - w \rangle - \Gamma_{ij}^* \right) \Theta \left(\langle \epsilon, v_{ij}^{\odot} - w_{ij}^{\odot} \rangle - \Gamma_{kl}^* \right) \langle \epsilon, v - w \rangle d\epsilon dw, \end{aligned} \tag{54}$$

where f_{i0}, $i = 1, \dots, 4$ are suitable nonnegative initial conditions that will be defined later and $\Omega \subseteq \mathbb{R}^3$ denotes the spatial domain of the gas mixture. We consider two choices for the set Ω: $\Omega = \mathbb{R}^3$, or Ω being a 3-dimensional torus $[0, L]^3$, $L > 0$. The latter choice corresponds to the case of the periodic boundary conditions on $[0, L]^3$. Also, $\Gamma_{ij}^* = \sqrt{2\gamma_i / \mu_{ij}}$ and Θ is the Heaviside step function.

As before, the pairs of post-reactive velocities are $(v_{ij}^{\odot}, w_{ij}^{\odot}) = (v^{\ddagger}, w^{\ddagger})$ for $i, j = 1, 2$, given in (11)-(12), and $(v_{ij}^{\odot}, w_{ij}^{\odot}) = (v^{\dagger}, w^{\dagger})$ for $i, j = 3, 4$, given in (18)-(19). The pairs of indices (i, j) and (k, l) are from the set of quadruples (i, j, k, l) : $\{(1, 2, 3, 4), (2, 1, 4, 3), (3, 4, 1, 2), (4, 3, 2, 1)\}$.

Proposition 3.1. *Assume that $\beta_{ij} = \beta_{ji}$ for $(i, j) \in \{(1, 2), (2, 1), (3, 4), (4, 3)\}$. For ϕ_i measurable on $\Omega \times \mathbb{R}^3$ and $f_i \in C_0(\Omega \times \mathbb{R}^3)$, $i = 1, \dots, 4$, we have:*

$$\begin{aligned} \sum_{i=1}^{4} \int_{\mathbb{R}^3} \phi_i J_i^E \, dv =& \sum_{i=1}^{4} \sum_{s=1}^{4} \sigma_{is}^2 \iiint_{\mathbb{R}^3 \times \mathbb{R}^3 \times \mathbb{S}_+^2} \left[\phi_i(x, v) + \phi_s(x, w) - \phi_i(x, v') - \phi_s(x, w') \right] \times \\ & \left[f_i(v') f_s(w') - f_i(v) f_s(w) \right] \langle \epsilon, v - w \rangle \Xi_{is} \, d\epsilon dw dv, \end{aligned} \tag{55}$$

$$\sum_{i=1}^{4}\int_{\mathbb{R}^3}\phi_i J_i^R\,dv=\iiint_{\mathbb{R}^3\times\mathbb{R}^3\times\mathbb{S}^2_+}\left[\beta_{12}\sigma_{12}^2\phi_1(x,v)+\beta_{21}\sigma_{21}^2\phi_2(x,w)-\beta_{34}\sigma_{34}^2\phi_3(x,v^{\ddagger})-\beta_{43}\sigma_{43}^2\phi_4(x,w^{\ddagger})\right]\times$$
$$\left[\left(\frac{\mu_{12}}{\mu_{34}}\right)^3 f_3(x,v^{\ddagger})f_4(x,w^{\ddagger})-f_1(x,v)f_2(x,w)\right]\Theta(\langle\epsilon,v-w\rangle-\Gamma_{12}^*)\Theta(\langle\epsilon,v^{\ddagger}-w^{\ddagger}\rangle-\Gamma_{34}^*)\langle\epsilon,v-w\rangle\,d\epsilon dw dv, \tag{56}$$

and

$$\sum_{i=1}^{4}\int_{\mathbb{R}^3}\phi_i J_i^R\,dv=\iiint_{\mathbb{R}^3\times\mathbb{R}^3\times\mathbb{S}^2_+}\left[\beta_{34}\sigma_{34}^2\phi_3(x,v)+\beta_{43}\sigma_{43}^2\phi_4(x,w)-\beta_{12}\sigma_{12}^2\phi_1(x,v^{\dagger})-\beta_{21}\sigma_{21}^2\phi_2(x,v^{\dagger})\right]\times$$
$$\left[\left(\frac{\mu_{34}}{\mu_{12}}\right)^3 f_1(x,v^{\dagger})f_2(x,w^{\dagger})-f_3(x,v)f_4(x,w)\right]\Theta(\langle\epsilon,v-w\rangle-\Gamma_{34}^*)\Theta(\langle\epsilon,v^{\dagger}-w^{\dagger}\rangle-\Gamma_{12}^*)\langle\epsilon,v-w\rangle\,d\epsilon dw dv, \tag{57}$$

where Ξ_{is}, appearing in (55), is given by

$$\Xi_{is}=\begin{cases}\frac{1}{2}\Theta(\langle\epsilon,v-w\rangle)+\frac{1}{2}(1-\beta_{is})\Theta\left(\langle\epsilon,v-w\rangle-\Gamma_{is}^*\right)\Theta\left(\langle\epsilon,v_{is}^{\odot}-w_{is}^{\odot}\rangle-\Gamma_{kl}^*\right) & \text{if } (i,s)\in I;\\ \frac{1}{4}\Theta(\langle\epsilon,v-w\rangle), & \text{if } i=s;\\ \frac{1}{2}\Theta(\langle\epsilon,v-w\rangle), & \text{otherwise,}\end{cases} \tag{58}$$

with $I=\{(1,2),(2,1),(3,4),(4,3)\}$ and the pairs of indices (i,s) and (k,l) are from the set of quadruples (i,s,k,l) : $\{(1,2,3,4),\ (2,1,4,3),\ (3,4,1,2),\ (4,3,2,1)\}$ and $(v_{is}^{\odot},w_{is}^{\odot})=(v^{\ddagger},w^{\ddagger})$ for $i,s=1,2$, and $(v_{is}^{\odot},w_{is}^{\odot})=(v^{\dagger},w^{\dagger})$ for $i,s=3,4$.
The post-collisional velocities, v' and w' are given in (3), while the post-reactive velocities, $v^{\ddagger}$, $w^{\ddagger}$ and $v^{\dagger}$, $w^{\dagger}$, are given in (11)-(12) and (18)-(19), respectively.

Proof. The proof of (55) is standard, see, for example, [27], for single specie treatment. The proof for gas mixtures is similar: it is based on the fact that the absolute value of the Jacobians of the transformations $(v,w)\mapsto(v',w')$ and $(v,w)\mapsto(w,v)$ is one, together with the identity $\langle\epsilon,v-w\rangle=\langle-\epsilon,w-v\rangle$. The change of variables, $(v,w)\mapsto(v',w')$, $(v,w)\mapsto(w,v)$, and $\epsilon\mapsto-\epsilon$, together with the fact that $\beta_{is}=\beta_{si}$, results in (55). The multiplicative factor Ξ_{is} comes from the fact that the second term of the reactive collisional integral (54), with β_{ij} in front of it, singles out those pre-collisional states that are energetic enough to result in the reaction, and thus preventing double counting of the events in the collisional integrals (53)–(54).

Next, we consider the integrals

$$\int_{\mathbb{R}^3}\phi_1 J_1^R\,dv=\beta_{12}\sigma_{12}^2\iiint_{\mathbb{R}^3\times\mathbb{R}^3\times\mathbb{S}^2_+}\phi_1(v)\left[\left(\frac{\mu_{12}}{\mu_{34}}\right)^3 f_3(v^{\ddagger})f_4(w^{\ddagger})-f_1(v)f_2(w)\right]\langle\epsilon,v-w\rangle\Theta_{1234}\,d\epsilon dw dv, \tag{59}$$

$$\int_{\mathbb{R}^3}\phi_2 J_2^R\,dv=\beta_{21}\sigma_{21}^2\iiint_{\mathbb{R}^3\times\mathbb{R}^3\times\mathbb{S}^2_+}\phi_2(v)\left[\left(\frac{\mu_{12}}{\mu_{34}}\right)^3 f_4(v^{\ddagger})f_3(w^{\ddagger})-f_2(v)f_1(w)\right]\langle\epsilon,v-w\rangle\Theta_{1234}\,d\epsilon dw dv, \tag{60}$$

$$\int_{\mathbb{R}^3}\phi_3 J_3^R\,dv=\beta_{34}\sigma_{34}^2\iiint_{\mathbb{R}^3\times\mathbb{R}^3\times\mathbb{S}^2_+}\phi_3(v)\left[\left(\frac{\mu_{34}}{\mu_{12}}\right)^3 f_1(v^{\dagger})f_2(w^{\dagger})-f_3(v)f_4(w)\right]\langle\epsilon,v-w\rangle\Theta_{3412}\,d\epsilon dw dv, \tag{61}$$

and

$$\int_{\mathbb{R}^3} \phi_4 J_4^R \, dv = \beta_{43}\sigma_{43}^2 \iiint_{\mathbb{R}^3\times\mathbb{R}^3\times\mathbb{S}_+^2} \phi_4(v) \left[\left(\frac{\mu_{34}}{\mu_{12}}\right)^3 f_2(v^\dagger) f_1(w^\dagger) - f_4(v) f_3(w) \right] \langle \epsilon, v-w\rangle \Theta_{3412} \, d\epsilon dw dv, \qquad (62)$$

appearing in the sum on the left hand side of (56). Also, $\Theta_{1234} = \Theta(\langle \epsilon, v-w\rangle - \Gamma_{12}^*)\Theta(\langle \epsilon, v^\ddagger - w^\ddagger\rangle - \Gamma_{34}^*)$, in (59)–(60), and $\Theta_{3412} = \Theta(\langle \epsilon, v-w\rangle - \Gamma_{34}^*)\Theta(\langle \epsilon, v^\dagger - w^\dagger\rangle - \Gamma_{12}^*)$, in (61)–(62). We also suppressed x dependence in ϕ_i and f_i. Changing the variables of integration in (61)–(62) from (v,w) to $(v^\dagger, w^\dagger)$ and using (43) together with the identity $\langle \epsilon, v^\dagger - w^\dagger\rangle = \left(\frac{\mu_{34}}{\mu_{12}}\right)^{1/2} \alpha^+$ of Lemma 2.1, one obtains,

$$\int_{\mathbb{R}^3} \phi_3 J_3^R \, dv = \beta_{34}\sigma_{34}^2 \iiint_{\mathbb{R}^3\times\mathbb{R}^3\times\mathbb{S}_+^2} \phi_3(v)\left[\left(\frac{\mu_{34}}{\mu_{12}}\right)^3 f_1(v^\dagger) f_2(w^\dagger) - f_3(v) f_4(w) \right]\left(\frac{\mu_{12}}{\mu_{34}}\right)^3 \langle \epsilon, v^\dagger - w^\dagger\rangle \Theta_{3412} \, d\epsilon dw^\dagger dv^\dagger \qquad (61')$$

and

$$\int_{\mathbb{R}^3} \phi_4 J_4^R \, dv = \beta_{43}\sigma_{43}^2 \iiint_{\mathbb{R}^3\times\mathbb{R}^3\times\mathbb{S}_+^2} \phi_4(v)\left[\left(\frac{\mu_{34}}{\mu_{12}}\right)^3 f_2(v^\dagger) f_1(w^\dagger) - f_4(v) f_3(w) \right]\left(\frac{\mu_{12}}{\mu_{34}}\right)^3 \langle \epsilon, v^\dagger - w^\dagger\rangle \Theta_{3412} \, d\epsilon dw^\dagger dv^\dagger. \qquad (62')$$

Next, from (41)-(42) of Lemma 2.1, the expressions for v and w (as the functions of $v^\dagger$, $w^\dagger$) are:

$$v = \frac{1}{M}\left[m_1 v^\dagger + m_2 w^\dagger + m_4 \frac{\mu_{12}}{\mu_{34}} \left\{ (v^\dagger - w^\dagger) - \epsilon\langle \epsilon, v^\dagger - w^\dagger\rangle \right\} + m_4 \epsilon \sqrt{\frac{\mu_{12}}{\mu_{34}}} \alpha^- \right] = v^\ddagger(v^\dagger, w^\dagger) \qquad (63)$$

and

$$w = \frac{1}{M}\left[m_1 v^\dagger + m_2 w^\dagger - m_3 \frac{\mu_{12}}{\mu_{34}} \left\{ (v^\dagger - w^\dagger) - \epsilon\langle \epsilon, v^\dagger - w^\dagger\rangle \right\} - m_3 \epsilon \sqrt{\frac{\mu_{12}}{\mu_{34}}} \alpha^- \right] = w^\ddagger(v^\dagger, w^\dagger). \qquad (64)$$

Furthermore, $\Theta_{3412} = \Theta(\langle \epsilon, v-w\rangle - \Gamma_{34}^*)\Theta(\langle \epsilon, v^\dagger - w^\dagger\rangle - \Gamma_{12}^*)$, in (61)′–(62)′, is equal to $\Theta(\langle \epsilon, v^\dagger - w^\dagger\rangle - \Gamma_{12}^*)\Theta(\langle \epsilon, v^\ddagger - w^\ddagger\rangle - \Gamma_{34}^*) = \Theta_{1234}$.
Now, combining (63)–(64), the expressions in (61)′–(62)′ take the form

$$\int_{\mathbb{R}^3} \phi_3 J_3^R \, dv = \beta_{34}\sigma_{34}^2 \iiint_{\mathbb{R}^3\times\mathbb{R}^3\times\mathbb{S}_+^2} \phi_3(v^\ddagger)\left[f_1(v^\dagger) f_2(w^\dagger) - \left(\frac{\mu_{12}}{\mu_{34}}\right)^3 f_3(v^\ddagger) f_4(w^\ddagger) \right] \langle \epsilon, v^\dagger - w^\dagger\rangle \Theta_{1234} \, d\epsilon dw^\dagger dv^\dagger \qquad (61'')$$

and

$$\int_{\mathbb{R}^3} \phi_4 J_4^R \, dv = \beta_{43}\sigma_{43}^2 \iiint_{\mathbb{R}^3\times\mathbb{R}^3\times\mathbb{S}_+^2} \phi_4(v^\ddagger)\left[f_2(v^\dagger) f_1(w^\dagger) - \left(\frac{\mu_{12}}{\mu_{34}}\right)^3 f_4(v^\ddagger) f_3(w^\ddagger) \right] \langle \epsilon, v^\dagger - w^\dagger\rangle \Theta_{1234} \, d\epsilon dw^\dagger dv^\dagger. \qquad (62'')$$

Next, change of the variables $(v, w, \epsilon) \mapsto (w, v, -\epsilon)$ in (60) and (62′′) together with renaming the integration variables from $(v^\dagger, w^\dagger)$ to (v, w) in (61′′)–(62′′), and finally summing up the resulting left hand sides of (59)–(62), results in (56).

Proof of (57) follows the same line of arguments; this time however, one changes the integration variables in (59)–(60) from (v, w) to $(v^\ddagger, w^\ddagger)$. In this process v and w, as the functions of $v^\ddagger$, $w^\ddagger$, become $v^\dagger$ and $w^\dagger$, respectively. □

Remark 3.1. *The assumption in Proposition 3.1 that $f_i \in C_0(\Omega \times \mathbb{R}^3)$, for $i = 1, \dots, 4$, is only needed to make sure that all the integrals exist and are finite.*

4 Conservation laws

Under the additional condition $\beta_{12}\sigma_{12}^2 = \beta_{34}\sigma_{34}^2$ that can be easily verified, Proposition 3.1 implies that for any $a, c \in \mathbb{R}$ and $b \in \mathbb{R}^3$,

$$\phi_i(x, v) = am_i + m_i\langle b, v\rangle + c\left(\frac{m_i v^2}{2} + E_i\right), \ i = 1, \dots, 4, \quad \Longrightarrow \quad \begin{cases} \sum_{i=1}^{4} \int_{\mathbb{R}^3} \phi_i J_i^E \, dv = 0, \\ \sum_{i=1}^{4} \int_{\mathbb{R}^3} \phi_i J_i^R \, dv = 0. \end{cases} \tag{65}$$

Property (65) implies that if f_i is a nonnegative smooth solution of (52) on $[0, T]$, $T > 0$, then, at least formally, we have the following conservation laws for $t \in [0, T]$:

$$\sum_{i=1}^{4} \iint_{\Omega\times\mathbb{R}^3} m_i f_i(t, x, v) \, dvdx = \sum_{i=1}^{4} \iint_{\Omega\times\mathbb{R}^3} m_i f_{i0}(x, v) \, dvdx, \quad \text{(mass)} \tag{66}$$

$$\sum_{i=1}^{4} \iint_{\Omega\times\mathbb{R}^3} m_i v f_i(t, x, v) \, dvdx = \sum_{i=1}^{4} \iint_{\Omega\times\mathbb{R}^3} m_i v f_{i0}(x, v) \, dvdx, \quad \text{(momentum)} \tag{67}$$

$$\sum_{i=1}^{4} \iint_{\Omega\times\mathbb{R}^3} \left(\frac{m_i v^2}{2} + E_i\right) f_i(t, x, v) \, dvdx = \sum_{i=1}^{4} \iint_{\Omega\times\mathbb{R}^3} \left(\frac{m_i v^2}{2} + E_i\right) f_{i0}(x, v) \, dvdx, \quad \text{(total energy)} \tag{68}$$

where $f_{i0}(x, v)$, $i = 1, \dots, 4$, are nonnegative initial conditions of the dilute MSRS kinetic system (52). The above conservation laws follow easily from multiplying the dilute MSRS system by corresponding ϕ_i, integrating with respect to $(t, x, v) \in [0, T] \times \Omega \times \mathbb{R}^3$, and using (65).

An additional conservation law (along the characteristics of the streaming operator in the left hand side of (52)) can be obtained from the following property:

$$\phi_i(x, v) = m_i \frac{(x - tv)^2}{2} + E_i, \ t \in [0, T], \ i = 1, \dots, 4, \quad \Longrightarrow \quad \begin{cases} \sum_{i=1}^{4} \int_{\mathbb{R}^3} \phi_i J_i^E \, dv = 0, \\ \sum_{i=1}^{4} \int_{\mathbb{R}^3} \phi_i J_i^R \, dv = 0. \end{cases} \tag{69}$$

Indeed, after multiplying dilute MSRS kinetic system (52) by $m_i \dfrac{(x - tv)^2}{2} + E_i$ and integrating by parts, one has, for $t \in [0, T]$,

$$\sum_{i=1}^{4} \iint_{\Omega\times\mathbb{R}^3} \left(\frac{m_i (x - tv)^2}{2} + E_i\right) f_i(t, x, v) \, dvdx = \sum_{i=1}^{4} \iint_{\Omega\times\mathbb{R}^3} \left(\frac{m_i x^2}{2} + E_i\right) f_{i0}(x, v) \, dvdx. \tag{70}$$

Next, identity (55) of Proposition 3.1 applied, for each $k = 1, \ldots, 4$, to $\phi_i(x, v) = \delta_{ik}$, $i = 1, \ldots, 4$, with δ_{ik} being the Kronecker delta, imply

$$\int_{\mathbb{R}^3} J_k^E dv = 0, \quad \text{a.e. in } x \in \Omega \text{ and for } k = 1, \ldots, 4 \tag{71}$$

and identities (56) or (57) of Proposition 3.1 applied successively to $\phi_i(x, v) = \delta_{i1}$, $\phi_i(x, v) = \delta_{i2}$, $\phi_i(x, v) = \delta_{i3}$ and $\phi_i(x, v) = \delta_{i4}$, yield

$$\int_{\mathbb{R}^3} J_1^R dv = \int_{\mathbb{R}^3} J_2^R dv = -\int_{\mathbb{R}^3} J_3^R dv = -\int_{\mathbb{R}^3} J_4^R dv, \quad \text{a.e. in } x \in \Omega. \tag{72}$$

Properties (71) and (72) result in the additional conservation laws:

$$n = \sum_{i=1}^{4} \iint_{\Omega\times\mathbb{R}^3} f_i(t, x, v)\, dvdx = \sum_{i=1}^{4} \iint_{\Omega\times\mathbb{R}^3} f_{i0}(x, v)\, dvdx = n_0, \tag{73}$$

$$n_1 + n_3 = \iint_{\Omega\times\mathbb{R}^3} \big[f_1(t, x, v) + f_3(t, x, v)\big]\, dvdx = \iint_{\Omega\times\mathbb{R}^3} \big[f_{10}(x, v) + f_{30}(x, v)\big]\, dvdx = n_{10} + n_{30}, \tag{74}$$

$$n_1 + n_4 = \iint_{\Omega\times\mathbb{R}^3} \big[f_1(t, x, v) + f_4(t, x, v)\big]\, dvdx = \iint_{\Omega\times\mathbb{R}^3} \big[f_{10}(x, v) + f_{40}(x, v)\big]\, dvdx = n_{10} + n_{40}, \tag{75}$$

$$n_2 + n_3 = \iint_{\Omega\times\mathbb{R}^3} \big[f_2(t, x, v) + f_3(t, x, v)\big]\, dvdx = \iint_{\Omega\times\mathbb{R}^3} \big[f_{20}(x, v) + f_{30}(x, v)\big]\, dvdx = n_{20} + n_{30}, \tag{76}$$

$$n_2 + n_4 = \iint_{\Omega\times\mathbb{R}^3} \big[f_2(t, x, v) + f_4(t, x, v)\big]\, dvdx = \iint_{\Omega\times\mathbb{R}^3} \big[f_{20}(x, v) + f_{40}(x, v)\big]\, dvdx = n_{20} + n_{40}, \tag{77}$$

where $f_{i0}(x, v)$, $i = 1, \ldots, 4$, are nonnegative initial conditions of the dilute MSRS kinetic system (52).

In other words, in addition to the conservation of the total density n, partial sums of reactant and product number densities are also preserved, according to the reaction law (1).

5 Balance equations

We now define the macroscopic quantities of the MSRS kinetic model as suitable moments of the distribution functions f_i and provide the evolution equations for the most relevant macroscopic quantities.

Macroscopic quantities

$$n_i(t, x) = \int_{\mathbb{R}^3} f_i(t, x, v) dv, \quad n(t, x) = \sum_{i=1}^{4} n_i(t, x), \tag{78}$$

$$\varrho_i(t, x) = \int_{\mathbb{R}^3} m_i f_i(t, x, v) dv, \quad \varrho(t, x) = \sum_{i=1}^{4} \varrho_i(t, x), \tag{79}$$

$$u_i(t,x) = \frac{1}{n_i(t,x)} \int_{\mathbb{R}^3} v f_i(t,x,v)dv, \quad u(t,x) = \frac{1}{\varrho(t,x)} \sum_{i=1}^{4} m_i n_i(t,x) u_i(t,x), \tag{80}$$

$$\overline{u}_i(t,x) = \frac{1}{\varrho_i(t,x)} \int_{\mathbb{R}^3} m_i\big(v - u(t,x)\big) f_i(t,x,v)dv, \qquad \text{with} \quad \sum_{i=1}^{4} \varrho_i(t,x)\overline{u}_i(t,x) = 0, \tag{81}$$

$$p_i^{(rs)}(t,x) = \int_{\mathbb{R}^3} m_i\big(v - u(t,x)\big)^{(r)}\big(v - u(t,x)\big)^{(s)} f_i(t,x,v)dv, \quad p^{(sr)}(t,x) = \sum_{i=1}^{4} p_i^{(sr)}(t,x), \tag{82}$$

$$p_i(t,x) = \frac{1}{3}\int_{\mathbb{R}^3} m_i\big(v - u(t,x)\big)^2 f_i(t,x,v)dv, \quad p(t,x) = \sum_{i=1}^{4} p_i(t,x), \tag{83}$$

$$\mathcal{T}_i(t,x) = \frac{p_i(t,x)}{kn_i(t,x)}, \quad \mathcal{T}(t,x) = \frac{1}{n(t,x)} \sum_{i=1}^{4} n_i(t,x)\mathcal{T}_i(t,x), \quad \mathcal{T}(t,x) = \frac{p(t,x)}{kn(t,x)}, \tag{84}$$

$$q_i(t,x) = \frac{1}{2}\int_{\mathbb{R}^3} m_i|v - u(t,x)|^2\big(v - u(t,x)\big) f_i(t,x,v)dv, \quad q(t,x) = \sum_{i=1}^{4}\big(q_i(t,x) + E_i n_i(t,x)\overline{u}_i(t,x)\big). \tag{85}$$

In the above expressions, n_i, ϱ_i, u_i, $\overline{u}_i$, $p_i^{(rs)}$, p_i, $\mathcal{T}_i$ and q_i denote the number density, mass density, mean velocity, diffusion velocity, pressure tensor components, pressure, temperature and heat flux of the ith component of the reactive mixture, respectively, and k is the Boltzmann constant. Also, the upper indices r and s indicate spatial directions in a given orthogonal reference system. Moreover, the symbols n, ϱ, u, $p^{(rs)}$, p, $\mathcal{T}$ and q represent the number density, mass density, mean velocity, pressure tensor components, pressure, temperature and heat flux of the whole mixture, respectively.

Note that the above definitions of the macroscopic quantities establish the connection between the properties of the mixture and those of its components. In particular, for what concerns the temperature, we will assume that all species have the same temperature $\mathcal{T}$, meaning that the macroscopic theory considered in this paper does not take into account the relaxation mechanism of exchanging internal energies among the species.

By multiplying the MSRS kinetic system (52) by certain functions ϕ_i chosen in a convenient but rather standard way in the kinetic theory [12], [27], and then integrating over v in $\mathbb{R}^3$, one can derive the balance equations for each ith component of the mixture, as well as the conservation laws for the whole mixture.

- Balance equation for the number density of each ith component (chemical rate equation)

$$\frac{\partial n_i}{\partial t} + \sum_{s=1}^{3} \frac{\partial}{\partial x_s}\left(n_i\overline{u}_i^{(s)} + n_i u^{(s)}\right) = \int_{\mathbb{R}^3} J_i^R dv, \quad i = 1,\dots,4, \tag{86}$$

where the integral on the right-hand-side defines the reaction rate of the MSRS kinetic system.

- Balance equation for the momentum of each ith component of the reactive mixture

$$\frac{\partial}{\partial t}\left(\varrho_i u_i^{(r)}\right) + \sum_{s=1}^{3} \frac{\partial}{\partial x_s}\left[p_i^{(rs)} + \varrho_i\overline{u}_i^{(r)}u^{(s)} + \varrho_i\overline{u}_i^{(s)}u^{(r)} + \varrho_i u^{(r)}u^{(s)}\right]$$
$$= \int_{\mathbb{R}^3} m_i\left(J_i^E + J_i^R\right)v^{(r)}dv, \quad i = 1,\dots,4 \quad r = 1,2,3. \tag{87}$$

• Balance equation for the total energy of each ith component of the reactive mixture

$$\begin{aligned}
&\frac{\partial}{\partial t}\left(\frac{3}{2}p_i + n_i E_i + \sum_{r=1}^{3} \varrho_i \overline{u}_i^{(r)} u^{(r)} + \frac{1}{2}\varrho_i u^2\right) \\
&\qquad + \sum_{s=1}^{3} \frac{\partial}{\partial x_s}\left[q_i^{(s)} + \sum_{r=1}^{3} p_i^{(sr)} u^{(r)} + n_i E_i \overline{u}_i^{(s)} + \frac{1}{2}\varrho_i \overline{u}_i^{(s)} u^2 \right. \\
&\qquad \left. + \left(\frac{3}{2}p_i + n_i E_i + \sum_{r=1}^{3} \varrho_i \overline{u}_i^{(r)} u^{(r)} + \frac{1}{2}\varrho_i u^2\right) u^{(s)} \right] \\
&\qquad = \int_{\mathbb{R}^3} \left(\frac{1}{2}m_i v^2 + E_i\right)\left(J_i^E + J_i^R\right) v dv, \quad i = 1, \ldots, 4.
\end{aligned} \tag{88}$$

• Conservation law for partial number densities

$$\frac{\partial}{\partial t}(n_i + n_k) + \sum_{s=1}^{3} \frac{\partial}{\partial x_s}\left[n_i \overline{u}_i^{(s)} + n_k \overline{u}_k^{(s)} + (n_i + n_k) u^{(s)} \right] = 0, \quad \text{for } \; i \in \{1,2\} \; \text{ and } \; k \in \{3,4\}. \tag{89}$$

• Conservation law for the mass density of the whole mixture

$$\frac{\partial \varrho}{\partial t} + \sum_{s=1}^{3} \frac{\partial}{\partial x_s}\left(\varrho u^{(s)}\right) = 0. \tag{90}$$

• Conservation law for the momentum components of the whole mixture

$$\frac{\partial}{\partial t}\left(\varrho u^{(r)}\right) + \sum_{s=1}^{3} \frac{\partial}{\partial x_s}\left[p^{(rs)} + \varrho u^{(r)} u^{(s)}\right] = 0, \qquad r = 1, 2, 3. \tag{91}$$

• Conservation law for the total energy of the whole mixture

$$\frac{\partial}{\partial t}\left(\frac{3}{2}nk\mathcal{T} + \sum_{i=1}^{4} n_i E_i + \frac{1}{2}\varrho u^2\right) + \sum_{r=1}^{3} \frac{\partial}{\partial x_r}\left[q^{(r)} + \sum_{s=1}^{3} p^{(rs)} u^{(s)} + \left(\frac{3}{2}nk\mathcal{T} + \sum_{i=1}^{4} n_i E_i + \frac{1}{2}\varrho u^2\right) u^{(s)} \right] = 0. \tag{92}$$

6 Entropy identity, H-function, and equilibrium solutions

Proposition 3.1 also implies existence of a Liapunov functional (an H-function) for (52), consistent with system's physical equilibrium. Assume that for $i, j = 1, \ldots, 4$, the conditions $\beta_{ij} = \beta_{ji}$ and $\beta_{12}\sigma_{12}^2 = \beta_{34}\sigma_{34}^2$ are satisfied. For f_i, a smooth nonnegative solution, we multiply (52) by $1 + \log\left(f_i/(\mu_{ij})^{3/2}\right)$ with

$i = 1, \ldots 4$ and $(i, j) \in \{(1,2), (2,1), (3,4), (4,3)\}$, and integrate over $\Omega \times \mathbb{R}^3$, and use (55)–(56) (with $\phi_i = \log\left(f_i/(\mu_{ij})^{3/2}\right)$) to obtain the following entropy identity:

$$\frac{d}{dt}\sum_{i=1}^{4} \iint\limits_{\Omega\times\mathbb{R}^3} f_i \log\left(f_i/(\mu_{ij})^{3/2}\right)\, dvdx$$

$$+\sum_{i,s=1}^{4} \sigma_{is}^2 \int\limits_{\Omega\times\mathbb{R}^3\times\mathbb{R}^3\times\mathbb{S}^2_+} \!\!\!\cdots\!\!\!\int \Big[f_i(v')f_s(w') - f_i(v)f_s(w)\Big] \log\left(\frac{f_i(v')f_s(w')}{f_i(v)f_s(w)}\right)\langle \epsilon, v-w\rangle \Xi_{is}\, d\epsilon dw dv dx$$

$$+\beta_{12}\sigma_{12}^2 \int\limits_{\Omega\times\mathbb{R}^3\times\mathbb{R}^3\times\mathbb{S}^2_+} \!\!\!\cdots\!\!\!\int \left\{\left[\left(\frac{\mu_{12}}{\mu_{34}}\right)^3 f_3(v^\ddagger)f_4(w^\ddagger) - f_1(v)f_2(w)\right]\times\right.$$

$$\left.\log\left[\left(\frac{\mu_{12}}{\mu_{34}}\right)^3 \frac{f_3(v^\ddagger)f_4(w^\ddagger)}{f_1(v)f_2(w)}\right]\Theta(\langle\epsilon, v-w\rangle - \Gamma_{12}^*)\Theta(\langle\epsilon, v^\ddagger - w^\ddagger\rangle - \Gamma_{34}^*)\langle\epsilon, v-w\rangle\right\} d\epsilon dw dv dx = 0, \quad (93)$$

with Ξ_{is} given in (58). We observe that the second and the third terms in the left hand side of (93) are nonnegative. Indeed, this follows from the inequalities

$$[f_i(v')f_s(w') - f_i(v)f_s(w)] \log\left(\frac{f_i(v')f_s(w')}{f_i(v)f_s(w)}\right) \geq 0, \quad (94)$$

$$\left[\left(\frac{\mu_{12}}{\mu_{34}}\right)^3 f_3(v^\ddagger)f_4(w^\ddagger) - f_1(v)f_2(w)\right] \log\left[\left(\frac{\mu_{12}}{\mu_{34}}\right)^3 \frac{f_3(v^\ddagger)f_4(w^\ddagger)}{f_1(v)f_2(w)}\right] \geq 0, \quad (95)$$

for any $i, s = 1, \ldots, 4$. Finally, integrating (93) over $0 \leq t_1 \leq \tau \leq t_2 \leq T$ and using (94)-(95), we obtain

$$\sum_{i=1}^{4} \iint\limits_{\Omega\times\mathbb{R}^3} f_i(t_2,x,v) \log\left[f_i(t_2,x,v)/(\mu_{ij})^{3/2}\right] dvdx \leq \sum_{i=1}^{4} \iint\limits_{\Omega\times\mathbb{R}^3} f_i(t_1,x,v) \log\left[f_i(t_1,x,v)/(\mu_{ij})^{3/2}\right] dvdx, \quad (96)$$

for any $0 \leq t_1 \leq t_2$. Inequality (96) implies that under the conditions $\beta_{ij} = \beta_{ji} > 0$ $(i = 1, \ldots, 4)$ and $\beta_{12}\sigma_{12}^2 = \beta_{34}\sigma_{34}^2$, the convex function $H(t)$, defined by

$$H(t) = \sum_{i=1}^{4} \iint\limits_{\Omega\times\mathbb{R}^3} f_i(t,x,v) \log\left[f_i(t,x,v)/(\mu_{ij})^{3/2}\right] dvdx, \quad (97)$$

is an H-function (Liapunov functional) for the system (52)-(54).

We have the following characterization of equilibrium solutions for the system (52)-(54):

Proposition 6.1. *Assume that for $i, j = 1, \ldots, 4$, the coefficients $0 < \beta_{ij} \leq 1$ satisfy the conditions $\beta_{ij} = \beta_{ji}$ and $\beta_{12}\sigma_{12}^2 = \beta_{34}\sigma_{34}^2$. For $n_i(t,x) \geq 0$, $u(t,x)$, and $\mathcal{T}(t,x) \geq 0$ measurable functions and $0 \leq f_i \in L^1(\Omega \times \mathbb{R}^3)$, the following statements are equivalent:*

1. $f_i = n_i \left(\frac{m_i}{2\pi k\mathcal{T}}\right)^{3/2} \exp\left(-\frac{m_i(v-u)^2}{2k\mathcal{T}}\right)$, *$i = 1, \ldots, 4$, and* $n_1 n_2 = \left(\frac{\mu_{12}}{\mu_{34}}\right)^{3/2} n_3 n_4 \exp\left(\frac{E_{abs}}{k\mathcal{T}}\right)$,

2. $J_i^E(\{f_i\}) = 0$ *and* $J_i^R(\{f_i\}) = 0$, $i = 1, \ldots, 4$,

3. $\sum_{i=1}^{4}\int_{\mathbb{R}^3}\left[J_i^E(\{f_i\})+J_i^R(\{f_i\})\right]\log\left(f_i/\mu_{ij}\right)\,dv=0.$

The notations $J_i^E(\{f_i\})$ and $J_i^R(\{f_i\})$ signify the fact that for $i=1,\ldots,4$, the collisional operators depend on the set one-particle distribution functions, f_1, f_2, f_3, and f_4.

Proposition 6.1 characterizes equilibrium solutions for the MSRS system (52)-(54). In particular, the condition on the partial number densities n_i and mixture temperature $\mathcal{T}$ appearing in item 1 of Proposition 6.1 represents the mass action law (m.a.l.) of the MSRS model. On the other hand, the expressions for the distribution functions f_i, given in item 1 of Proposition 6.1, indicate that when the reactive mixture evolves towards the equilibrium, all species relax to the same temperature, which is the temperature $\mathcal{T}$ of the mixture.

Now, if we disregard the chemical reaction, the mixture becomes non-reactive or chemically inert and the previous Proposition 6.1 reduces to the following result.

Corollary 6.1. *Assume that $\beta_{ij}=0$ for $i,j=1,\ldots,4$, i.e., $J_i^R\equiv 0$ and the corresponding system (52)-(54) is chemically inert. For $n_i(t,x)\geq 0$, $u(t,x)$, and $\mathcal{T}(t,x)\geq 0$ measurable functions and $0\leq f_i\in L^1(\Omega\times\mathbb{R}^3)$, the following statements are equivalent:*

1. $f_i=n_i\left(\dfrac{m_i}{2\pi k\mathcal{T}}\right)^{3/2}\exp\left(-\dfrac{m_i(v-u)^2}{2k\mathcal{T}}\right)$, $i=1,\ldots,4$,

2. $J_i^E(\{f_i\})=0$, $i=1,\ldots,4$,

3. $\sum_{i=1}^{4}\int_{\mathbb{R}^3}J_i^E(\{f_i\})\log f_i\,dv=0$,

with the corresponding H-function given by

$$H_E(t)=\sum_{i=1}^{4}\iint_{\Omega\times\mathbb{R}^3}f_i(t,x,v)\log f_i(t,x,v)\,dvdx. \tag{98}$$

The proofs of Proposition 6.1 and Corollary (6.1) follow a very similar line of arguments as the proof of Proposition 3.2 in [10] and are not given here.

7 Spatially homogeneous evolution

In this section we consider spatially homogeneous conditions, so that the various quantities describing the mixture and appearing in the system (52)-(54) do not depend on x. We are interested in the macroscopic state of the mixture characterized in terms of macroscopic quantities and balance equations.

7.1 Balance equations

In the spatially homogeneous case, the balance equations (86)–(92) take the form

$$\frac{dn_i}{dt} = \int_{\mathbb{R}^3} J_i^R dv, \quad i = 1, \dots, 4, \tag{99}$$

$$\frac{dn}{dt} = 0, \tag{100}$$

$$\frac{d\rho}{dt} = 0, \tag{101}$$

$$\frac{d}{dt}\big(\varrho u\big) = 0, \tag{102}$$

$$\frac{d}{dt}\left(\frac{3}{2}nk\mathcal{T} + \sum_{i=1}^{4} n_i E_i + \frac{1}{2}\varrho u^2\right) = 0. \tag{103}$$

Equations (100), (101), and (102) yield $n =$ constant, $\rho =$ constant, and $u =$ constant while equation (103), with ρ and u being constants, implies

$$\frac{3}{2}nk\mathcal{T} + \sum_{i=1}^{4} n_i E_i = \text{constant}. \tag{104}$$

If we choose the reference frame for which the mixture is stationary, we have $u = 0$ and the macroscopic state of the reactive mixture is then defined by the set $\{n_1, n_2, n_3, n_4, \mathcal{T}\}$. If we consider an initial state defined by $\{n_{10}, n_{20}, n_{30}, n_{40}, \mathcal{T}_0\}$, from Eqs. (99) and (104), with $n = n_0$, we obtain

$$n_1 - n_{10} = n_2 - n_{20} = -\big(n_3 - n_{30}\big) = -\big(n_4 - n_{40}\big) \tag{105}$$

and

$$\frac{3}{2}n_0 k\mathcal{T} + \sum_{i=1}^{4} n_i E_i = \frac{3}{2}n_0 k\mathcal{T}_0 + \sum_{i=1}^{4} n_{i0} E_i. \tag{106}$$

Therefore, (105) and (106) yield the following expressions for partial number density n_i in terms of the mixture temperature:

$$n_i(t) = n_{i0} + \frac{3n_0 k\big[\mathcal{T}(t) - \mathcal{T}_0\big]}{2E_{abs}}, \quad i = 1, 2, \qquad \text{and} \qquad n_i(t) = n_{i0} - \frac{3n_0 k\big[\mathcal{T}(t) - \mathcal{T}_0\big]}{2E_{abs}}, \quad i = 3, 4, \tag{107}$$

where $E_{abs} = E_3 + E_4 - E_1 - E_2$ has been introduced in section 2.2.

7.2 Uniqueness of equilibrium state

The macroscopic state of the mixture is fully described by the partial densities n_i, $i = 1, 2, 3, 4$, and the temperature $\mathcal{T}$ of the mixture. In equilibrium (described in the general case of spatially inhomogeneous conditions by Proposition 6.1), the balance equations (99)–(103) have a unique positive solution that depends only on initial partial densities, n_{i0}, $i = 1, 2, 3, 4$, and the initial temperature $\mathcal{T}_0$. We have

Proposition 7.1. *In equilibrium, the macroscopic state of the mixture governed by the system* (52)-(54) *is uniquely determined by the initial partial densities, $n_{i0} > 0$, $i = 1, 2, 3, 4$, and the initial temperature $\mathcal{T}_0 > 0$.*

Proof. In contrast to the proof of the similar result in [1] (Proposition 1), we do not assume positivity of the sought equilibrium solution.

In addition to (107), in equilibrium, the partial densities and temperature satisfy the mass action law (see (1) of Proposition 6.1):

$$n_1 n_2 = \left(\frac{\mu_{12}}{\mu_{34}}\right)^{3/2} n_3 n_4 \exp\left(\frac{E_{abs}}{k\mathcal{T}}\right). \tag{108}$$

We want to show that equations (107) and (108) have a unique non-negative solution determined by the initial macroscopic values n_{10}, n_{20}, n_{30}, n_{40}, and $\mathcal{T}_0$.

After rescaling of both temperature and partial densities to $\hat{\mathcal{T}} = k\mathcal{T}/E_{abs}$ and $\hat{n}_i = 2n_i/3n_0$ for $i = 1, 2, 3, 4$, respectively, and with $n_0 = n_{10} + n_{20} + n_{30} + n_{40} = n_1 + n_2 + n_3 + n_4$, equations (107) and (108) become

$$\hat{n}_i = \hat{n}_{i0} + (\hat{\mathcal{T}} - \hat{\mathcal{T}}_0), \quad i = 1, 2, \tag{109}$$

$$\hat{n}_i = \hat{n}_{i0} - (\hat{\mathcal{T}} - \hat{\mathcal{T}}_0), \quad i = 3, 4, \tag{110}$$

$$\hat{n}_1 \hat{n}_2 = \left(\frac{\mu_{12}}{\mu_{34}}\right)^{3/2} \hat{n}_3 \hat{n}_4 \exp\left(\frac{1}{\hat{\mathcal{T}}}\right), \tag{111}$$

together with the constraint $\hat{n}_1 + \hat{n}_2 + \hat{n}_3 + \hat{n}_4 = \hat{n}_{10} + \hat{n}_{20} + \hat{n}_{30} + \hat{n}_{40} = 2/3$. We have

Lemma 7.1. *Function*

$$F(\hat{\mathcal{T}}) = \left(\hat{n}_{10} + (\hat{\mathcal{T}} - \hat{\mathcal{T}}_0)\right)\left(\hat{n}_{20} + (\hat{\mathcal{T}} - \hat{\mathcal{T}}_0)\right)\left(\frac{\mu_{34}}{\mu_{12}}\right)^{3/2} \exp\left(-\frac{1}{\hat{\mathcal{T}}}\right) - \left(\hat{n}_{30} - (\hat{\mathcal{T}} - \hat{\mathcal{T}}_0)\right)\left(\hat{n}_{40} - (\hat{\mathcal{T}} - \hat{\mathcal{T}}_0)\right), \tag{112}$$

defined on the interval (L_1, L_2), with $L_1 = \max\left(0, \hat{\mathcal{T}}_0 - \min(\hat{n}_{10}, \hat{n}_{20})\right)$ and $L_2 = \hat{\mathcal{T}}_0 + \min(\hat{n}_{30}, \hat{n}_{40})$, has only one (positive) zero.

Proof of Lemma 7.1. For given initial partial densities $n_{i0} > 0$, $i = 1, 2, 3, 4$, and the initial temperature $\mathcal{T}_0 > 0$, we consider two cases: (1) $\hat{\mathcal{T}}_0 - \min(\hat{n}_{10}, \hat{n}_{20}) \le 0$ and (2) $\hat{\mathcal{T}}_0 - \min(\hat{n}_{10}, \hat{n}_{20}) > 0$. In case (1), $L_1 = 0$ and

$$\lim_{\hat{\mathcal{T}} \to 0^+} F(\hat{\mathcal{T}}) = -(\hat{n}_{30} + \hat{\mathcal{T}}_0)(\hat{n}_{40} + \hat{\mathcal{T}}_0) < 0, \tag{113}$$

$$\lim_{\hat{\mathcal{T}} \to L_2^-} F(\hat{\mathcal{T}}) = (\hat{n}_{10} + \min(\hat{n}_{30}, \hat{n}_{40}))\,(\hat{n}_{20} + \min(\hat{n}_{30}, \hat{n}_{40}))\left(\frac{\mu_{34}}{\mu_{12}}\right)^{3/2} \exp\left(-\frac{1}{\hat{\mathcal{T}}_0 + \min(\hat{n}_{30}, \hat{n}_{40})}\right) > 0, \tag{114}$$

while in case (2), we have $L_1 = \hat{\mathcal{T}}_0 - \min(\hat{n}_{10}, \hat{n}_{20}) > 0$ and property (113) is replaced by the property

$$\lim_{\hat{\mathcal{T}} \to L_1^+} F(\hat{\mathcal{T}}) = -\,(\hat{n}_{30} + \min(\hat{n}_{10}, \hat{n}_{20}))\,(\hat{n}_{40} + \min(\hat{n}_{10}, \hat{n}_{20})) < 0. \tag{115}$$

Additionally, in both cases, the derivative of $F(\hat{\mathcal{T}})$,

$$F'(\hat{\mathcal{T}}) = \left\{ \left(\hat{n}_{10} + (\hat{\mathcal{T}} - \hat{\mathcal{T}}_0)\right) + \left(\hat{n}_{20} + (\hat{\mathcal{T}} - \hat{\mathcal{T}}_0)\right) \right\} \left(\frac{\mu_{34}}{\mu_{12}}\right)^{3/2} \exp\left(-\frac{1}{\hat{\mathcal{T}}}\right)$$
$$+ \frac{\left(\hat{n}_{10} + (\hat{\mathcal{T}} - \hat{\mathcal{T}}_0)\right)\left(\hat{n}_{20} + (\hat{\mathcal{T}} - \hat{\mathcal{T}}_0)\right)\left(\frac{\mu_{34}}{\mu_{12}}\right)^{3/2} \exp\left(-\frac{1}{\hat{\mathcal{T}}}\right)}{\hat{\mathcal{T}}^2} + \left(\hat{n}_{30} - (\hat{\mathcal{T}} - \hat{\mathcal{T}}_0)\right) + \left(\hat{n}_{40} - (\hat{\mathcal{T}} - \mathcal{T}_0)\right), \tag{116}$$

is positive on the interval (L_1, L_2). Indeed, the terms $\left(\hat{n}_{10} + (\hat{\mathcal{T}} - \hat{\mathcal{T}}_0)\right)$, $\left(\hat{n}_{20} + (\hat{\mathcal{T}} - \hat{\mathcal{T}}_0)\right)$, $\left(\hat{n}_{30} - (\hat{\mathcal{T}} - \hat{\mathcal{T}}_0)\right)$, and $\left(\hat{n}_{40} - (\hat{\mathcal{T}} - \hat{\mathcal{T}}_0)\right)$ in (116) are all non-negative on (L_1, L_2), with at least three of them being positive. Properties (113)-(114) in case (1), or properties (115)-(114) in case (2), together with $F(\hat{\mathcal{T}})$ being strictly increasing, imply the existence of a unique zero of function $F(\hat{\mathcal{T}})$ on (L_1, L_2). □

Now, for $\hat{\mathcal{T}} = \hat{\mathcal{T}}^{eq}$, the unique positive zero of $F(\hat{\mathcal{T}})$ obtained in Lemma 7.1, we define the unique equilibrium partial densities (see (109)-(110)) by

$$\hat{n}_i^{eq} = \hat{n}_{i0} + (\hat{\mathcal{T}}^{eq} - \hat{\mathcal{T}}_0), \quad i = 1, 2, \tag{117}$$
$$\hat{n}_i^{eq} = \hat{n}_{i0} - (\hat{\mathcal{T}}^{eq} - \hat{\mathcal{T}}_0), \quad i = 3, 4. \tag{118}$$

Next, since $\hat{\mathcal{T}}_0 - \min(\hat{n}_{10}, \hat{n}_{20}) < \hat{\mathcal{T}}^{eq} < \hat{\mathcal{T}}_0 + \min(\hat{n}_{30}, \hat{n}_{40})$, we observe that $\hat{n}_i^{eq} \geq 0$, for $i = 1, 2, 3, 4$. Therefore, $\hat{n}_i = \hat{n}_i^{eq}$ and $\hat{\mathcal{T}} = \hat{\mathcal{T}}^{eq} > 0$ is the unique non-negative solution of the system (109)-(111), while the densities $n_i^{eq} = (3/2)n_0\hat{n}_i^{eq}$, for $i = 1, 2, 3, 4$ and the temperature $T^{eq} = (E_{abs}/k)\hat{\mathcal{T}}^{eq}$ is the unique equilibrium solution of equations (107) and (108). □

8 Appendix: SRS model

In the simple reacting spheres (SRS) kinetic model, the reactive collision between particles of species i and s occur ($i, s = 1, \ldots, 4$) when the kinetic energy associated with the relative motion along the line of centers exceeds the activation energy γ_i,

$$(1/2)\mu_{is}\big(\langle \epsilon, v - w\rangle\big)^2 \geq \gamma_i. \tag{119}$$

Now, combining the assumed conservations of momentum and total energy for the reactive events:

$$\begin{aligned} m_1 v + m_2 w &= m_3 v^\ddagger + m_4 w^\ddagger \\ m_1 v^2 + m_2 w^2 &= m_3 v^{\ddagger 2} + m_4 w^{\ddagger 2} + 2E_{abs}, \end{aligned} \tag{120}$$

where $v^\ddagger$ and $w^\ddagger$ are post-reactive values of the velocities v and w and E_{abs} is the energy absorbed by the internal degrees of freedom, we obtain the relation (see also [3])

$$\left(\sqrt{\frac{\mu_{34}}{2}}(v^\ddagger - w^\ddagger)\right)^2 = \left(\sqrt{\frac{\mu_{12}}{2}}(v - w)\right)^2 - E_{abs}. \tag{121}$$

The resulting connection between the pre- and post-reactive relative velocities can be written in the form

$$\sqrt{\frac{\mu_{34}}{2}}(v^\ddagger - w^\ddagger) = \sqrt{\frac{\mu_{12}}{2}}(v - w) + \Lambda\epsilon, \tag{122}$$

where

$$\Lambda = -\left\langle \sqrt{\frac{\mu_{12}}{2}}(v-w), \epsilon \right\rangle + \sqrt{\left\langle \sqrt{\frac{\mu_{12}}{2}}(v-w), \epsilon \right\rangle^2 - E_{abs}} \tag{123}$$

And finally, in the case of the reaction $A + B \to A^* + B^*$, the post-reactive values of velocities v, w

$$v^\ddagger = \frac{1}{M}\left[m_1 v + m_2 w + m_4 \sqrt{\frac{\mu_{12}}{\mu_{34}}} \left\{ (v-w) - \epsilon\langle \epsilon, v-w\rangle + \epsilon\alpha^- \right\} \right], \tag{124}$$

$$w^\ddagger = \frac{1}{M}\left[m_1 v + m_2 w - m_3 \sqrt{\frac{\mu_{12}}{\mu_{34}}} \left\{ (v-w) - \epsilon\langle \epsilon, v-w\rangle + \epsilon\alpha^- \right\} \right], \tag{125}$$

with $\alpha^- = \sqrt{\big(\langle \epsilon, v-w\rangle\big)^2 - 2E_{abs}/\mu_{12}}$ and, E_{abs}, the energy absorbed by the internal degrees of freedom. The absorbed energy E_{abs} has the property $E_{abs} = E_3 + E_4 - E_1 - E_2 > 0$, where $E_i > 0$, $i = 1, \ldots 4$, is the energy of i-th particle associated with its internal degrees of freedom.

The activation energies γ_1, γ_2 for A and B are chosen to satisfy $\gamma_1 \geq E_{abs} > 0$, and by symmetry, $\gamma_2 = \gamma_1$.

For the inverse reaction $A^* + B^* \to A + B$, we proceed in a similar with the expressions and obtain the following expressions for $v^\dagger$ and $w^\dagger$

$$v^\dagger = \frac{1}{M}\left[m_3 v + m_4 w + m_2 \sqrt{\frac{\mu_{34}}{\mu_{12}}} \left\{ (v-w) - \epsilon\langle \epsilon, v-w\rangle + \epsilon\alpha^+ \right\} \right], \tag{126}$$

$$w^\dagger = \frac{1}{M}\left[m_3 v + m_4 w - m_1 \sqrt{\frac{\mu_{34}}{\mu_{12}}} \left\{ (v-w) - \epsilon\langle \epsilon, v-w\rangle + \epsilon\alpha^+ \right\} \right], \tag{127}$$

with $\alpha^+ = \sqrt{\big(\langle \epsilon, v-w\rangle\big)^2 + 2E_{abs}/\mu_{34}}$, and the activation energies for A^* and B^*, $\gamma_3 = \gamma_1 - E_{abs}$ and, $\gamma_4 = \gamma_3$.

Post- and pre-collisional velocities of the reactive pairs satisfy conservation of the momentum

$$m_1 v + m_2 w = m_3 v^\ddagger + m_4 w^\ddagger, \qquad m_3 v + m_4 w = m_1 v^\dagger + m_2 w^\dagger. \tag{128}$$

A part of kinetic energy is exchanged with the energy absorbed by the internal states. The following equalities hold:

$$\begin{aligned} m_1 v^2 + m_2 w^2 &= m_3 v^{\ddagger 2} + m_4 w^{\ddagger 2} + 2E_{abs}, \\ m_3 v^2 + m_4 w^2 &= m_1 v^{\dagger 2} + m_2 w^{\dagger 2} - 2E_{abs}. \end{aligned} \tag{129}$$

In the SRS kinetic model, the angular momentum is not conserved during the reactive collisional process, unless $\mu_{12} = \mu_{34}$.

8.1 SRS' version of Lemma 2.1

Lemma 8.1.

(1) *The inverse velocities to $v^\ddagger$, $w^\ddagger$ are given by*

$$v = \frac{1}{M}\left[m_3 v^\ddagger + m_4 w^\ddagger + m_2 \sqrt{\frac{\mu_{34}}{\mu_{12}}} \left\{ (v^\ddagger - w^\ddagger) - \epsilon\langle \epsilon, v^\ddagger - w^\ddagger\rangle + \epsilon\alpha^+ \right\} \right], \tag{130}$$

$$w = \frac{1}{M}\left[m_3 v^\ddagger + m_4 w^\ddagger - m_1 \sqrt{\frac{\mu_{34}}{\mu_{12}}} \left\{ (v^\ddagger - w^\ddagger) - \epsilon\langle \epsilon, v^\ddagger - w^\ddagger\rangle + \epsilon\alpha^+ \right\} \right], \tag{131}$$

and the inverse velocities to $v^\dagger$, $w^\dagger$ are given by

$$v = \frac{1}{M}\left[m_1 v^\dagger + m_2 w^\dagger + m_4\sqrt{\frac{\mu_{12}}{\mu_{34}}}\left\{(v^\dagger - w^\dagger) - \epsilon\langle\epsilon, v^\dagger - w^\dagger\rangle + \epsilon\alpha^-\right\}\right], \tag{132}$$

$$w = \frac{1}{M}\left[m_1 v^\dagger + m_2 w^\dagger - m_3\sqrt{\frac{\mu_{12}}{\mu_{34}}}\left\{(v^\dagger - w^\dagger) - \epsilon\langle\epsilon, v^\dagger - w^\dagger\rangle + \epsilon\alpha^-\right\}\right]. \tag{133}$$

(2) *For fixed ϵ, the Jacobians of the transformations $(v, w) \mapsto (v^\dagger, w^\dagger)$ and $(v, w) \mapsto (v^\ddagger, w^\ddagger)$ are given by*

$$\left(\frac{\mu_{34}}{\mu_{12}}\right)^{3/2}\frac{\langle\epsilon, v - w\rangle}{\alpha^+} \quad \text{and} \quad \left(\frac{\mu_{12}}{\mu_{34}}\right)^{3/2}\frac{\langle\epsilon, v - w\rangle}{\alpha^-}, \tag{134}$$

respectively.

(3) Furthermore, $\langle\epsilon, v^\dagger - w^\dagger\rangle = \left(\frac{\mu_{34}}{\mu_{12}}\right)^{1/2}\alpha^+$, $\langle\epsilon, v^\ddagger - w^\ddagger\rangle = \left(\frac{\mu_{12}}{\mu_{34}}\right)^{1/2}\alpha^-$, $\frac{1}{2}\mu_{12}\big(\langle\epsilon, v - w\rangle\big)^2 - \gamma_1 = \frac{1}{2}\mu_{34}\big(\langle\epsilon, v^\ddagger - w^\ddagger\rangle\big)^2 - \gamma_3$, *and* $\frac{1}{2}\mu_{34}\big(\langle\epsilon, v - w\rangle\big)^2 - \gamma_3 = \frac{1}{2}\mu_{12}\big(\langle\epsilon, v^\dagger - w^\dagger\rangle\big)^2 - \gamma_1$.

8.2 The dilute SRS kinetic system

$$\frac{\partial f_i}{\partial t} + v\frac{\partial f_i}{\partial x} = J_i^E + J_i^R, \quad f_i(0, x, v) = f_{i0}(x, v), \quad i = 1, \ldots, 4, \quad (x, v) \in \Omega \times \mathbb{R}^3, \tag{135}$$

with

$$J_i^E = \sum_{s=1}^{4}\left\{\sigma_{is}^2 \iint_{\mathbb{R}^3\times\mathbb{S}_+^2}\Big[f_i(t,x,v')f_s(t,x,w') - f_i(t,x,v)f_s(t,x,w)\Big]\langle\epsilon, v - w\rangle\, d\epsilon dw\right\}$$
$$- \beta_{ij}\sigma_{ij}^2 \iint_{\mathbb{R}^3\times\mathbb{S}_+^2}\Big[f_i(t,x,v')f_j(t,x,w') - f_i(t,x,v)f_j(t,x,w)\Big]\Theta(\langle\epsilon, v - w\rangle - \Gamma_{ij})\,\langle\epsilon, v-w\rangle d\epsilon dw, \tag{136}$$

and

$$J_i^R = \beta_{ij}\sigma_{ij}^2 \iint_{\mathbb{R}^3\times\mathbb{S}_+^2}\left[\left(\frac{\mu_{ij}}{\mu_{kl}}\right)^2 f_k(t,x,v_{ij}^\odot)f_l(t,x,w_{ij}^\odot) - f_i(t,x,v)f_j(t,x,w)\right]\Theta(\langle\epsilon, v - w\rangle - \Gamma_{ij})\,\langle\epsilon, v-w\rangle d\epsilon dw, \tag{137}$$

where f_{i0}, $i = 1, \ldots, 4$ are suitable nonnegative initial conditions and $\Omega \subseteq \mathbb{R}^3$ denotes the spatial domain of the gas mixture. $\Gamma_{ij} = \sqrt{2\gamma_i/\mu_{ij}}$ and Θ is the Heaviside step function. As before, the pairs of post-reactive velocities, $(v_{ij}^\odot, w_{ij}^\odot) = (v^\ddagger, w^\ddagger)$ for $i, j = 1, 2$, and $(v_{ij}^\odot, w_{ij}^\odot) = (v^\dagger, w^\dagger)$ for $i, j = 3, 4$. The pairs of indices (i, j) and (k, l) are from the set of quadruples (i, j, k, l) : $\{(1, 2, 3, 4), (2, 1, 4, 3), (3, 4, 1, 2), (4, 3, 2, 1)\}$.

8.3 SRS' version of Proposition 3.1

Proposition 8.1. *Assume that $\beta_{ij} = \beta_{ji}$ for $(i, j) \in \{(1, 2), (2, 1), (3, 4), (4, 3)\}$. For ϕ_i measurable on $\Omega \times \mathbb{R}^3$ and $f_i \in C_0(\Omega \times \mathbb{R}^3)$, $i = 1, \ldots, 4$, we have:*

$$\sum_{i=1}^{4}\int_{\mathbb{R}^3}\phi_i J_i^E\,dv = \sum_{i=1}^{4}\sum_{s=1}^{4}\sigma_{is}^2 \iiint_{\mathbb{R}^3\times\mathbb{R}^3\times\mathbb{S}_+^2} \left[\phi_i(x,v)+\phi_s(x,w)-\phi_i(x,v')-\phi_s(x,w')\right]\times \left[f_i(v')f_s(w')-f_i(v)f_s(w)\right]\langle\epsilon, v-w\rangle \Xi_{is}\,d\epsilon dw dv, \tag{138}$$

$$\sum_{i=1}^{4}\int_{\mathbb{R}^3}\phi_i J_i^R\,dv = \iiint_{\mathbb{R}^3\times\mathbb{R}^3\times\mathbb{S}_+^2} \left[\beta_{12}\sigma_{12}^2\phi_1(x,v)+\beta_{21}\sigma_{21}^2\phi_2(x,w)-\beta_{34}\sigma_{34}^2\phi_3(x,v^{\ddagger})-\beta_{43}\sigma_{43}^2\phi_4(x,w^{\ddagger})\right]\times \left[\left(\frac{\mu_{12}}{\mu_{34}}\right)^2 f_3(x,v^{\ddagger})f_4(x,w^{\ddagger})-f_1(x,v)f_2(x,w)\right]\Theta(\langle\epsilon,v-w\rangle-\Gamma_{12})\langle\epsilon,v-w\rangle\,d\epsilon dw dv, \tag{139}$$

and

$$\sum_{i=1}^{4}\int_{\mathbb{R}^3}\phi_i J_i^R\,dv = \iiint_{\mathbb{R}^3\times\mathbb{R}^3\times\mathbb{S}_+^2} \left[\beta_{34}\sigma_{34}^2\phi_3(x,v)+\beta_{43}\sigma_{43}^2\phi_4(x,w)-\beta_{12}\sigma_{12}^2\phi_1(x,v^{\dagger})-\beta_{21}\sigma_{21}^2\phi_2(x,v^{\dagger})\right]\times \left[\left(\frac{\mu_{34}}{\mu_{12}}\right)^2 f_1(x,v^{\dagger})f_2(x,w^{\dagger})-f_3(x,v)f_4(x,w)\right]\Theta(\langle\epsilon,v-w\rangle-\Gamma_{34})\langle\epsilon,v-w\rangle\,d\epsilon dw dv, \tag{140}$$

where Ξ_{is}, appearing in (138), is given by

$$\Xi_{is} = \begin{cases} \frac{1}{2}\Theta(\langle\epsilon,v-w\rangle)+\frac{1}{2}(1-\beta_{is})\Theta(\Gamma_{is}-\langle\epsilon,v-w\rangle), & \text{if } (i,s)\in I;\\ \frac{1}{4}\Theta(\langle\epsilon,v-w\rangle), & \text{if } i=s;\\ \frac{1}{2}\Theta(\langle\epsilon,v-w\rangle), & \text{otherwise,} \end{cases} \tag{141}$$

with $I=\{(1,2),(2,1),(3,4),(4,3)\}$.
The post-collisional velocities, v' and w' are given in (3), while the post-reactive velocities, $v^{\ddagger}$, $w^{\ddagger}$ and $v^{\dagger}$, $w^{\dagger}$, are given in (130)-(131) and (132)-(133), respectively.

As in the case of MSRS, Proposition 8.1 for SRS model implies that when $\beta_{ij}=\beta_{ji}>0$ $(i=1,\ldots,4)$ and $\beta_{12}\sigma_{12}^2=\beta_{34}\sigma_{34}^2$, the convex function $H(t)$, defined by

$$H(t)=\sum_{i=1}^{4}\iint_{\Omega\times\mathbb{R}^3} f_i(t,x,v)\log\left[f_i(t,x,v)/\mu_{ij}\right]\,dvdx, \tag{142}$$

is an H-function (Liapunov functional) for the SRS model and the following result holds:

Proposition 8.2. *Assume that for $i,j=1,\ldots,4$, the coefficients $0<\beta_{ij}\le 1$ satisfy the conditions $\beta_{ij}=\beta_{ji}$ and $\beta_{12}\sigma_{12}^2=\beta_{34}\sigma_{34}^2$. For $n_i(t,x)\ge 0$, $u(t,x)$, and $\mathcal{T}(t,x)\ge 0$ measurable functions and $0\le f_i\in L^1(\Omega\times\mathbb{R}^3)$, the following statements are equivalent:*

1. $f_i = n_i\left(\frac{m_i}{2\pi k\mathcal{T}}\right)^{3/2}\exp\left(-\frac{m_i(v-u)^2}{2k\mathcal{T}}\right)$, $i=1,\ldots,4$, *and* $n_1n_2=\left(\frac{\mu_{12}}{\mu_{34}}\right)^{1/2} n_3n_4\exp\left(\frac{E_{abs}}{k\mathcal{T}}\right)$,

2. $J_i^E(\{f_i\})=0$ *and* $J_i^R(\{f_i\})=0$, $i=1,\ldots,4$,

3. $\sum_{i=1}^{4} \int_{\mathbb{R}^3} \left[J_i^E(\{f_i\}) + J_i^R(\{f_i\}) \right] \log\left(f_i/\mu_{ij}\right)\, dv = 0.$

The notations $J_i^E(\{f_i\})$ and $J_i^R(\{f_i\})$ signify the fact that for $i = 1, \ldots, 4$, the collisional operators depend on the set one-particle distribution functions, f_1, f_2, f_3, and f_4.

We observe that the post-reactive velocities in the SRS model (see (124)-(125) and (126)-(127)) yield the factor $\left(\frac{\mu_{ij}}{\mu_{kl}}\right)^2$ in (137), while in the MSRS model this factor is $\left(\frac{\mu_{ij}}{\mu_{kl}}\right)^3$. This difference also results in different forms of the mass-action law:

$$n_1 n_2 = \left(\frac{\mu_{12}}{\mu_{34}}\right)^{1/2} n_3 n_4 \exp\left(\frac{E_{abs}}{k\mathcal{T}}\right) \qquad \text{(SRS model)}$$
$$n_1 n_2 = \left(\frac{\mu_{12}}{\mu_{34}}\right)^{3/2} n_3 n_4 \exp\left(\frac{E_{abs}}{k\mathcal{T}}\right) \qquad \text{(MSRS model)}$$

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