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On Two Kinetic Models for Chemical Reactions: Comparisons and Existence Results

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Two kinetic theories for bimolecular chemical reactions in dilute gases are analyzed and compared. Reactive scattering kernels are constructed, satisfying microreversibility principles and yielding a physically plausible link between the two models. Mathematical properties and in particular the role played by microreversibility conditions and by certain elastic collisional terms on existence of solutions are also investigated.

KEY WORDS: Kinetic theory of gas mixtures; chemical reactions; hard-sphere systems.

1. INTRODUCTION

A microscopic description of chemical reactions in dense phase requires knowledge of the coupling between the dynamics of the solute molecules and the dynamics of the solvent molecules. This very challenging goal is avoided in the models where the solute molecules are governed by diffusive type equation (Fokker–Planck, Langevin, or Smoluchowski equations), with the reactive events generated by the boundary conditions, and

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with the dynamics of the solvent molecules absent. Also, in the transition state theory the knowledge of dynamics of particles is replaced in favor of calculating only equilibrium rate coefficients, while the solvent effects appear in the free energy of the transition state.

The kinetic models considered in this note consider chemical reactions in dilute gases only, where the assumption of uncorrelated binary collisions is used to obtain the Boltzmann-type kinetic equations. As in the above mentioned models, presence of the solvent is avoided. However, in contrast to the Fokker–Planck approach for the solute molecules and the transition state theory, two models in the note deal with the microscopic (nonequilibrium) basis for the macroscopic chemical action law and the development of the kinetic theory of chemical reactions that has built-in trend to equilibrium (H-function).

It was first Prigogine and Xhrouet[1] who considered the kinetic theory of chemically reacting gases where the reactive terms are perturbations of nonreactive collisional terms. This approach is only justified when the cross sections of gas phase reactions are much smaller than those for non-reactive events. In all other cases, the reactive and nonreactive collisional terms must be treated on equal par. The article by Kapral[2] reviews many theories introduced after the work of Light *et al.*[3]

In this work we compare two kinetic models for bimolecular reversible chemical reactions in dilute gases, where the reactive and the nonreactive terms are treated on equal par. In both models the molecules are structureless point masses, with one internal state of excitation, that experience a strong short-range repulsion due to the chemical activation barrier. The reactions take place only if the kinetic energy of the colliding pair of molecules surmounts this barrier; otherwise the molecules scatter elastically. Although, simplistic in its nature, these types of models can be helpful in studying certain aspects of condensed phase chemical reactions.

In ref. 4, Rossani and Spiga constructed a formal reactive kinetic theory (based on work in refs. 3 and 5) that has built-in trend to equilibrium (H-Theorem). This theory, based on the Boltzmann equation is a natural extension of classic gas kinetic theory to nonconservative interactions. Rossani–Spiga model is compared here with the simple reacting spheres (SRS) kinetic theory, considered by Marron in ref. 6 and Xystris and Dahler in ref. 7. In the SRS model both elastic and reactive interaction are hard-spheres-like. The SRS model has its origin in particle system dynamics, since it can be derived from the Liouville equation or from the corresponding BBGKY hierarchy equations (see, refs. 2 and 8). Additional bibliography on this matter can be found in ref. 9.

The paper is organized as follows. First, the Rossani–Spiga and the SRS kinetic theories are presented and discussed in Sections 2 and 3, respectively. In Section 4, we combine the techniques developed in refs. 4 and 7 to construct new reactive scattering kernels corresponding to the hard-spheres-like model. The model distinguishes between *elastic* and *reactive* mean hard-spheres' diameters and, in contrast to the SRS model, allows for a nonzero mass exchange in reactions. The reactive scattering kernels satisfy the microreversibility conditions; furthermore, they reduce themselves to reactive kernels of hard-spheres type, when no net mass and no hard sphere diameter changes are present in the reactions. These are the first, physically plausible, scattering kernels that satisfy the required microreversibility conditions of the Rossani–Spiga kinetic theory. We also discuss a new variant of the reactive kinetic theory that has its roots in the framework of the SRS and the Rossani–Spiga models.

Finally, in Section 5, we present detailed analysis of the properties of the Rossani–Spiga model, with particular emphasis on those properties that do not require the microreversibility conditions (10). We also discuss importance of the microreversibility conditions (10) and inclusion of certain elastic collisional terms on existence of the equilibrium solutions. Finally, we state a global in time existence result for the system (2)–(3)–(11).

2. THE ROSSANI–SPIGA KINETIC THEORY

Rossani and Spiga have shown in ref. 4 that one can construct a kinetic theory of chemically reactive dilute gases with built-in trend to equilibrium (H-Theorem). They considered a four component mixture of structureless particles A_1, A_2, A_3, A_3 and the chemical reactions of the type

$$A_1 + A_2 \rightleftharpoons A_3 + A_4. \tag{1}$$

In addition to the bimolecular chemical reactions (1), the elastic collisional events $A_i + A_j \rightleftharpoons A_i + A_j, i, j = 1, \dots, 4$ have also been included in the model. In fact, as we will show later, inclusion of at least some elastic collisions appears to be necessary for gas equilibration.

The reactions (1) can occur only when the kinetic energy associated with the relative motion along the line of mass centers of particles exceeds the activation energy. This threshold energy depends on the internal energies E_i of particles A_i.

For each i ($i = 1, \dots, 4$), let $f_i(t, x, v)$ denote the one-particle distribution function of the ith component of the reactive mixture. The function $f_i(t, x, v)$ changes in time due to free streaming and collisions (both elastic and reactive), and at time t, it represents the number density of particles of species i at point x with velocity v. The system has the form

$$\frac{\partial f_i}{\partial t} + v \cdot \frac{\partial f_i}{\partial x} = J_i^E + J_i^R, \quad f_i(0, x, v) = f_{i0}(x, v), (x, v) \in D \times \mathbb{R}^3, \quad (2)$$

where f_{i0}, $i = 1, \ldots, 4$ are suitable nonnegative initial conditions. The gas mixture is confined in $D \subseteq \mathbb{R}^3$. We consider two choices for the set D: $D = \mathbb{R}^3$, or D being a three-dimensional torus $[0, L]^3$, $L > 0$. The latter choice corresponds to case of the periodic boundary conditions on $[0, L]^3$. Here, J_i^E, J_i^R, $i = 1, \ldots, 4$, denote the elastic and reactive collisional terms, respectively. They are given by

$$\begin{aligned} J_i^E &= \sum_{j=1}^{4} J_{ij}^E = \sum_{j=1}^{4} \iint_{\mathbb{R}^3 \times \mathbb{S}^2} B_{ij}(g, \Omega \cdot \Omega') \\ &\qquad \times \Big[f_i(t, x, v_{ij}^{ij}) f_j(t, x, w_{ij}^{ij}) - f_i(t, x, v) f_j(t, x, w) \Big] \, \mathrm{d}w \, \mathrm{d}\Omega' \\ &= J_i^{E+} - J_i^{E-} \end{aligned} \quad (3)$$

and

$$\begin{aligned} J_i^R = \iint_{\mathbb{R}^3 \times \mathbb{S}^2} \Theta(g^2 - \delta_{ij}^{hk}) \Bigg[&\frac{\mu_{ij}}{\mu_{hk}} \frac{g_{ij}^{hk}}{g} B_{hk}^{ij}(g_{ij}^{hk}, \Omega \cdot \Omega') f_h(t, x, v_{ij}^{hk}) f_k(t, x, w_{ij}^{hk}) \\ &- B_{ij}^{hk}(g, \Omega \cdot \Omega') f_i(t, x, v) f_j(t, x, w) \Bigg] \mathrm{d}w \, \mathrm{d}\Omega', \end{aligned} \quad (4)$$

where Ω is the unit vector in the direction of the relative pre-collisional velocity $V = v - w$, whereas $g = |v - w|$ denotes its modulus; in this way, the vector V is split as $V = g\Omega$, with $g = |V|$ and $|\Omega| = 1$. Analogously, Ω' denotes the unit vector in the direction of the relative post-collisional velocity. Finally, Θ is the Heaviside step function, and $\mu_{ij} = m_i m_j / (m_i + m_j)$ are reduced masses of the colliding pairs, with m_i and m_j being the masses of particles from ith and jth species, respectively.

In (4), the pre-collisional pairs (i, j) and the post-collisional pairs (h, k) are associated with the following set of indices (i, j, h, k),

$$(1, 2, 3, 4), \quad (2, 1, 4, 3), \quad (3, 4, 1, 2), \quad (4, 3, 2, 1). \quad (5)$$

The quadruplets in (5) represent all possible reactive encounters. We note that the reactive terms are represented by a single collision integral. This is due to the fact that there is a unique chemical reaction in which species i is gained or lost.

The threshold energies are given by $\delta_{ij}^{hk} = 2\Delta E_{ij}^{hk}/\mu_{ij}$, with $\Delta E_{ij}^{hk} = E_h + E_k - E_i - E_j$ defined as

$$\Delta E_{ij}^{hk} = \begin{cases} \Delta E & \text{for } (i, j, h, k) = (1, 2, 3, 4),\ (2, 1, 4, 3); \\ -\Delta E & \text{for } (i, j, h, k) = (3, 4, 1, 2),\ (4, 3, 2, 1), \end{cases} \tag{6}$$

where $\Delta E > 0$. Finally, the post-collisional velocities appearing in (4) are defined by

$$v_{ij}^{hk} = \frac{\mu_{ij}}{m_j} v + \frac{\mu_{ij}}{m_i} w + \frac{\mu_{hk}}{m_h} g_{ij}^{hk} \Omega', \quad w_{ij}^{hk} = \frac{\mu_{ij}}{m_j} v + \frac{\mu_{ij}}{m_i} w - \frac{\mu_{hk}}{m_k} g_{ij}^{hk} \Omega', \tag{7}$$

with

$$g_{ij}^{hk} = \left[\frac{\mu_{ij}}{\mu_{hk}} (g^2 - \delta_{ij}^{hk}) \right]^{1/2}. \tag{8}$$

We observe that the expressions in (7) also include post-collisional velocities appearing in elastic collisional terms (3). Indeed, in this case, $(h, k) = (i, j)$ and $\delta_{ij}^{ij} = 0$, yielding $g_{ij}^{ij} = g$. For simplicity, we also eliminated the upper indices in the elastic scattering kernels.

The reactive and elastic scattering kernels B_{hk}^{ij} are assumed to satisfy the following (time reversal) symmetry relations,

$$\begin{aligned} B_{ij}^{hk}(g, \Omega \cdot \Omega') &= B_{ji}^{kh}(g, \Omega \cdot \Omega') = B_{ji}^{hk}(g, -\Omega \cdot \Omega') = B_{ij}^{kh}(g, -\Omega \cdot \Omega'), \\ B_{ij}(g, \Omega \cdot \Omega') &= B_{ji}(g, \Omega \cdot \Omega') = B_{ji}(g, -\Omega \cdot \Omega') = B_{ij}(g, -\Omega \cdot \Omega'). \end{aligned} \tag{9}$$

The scattering kernels are related to the elastic and reactive differential cross-sections[(4)], $I_{ij}^{hk}(g, \Omega \cdot \Omega')$, through the formulas $B_{ij}^{hk}(g, \Omega \cdot \Omega') = g I_{ij}^{hk}(g, \Omega \cdot \Omega')$.

Although the system (2)–(3)–(4) has built-in conservation laws, the H-Theorem in ref. 4 is obtained under additional microreversibility conditions on the reactive scattering kernels B_{ij}^{hk},

$$\mu_{ij}^2\, g\, B_{ij}^{hk}(g, \Omega \cdot \Omega') = \mu_{hk}^2\, g_{ij}^{hk}\, B_{hk}^{ij}(g_{ij}^{hk}, \Omega \cdot \Omega'). \tag{10}$$

Conditions (10) relate the differential cross-sections for forward and reverse reactions and have their roots in the symmetry of the Schrödinger (or Liouville) equation under time reversal (see, ref. 3).

When the microreversibility conditions (10) are assumed, the reactive collisional terms (4) have the following simpler form:

$$J_i^R = \iint_{\mathbb{R}^3\times\mathbb{S}^2} \Theta(g^2-\delta_{ij}^{hk})B_{ij}^{hk}(g,\Omega\cdot\Omega') \times\left[\left(\frac{\mu_{ij}}{\mu_{hk}}\right)^3 f_h(v_{ij}^{hk})f_k(w_{ij}^{hk})-f_i(v)f_j(w)\right]\mathrm{d}w\,\mathrm{d}\Omega' = J_i^{R+}-J_i^{R-}. \tag{11}$$

The system (2), although quite general in its scope, has not yet been compared to other known reactive kinetic theories. Furthermore, except for one example given in ref. 10 (or ref. 11), it has not been known whether the microreversibility conditions (10) can be satisfied for other, more realistic, particle potentials. In the next section, we compare the Rossani–Spiga model (2) to the SRS model[(7)]. In Section 4, we construct the reactive scattering kernels, B_{ij}^{hk}, (satisfying the microreversibility conditions (10)) for the generalization of the SRS model in which mass exchanges before and after reaction are allowed.

3. THE KINETIC THEORY OF SIMPLE REACTING SPHERES

The kinetic theory of SRSs has been proposed by Marron[(6)] and further developed by Xystris and Dahler[(7)] (see also refs. 2 and 8). The SRS is a natural extension of the hard spheres collision model that, in the dilute gas limit, can be analyzed from the point of view of Rossani–Spiga model. In the SRS model, as well as in the Rossani–Spiga model, internal degrees variables do not appear explicitly in the collisional integrals. Furthermore, the SRS reduces itself to the revised Enskog equation (or to the hard-sphere Boltzmann equation in the dilute gas limit), when the chemical reactions are turned off.

In the SRS model, both elastic and reactive interactions take place only when the particles are separated by a distance $\sigma_{rs}=\frac{1}{2}(d_r+d_s)$, where d_i denotes the diameter of the ith particle. Additionally, for the reactive collision between particles of species r and s to occur, the kinetic energy associated with the relative motion along the line of centers must exceed certain activation energy.

In the case of hard-sphere elastic encounters between a pair of particles from species r and s, the relative velocity $V=v-w$ before collision takes the post-collisional value $V'=v'-w'$ (see Fig. 1):

$$\langle \mathsf{n}, v'-w'\rangle = -\langle \mathsf{n}, v-w\rangle, \quad \langle \tau, v'-w'\rangle = \langle \tau, v-w\rangle, \tag{12}$$

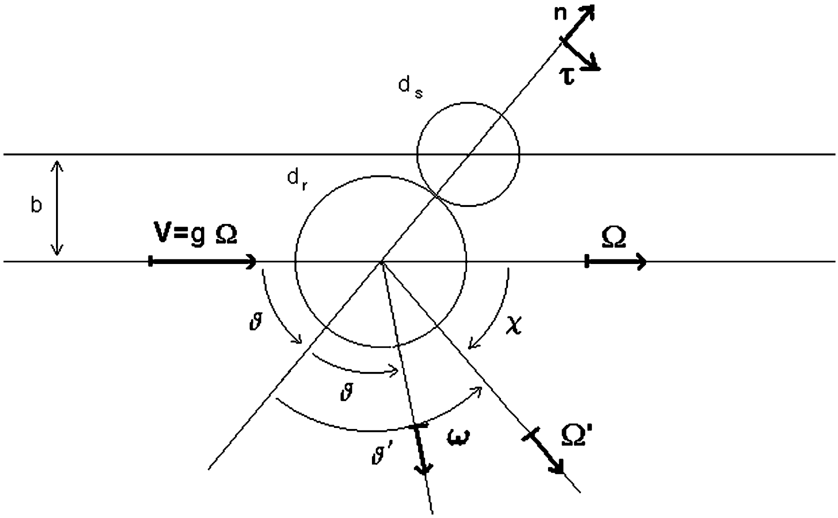

Fig. 1. Model for elastic and reactive collision between hard spheres (diameter d_r, d_s) in the relative motion reference frame.

where $\langle\cdot,\cdot\rangle$ is the inner product in $\mathbb{R}^3$, n is the unit vector along the line passing through the centers of the spheres at the moment of impact (apse line), i.e., $\mathsf{n}\in\mathbb{S}^2_+=\{\mathsf{n}\in\mathbb{R}^3:|\mathsf{n}|=1, \langle\mathsf{n}, v-w\rangle\geqslant 0\}$. In (12), τ denotes the unit vector orthogonal to n in the plane of the relative motion. Then conservations of momentum and kinetic energy lead to the following expressions for post-collisional velocities

$$v'=v-2\frac{\mu_{rs}}{m_r}\mathsf{n}\langle\mathsf{n}, v-w\rangle, \quad w'=w+2\frac{\mu_{rs}}{m_s}\mathsf{n}\langle\mathsf{n}, v-w\rangle. \tag{13}$$

As in (7), $\mu_{rs}=m_r m_s/(m_r+m_s)$ is the reduced mass of the colliding pair, where m_r and m_s are the masses of particles from rth and sth species, respectively. We note that in (13) the unit vector n, in the direction of the apse line, is used to describe the post-collisional velocities appearing in the collisional terms of the SRS model, while the unit vector Ω', in the direction of the relative post-collisional velocity, is used in Rossani–Spiga model.

The reactive encounters are accounted differently in the SRS and Rossani–Spiga models. The starting point in both cases is the conservation of momentum and total energy (the kinetic energy is not conserved in the reactive collisions). By designating the reaction $A_1+A_2\to A_3+A_4$ as an endothermic, we have

$$\frac{1}{2}\mu_{12}\,g^2=\frac{1}{2}\mu_{34}(g')^2+\Delta E, \tag{14}$$

where $g=|v-w|$ and $g'=|v'-w'|$.

In the case of the SRS model (hard-sphere-like collisions) the conservation of the tangential component of the relative velocity

$$\langle\tau, v'-w'\rangle=\langle\tau, v-w\rangle, \tag{15}$$

together with (14) yield

$$\begin{aligned}(g'_{\mathsf{n}})^2 &= (\langle\mathsf{n}, v'-w'\rangle)^2\\ &= (\langle\tau, v-w\rangle)^2\,\frac{\mu_{12}-\mu_{34}}{\mu_{34}}+\frac{\mu_{12}}{\mu_{34}}\left((\langle\mathsf{n}, v-w\rangle)^2-\frac{2\Delta E}{\mu_{12}}\right).\end{aligned} \tag{16}$$

We point out that similar conditions can be also found in the kinetic equations for granular media. In such theories in-elasticity of collisions between grains is modeled by reducing the normal relative velocity after collision by a restitution factor (see for instance ref. 12 and the references therein).

The right-hand-side of (16) must be nonnegative, thus the equation (16) implicitly defines a condition for the reactive collision to occur.

At this point two simplifications take place in the SRS model: there is no hard-sphere diameter change upon reaction, implying $\sigma_{12}=\sigma_{34}$, and there is no net mass exchange in the reaction ($m_1=m_3,\ m_2=m_4$). We note that the former assumption (see refs. 2 and 8) avoids complications in dealing with overlapping configurations, while the latter implies $\mu_{12}=\mu_{34}$. As the result of these assumptions the expression in (16) reduces to

$$\langle\mathsf{n}, v'-w'\rangle=-\sqrt{(\langle\mathsf{n}, v-w\rangle)^2-\frac{2\Delta E}{\mu_{12}}}=\alpha^-. \tag{17}$$

We note that the minus sign in front of the square root reduces (17) to the first identity in (12) when $\Delta E=0$. From (17), the energy threshold for the reactive collision to take place must be such that $(\langle\mathsf{n}, v-w\rangle)^2\geqslant 2\Delta E/\mu_{12}$, or in terms of the kinetic energy associated with the relative motion along the line of centers

$$\frac{1}{2}\mu_{12}\big(\langle\mathsf{n}, v-w\rangle\big)^2\geqslant\gamma_{12}, \tag{18}$$

with $\gamma_{12} = \gamma_{21} \geqslant \Delta E > 0$. Finally, using the same notation as in ref. 13, the endothermic reaction velocities v, w take their post-reactive values

$$v^{\ddagger} = v - \frac{\mu_{12}}{m_1}\mathsf{n}\Big[\langle \mathsf{n}, v-w\rangle - \alpha^{-}\Big], \quad w^{\ddagger} = w + \frac{\mu_{12}}{m_2}\mathsf{n}\Big[\langle \mathsf{n}, v-w\rangle - \alpha^{-}\Big]. \tag{19}$$

Analogously for the inverse exothermic reaction $A_3 + A_4 \rightarrow A_1 + A_2$, the post-reactive velocities are given by

$$v^{\dagger} = v - \frac{\mu_{34}}{m_3}\mathsf{n}\Big[\langle \mathsf{n}, v-w\rangle - \alpha^{+}\Big], \quad w^{\dagger} = w + \frac{\mu_{34}}{m_4}\mathsf{n}\Big[\langle \mathsf{n}, v-w\rangle - \alpha^{+}\Big], \tag{20}$$

with $\alpha^{+} = -\sqrt{\big(\langle \mathsf{n}, v-w\rangle\big)^2 + 2\Delta E/\mu_{34}}$, and the activation energy for A_3 and A_4 given by $\gamma_{34} = \gamma_{43} = \gamma_{12} - \Delta E$.

The dilute-gas SRS kinetic system has the form

$$\frac{\partial f_i}{\partial t} + v\frac{\partial f_i}{\partial x} = J_i^E + J_i^R, \quad i = 1, \ldots, 4, \tag{21}$$

with

$$\begin{aligned} J_i^E = {} & \sum_{s=1}^{4}\Bigg\{\sigma_{is}^2 \iint_{\mathbb{R}^3\times\mathbb{S}^2}\Big[f_i(t,x,v')f_s(t,x,w') - f_i(t,x,v)f_s(t,x,w)\Big] \\ & \qquad \Theta\left(\langle \mathsf{n}, v-w\rangle\right)\langle \mathsf{n}, v-w\rangle\, \mathrm{d}\mathsf{n}\,\mathrm{d}w\Bigg\} \\ & -\beta_{ij}\sigma_{ij}^2 \iint_{\mathbb{R}^3\times\mathbb{S}^2}\Big[f_i(t,x,v')f_s(t,x,w') - f_i(t,x,v)f_s(t,x,w)\Big] \\ & \qquad \Theta\big(\langle \mathsf{n}, v-w\rangle - \Gamma_{ij}\big)\langle \mathsf{n}, v-w\rangle\, \mathrm{d}\mathsf{n}\,\mathrm{d}w, \end{aligned} \tag{22}$$

and

$$\begin{aligned} J_i^R = {} & \beta_{ij}\sigma_{ij}^2 \iint_{\mathbb{R}^3\times\mathbb{S}^2}\Big[f_k(t,x,v_{ij}^{\odot})f_l(t,x,w_{ij}^{\odot}) - f_i(t,x,v)f_j(t,x,w)\Big] \\ & \qquad \Theta\big(\langle \mathsf{n}, v-w\rangle - \Gamma_{ij}\big)\langle \mathsf{n}, v-w\rangle\, \mathrm{d}\mathsf{n}\,\mathrm{d}w. \end{aligned} \tag{23}$$

Here, $\Gamma_{ij} = \sqrt{2\gamma_{ij}/\mu_{ij}}$, and, as before, Θ is the Heaviside step function. The coefficients $0 \leqslant \beta_{ij} = \beta_{ji} < 1$ are the steric factors for reactive collisions between species i and j; they represent the fractions of energetic enough pre-collisional pairs that actually undergo the reactions. The prime velocities in (22) are given in (13). The pair of velocities $(v_{ij}^{\odot}, w_{ij}^{\odot})$ refers to post-reactive velocities described either in (19) or (20), i.e., $(v_{ij}^{\odot}, w_{ij}^{\odot}) = (v^{\ddagger}, w^{\ddagger})$ for $i, j = 1, 2$, and $(v_{ij}^{\odot}, w_{ij}^{\odot}) = (v^{\dagger}, w^{\dagger})$ for $i, j = 3, 4$. Also, the index pairs (i, j) and (k, l) appearing in (23) are associated with the set of indices (i, j, k, l) given in (5).

We note that the first term of (22) is the hard-spheres collision operator with the usual pre-collisional range of integration, while the second term of (22) singles out those pre-collisional states that are energetic enough to result in reaction. The collision operator in (23) is purely reactive.

4. CONSTRUCTION OF ROSSANI–SPIGA'S SCATTERING KERNELS

There are two drawbacks of the SRS model: no net mass and no hard sphere diameters changes in the reactions. Moreover, at present, it is not clear how to remove these assumptions from the SRS kinetic theory and still preserve its simplicity. Instead, we start with the hard-sphere-like collisions of the SRS model, in which the tangential components of the relative velocities before and after reaction are preserved (see identity (15)), but as in the Rossani–Spiga approach, we use the unit vector of the post-collisional relative velocity Ω', to find the expressions for the corresponding reactive scattering kernels. This approach, however, requires introduction of the *reactive* diameters of molecules involved in the reaction. In general, these (fictitious) *reactive* diameters are different from the nonreactive mean diameters of the molecules (see, for example, ref. 14). Finally, as an application of our construction, we reproduce the reactive scattering kernels for the SRS model in the Rossani–Spiga formalism and compute the total reactive cross sections for both models.

The SRS and Rossani–Spiga models use different quantities to represent the scattering kernels. The apse line n is used in the former, while the unit vector of the post-collisional relative velocity Ω' is employed in the latter model. The quantity that gives the number of molecules involved in a collision is $gb\,db\,\mathrm{d}\varphi = B\,\mathrm{d}\Omega'$, where b is the impact parameter, φ is an azimuthal angle specifying the position of the plane of the relative motion in space, and B is defined as $B = (g\,b\,|\partial b/\partial\chi|)/\sin\chi$, with χ deflection angle[15]. The quantity $gb\,db\,\mathrm{d}\varphi$ is the volume per unit of time of the so called collisional cylinder associated with the particular collision under construction[16].

Now, as in the SRS model, we consider a mixture of four species, $A_i, i = 1, 2, 3, 4$, undergoing reactive interactions that occur when the kinetic energy associated with the relative motion along the line of centers exceeds certain activation energy. Furthermore, the reactions take place when the particles are separated by a distance $\tilde{\sigma}_{ij} = \frac{1}{2}(\tilde{d}_i + \tilde{d}_j)$, where $\tilde{d}_i$ is the reactive (fictitious) diameter of particle i [14]. As before, the *reactive* mean diameters $\tilde{\sigma}_{ij}$ of the pre-collisional pairs, associated with the set in (5), enjoy the natural symmetry relations $\tilde{\sigma}_{ij} = \tilde{\sigma}_{ji}$. Using the geometry of the collision (see Fig. 1), we have $b = \tilde{\sigma}_{ij} \sin\theta$, with $0 \leqslant \theta \leqslant \pi/2$; this yields $b\,\mathrm{d}b\,\mathrm{d}\varphi = \tilde{\sigma}_{ij}^2 \cos\theta\,\mathrm{dn}$, and then, as in the SRS framework, we require

$$g\,b\,\mathrm{d}b\;\mathrm{d}\varphi = \tilde{\sigma}_{ij}^2\,\langle \mathsf{n}, v - w\rangle\,\mathrm{d}\mathsf{n} = B_{ij}^{hk}(g, \cos\chi)\,\mathrm{d}\Omega'. \tag{24}$$

Here, $\langle \mathsf{n}, v - w\rangle \geqslant 0$, $\cos\chi = \Omega \cdot \Omega'$, and the pre-collisional pair (i, j) and the post-collisional pair (h, k) are associated with the set of indices (i, j, h, k) given in (5). The identity (24) constitutes a bridge between the SRS and Rossani–Spiga formulations. Furthermore, determination of $b(g, \chi)$ in (24) together with the relation $B = (b|\partial b/\partial\chi|)/\sin\chi$ will result in the expressions for the scattering kernels $B_{ij}^{hk}(g, \cos\chi)$ in the Rossani–Spiga kinetic theory.

For the $A_1 + A_2 \rightarrow A_3 + A_4$ reaction, the relative speed after collision is given by $g' = g_{12}^{34} = \sqrt{\mu_{12}/\mu_{34}\left(g^2 - \delta_{12}^{34}\right)}$ with $g^2 \geqslant \delta_{12}^{34} = 2\Delta E/\mu_{12}$. As in the SRS model, dissipation of the kinetic energy is specified by (15) and (16). Our aim is to express the impact parameter, and then the scattering kernel, in terms of $\cos\chi$ and g. We have,

$$\cos\chi = \frac{\langle v - w, v' - w'\rangle}{g\,g'}$$
$$= \frac{(\langle\tau, v - w\rangle)^2 - \langle \mathsf{n}, v - w\rangle\sqrt{(\langle\tau, v - w\rangle)^2\,\dfrac{\mu_{12} - \mu_{34}}{\mu_{34}} + \dfrac{\mu_{12}}{\mu_{34}}\left((\langle \mathsf{n}, v - w\rangle)^2 - \dfrac{2\Delta E}{\mu_{12}}\right)}}{g\sqrt{\dfrac{\mu_{12}}{\mu_{34}}\left(g^2 - \dfrac{2\Delta E}{\mu_{12}}\right)}}. \tag{25}$$

The relations (see Fig. 1)

$$\langle\tau, v - w\rangle = g\sin\theta, \qquad \langle \mathsf{n}, v - w\rangle = g\cos\theta, \qquad \text{and } \sin\theta = \frac{b}{\tilde{\sigma}_{12}}, \tag{26}$$

yield

$$\cos\chi = \frac{1}{\sqrt{\frac{\mu_{12}}{\mu_{34}}\left(g^2-\frac{2\Delta E}{\mu_{12}}\right)}}\left\{g\left(\frac{b}{\tilde{\sigma}_{12}}\right)^2 - \sqrt{\left[1-\left(\frac{b}{\tilde{\sigma}_{12}}\right)^2\right]\left[\frac{\mu_{12}}{\mu_{34}}\left(g^2-\frac{2\Delta E}{\mu_{12}}\right)-g^2\left(\frac{b}{\tilde{\sigma}_{12}}\right)^2\right]}\right\}. \quad (27)$$

The argument in the square root appearing in the numerator of equation (27) is nonnegative if

$$\sin\theta = \frac{b}{\tilde{\sigma}_{12}} \leqslant \min\left\{1, \frac{1}{g}\sqrt{\frac{\mu_{12}}{\mu_{34}}\left(g^2-\frac{2\Delta E}{\mu_{12}}\right)}\right\} = \min\left\{1, \frac{g_{12}^{34}}{g}\right\}. \quad (28)$$

This bound corresponds to the condition needed for (16) to be well defined (i.e. $(\langle \mathsf{n}, v'-w'\rangle)^2 \geqslant 0$). Moreover, when (28) holds, $\cos\chi$ is an increasing continuous function of $b/\tilde{\sigma}_{12} \geqslant 0$ (as physically expected) with the range

$$\begin{aligned} -1 \leqslant \cos\chi \ &\leqslant \min\left\{\frac{1}{g}\sqrt{\frac{\mu_{12}}{\mu_{34}}\left(g^2-\frac{2\Delta E}{\mu_{12}}\right)}, \left[\frac{1}{g}\sqrt{\frac{\mu_{12}}{\mu_{34}}\left(g^2-\frac{2\Delta E}{\mu_{12}}\right)}\right]^{-1}\right\} \\ &= \min\left\{\frac{g_{12}^{34}}{g}, \frac{g}{g_{12}^{34}}\right\} = \ell_{12}^{34}. \end{aligned} \quad (29)$$

The upper bound for $\cos\chi$ is essentially given by the ratio between g' and g (that could be less or greater than 1 depending on the relation between the reduced masses) and represents an effective constraint on the deflection angle for the chemical reaction to occur.

In the case of the SRS model, i.e., when $\mu_{12} = \mu_{34}$ (implying $m_1 = m_3$, $m_2 = m_4$), ℓ_{12}^{34} in the right-hand side of (29) becomes $\ell_{12}^{34} = \sqrt{g^2 - 2/\Delta E/\mu_{12}}/g$, which corresponds to the required threshold energy, $\langle \mathsf{n}, v-w\rangle \geqslant \sqrt{\Delta E/\mu_{12}}$ of the original SRS model (see, also inequality (18)).

Now, from (27), the impact parameter b, in terms of g and χ, is given by

$$b(g,\chi) = \tilde{\sigma}_{12}\left[\frac{\frac{\mu_{12}}{\mu_{34}}\left(g^2-\frac{2\Delta E}{\mu_{12}}\right)\sin^2\chi}{\left(g-\sqrt{\frac{\mu_{12}}{\mu_{34}}\left(g^2-\frac{2\Delta E}{\mu_{12}}\right)}\right)^2+2g(1-\cos\chi)\sqrt{\frac{\mu_{12}}{\mu_{34}}\left(g^2-\frac{2\Delta E}{\mu_{12}}\right)}}\right]^{1/2}, \tag{30}$$

for χ satisfying inequality (29).

Finally, differentiation of the right side (30) with respect to χ yields the expression for the scattering kernel B_{12}^{34}:

$$B_{12}^{34}(g,\chi) = g\,b\,\frac{\left|\frac{\partial b}{\partial\chi}\right|}{\sin\chi} = g\,\tilde{\sigma}_{12}^2\Theta(g^2-\delta_{12}^{34})\Theta(\ell_{12}^{34}-\cos\chi)$$
$$\times\frac{\frac{\mu_{12}}{\mu_{34}}\left(g^2-\frac{2\Delta E}{\mu_{12}}\right)\left\{g\sqrt{\frac{\mu_{12}}{\mu_{34}}\left(g^2-\frac{2\Delta E}{\mu_{12}}\right)}(1+\cos^2\chi)-\cos\chi\left[g^2+\frac{\mu_{12}}{\mu_{34}}\left(g^2-\frac{2\Delta E}{\mu_{12}}\right)\right]\right\}}{\left[\left(g-\sqrt{\frac{\mu_{12}}{\mu_{34}}\left(g^2-\frac{2\Delta E}{\mu_{12}}\right)}\right)^2+2g(1-\cos\chi)\sqrt{\frac{\mu_{12}}{\mu_{34}}\left(g^2-\frac{2\Delta E}{\mu_{12}}\right)}\right]^2}. \tag{31}$$

The scattering kernel $B_{12}^{34}(g,\chi)$ is positive if (29) holds. In the case of the SRS model, i.e., when $\mu_{12}=\mu_{34}$, the expression for the scattering kernel becomes:

$$B_{12}^{34\,\mathrm{SRS}}(g,\chi) = g\,\tilde{\sigma}_{12}^2\Theta\left(g-\sqrt{2\Delta E/\mu_{12}}\right)\Theta\left(\frac{\sqrt{g^2-2\Delta E/\mu_{12}}}{g}-\cos\chi\right)$$
$$\times\frac{g(g^2-2\Delta E/\mu_{12})^{3/2}(1+\cos^2\chi)-(g^2-2\Delta E/\mu_{12})(2g^2-2\Delta E/\mu_{12})\cos\chi}{\left(2g^2-2\Delta E/\mu_{12}-2g\sqrt{g^2-2\Delta E/\mu_{12}}\cos\chi\right)^2}. \tag{32}$$

Very similar arguments yield the expression for $B_{34}^{12}(g,\cos\chi)$ in the reaction $A_3+A_4\to A_1+A_2$. Indeed, the relative speed after collision is given by $g'=g_{34}^{12}=\sqrt{\frac{\mu_{34}}{\mu_{12}}\left(g^2-\delta_{34}^{12}\right)}$, where $\delta_{34}^{12}=-2\Delta E/\mu_{34}$ and the SRS-like collision mechanism is defined by (15) and by

$$(g'_{\mathsf{n}})^2 = (\langle \mathsf{n}, v - w' \rangle)^2 = (\langle \tau, v - w \rangle)^2 \frac{\mu_{34} - \mu_{12}}{\mu_{12}} + \frac{\mu_{34}}{\mu_{12}} \left((\langle \mathsf{n}, v - w \rangle)^2 + \frac{2\Delta E}{\mu_{34}} \right). \quad (33)$$

As before, from (26), we get the expression for $\cos\chi$ similar to (27),

$$\cos\chi = \frac{1}{\sqrt{\frac{\mu_{34}}{\mu_{12}} \left(g^2 + \frac{2\Delta E}{\mu_{34}} \right)}} \times \left\{ g \left(\frac{b}{\tilde{\sigma}_{34}} \right)^2 - \sqrt{\left[1 - \left(\frac{b}{\tilde{\sigma}_{34}} \right)^2 \right] \left[\frac{\mu_{34}}{\mu_{12}} \left(g^2 + \frac{2\Delta E}{\mu_{34}} \right) - g^2 \left(\frac{b}{\tilde{\sigma}_{34}} \right)^2 \right]} \right\}, \quad (34)$$

which is well defined for

$$\frac{b}{\tilde{\sigma}_{34}} \leqslant \min \left\{ 1, \frac{1}{g} \sqrt{\frac{\mu_{34}}{\mu_{12}} \left(g^2 + \frac{2\Delta E}{\mu_{34}} \right)} \right\} = \min \left\{ 1, \frac{g_{34}^{12}}{g} \right\}. \quad (35)$$

Again, $\cos\chi$ is an increasing function of $b/\tilde{\sigma}_{34}$ with the range

$$-1 \leqslant \cos\chi \leqslant \min \left\{ \frac{1}{g} \sqrt{\frac{\mu_{34}}{\mu_{12}} \left(g^2 + \frac{2\Delta E}{\mu_{34}} \right)}, \left[\frac{1}{g} \sqrt{\frac{\mu_{34}}{\mu_{12}} \left(g^2 + \frac{2\Delta E}{\mu_{34}} \right)} \right]^{-1} \right\} = \min \left\{ \frac{g_{34}^{12}}{g}, \frac{g}{g_{34}^{12}} \right\} = \ell_{34}^{12}. \quad (36)$$

Following the steps described above for the direct reaction, we finally get the expression for the scattering kernel $B_{34}^{12}(g, \cos\chi)$

$$B_{34}^{12}(g,\chi) = g\,\tilde{\sigma}_{34}^2 \Theta(\ell_{34}^{12} - \cos\chi) \times \frac{\frac{\mu_{34}}{\mu_{12}} \left(g^2 + \frac{2\Delta E}{\mu_{34}} \right) \left\{ g \sqrt{\frac{\mu_{34}}{\mu_{12}} \left(g^2 + \frac{2\Delta E}{\mu_{34}} \right)} (1 + \cos^2\chi) - \cos\chi \left[g^2 + \frac{\mu_{34}}{\mu_{12}} \left(g^2 + \frac{2\Delta E}{\mu_{34}} \right) \right] \right\}}{\left[\left(g - \sqrt{\frac{\mu_{34}}{\mu_{12}} \left(g^2 + \frac{2\Delta E}{\mu_{34}} \right)} \right)^2 + 2g(1 - \cos\chi) \sqrt{\frac{\mu_{34}}{\mu_{12}} \left(g^2 + \frac{2\Delta E}{\mu_{34}} \right)} \right]^2}. \quad (37)$$

The scattering kernel $B_{34}^{12}(g,\chi)$ is positive if (36) holds. As before, in the SRS case, i.e., when $\mu_{12}=\mu_{34}$, kernel (37) becomes

$$B_{34}^{12\,\mathrm{SRS}}(g,\chi)=g\,\tilde{\sigma}_{34}^2\Theta\left(\frac{g}{\sqrt{g^2+2\Delta E/\mu_{12}}}-\cos\chi\right)$$
$$\times\frac{g(g^2+2\Delta E/\mu_{12})^{3/2}(1+\cos^2\chi)-(g^2+2\Delta E/\mu_{12})(2g^2+2\Delta E/\mu_{12})\cos\chi}{\left(2g^2+2\Delta E/\mu_{12}-2g\sqrt{g^2+2\Delta E/\mu_{12}}\,\cos\chi\right)^2}. \tag{38}$$

The expressions (31) and (37) were obtained only from the geometry of the reactive encounters and the identities (24). These expressions can be put in the following compact form

$$B_{ij}^{hk}(g,\chi)=g\,I_{ij}^{hk}(g,\Omega\cdot\Omega')=g\,\tilde{\sigma}_{ij}^2\Theta(g^2-\delta_{ij}^{hk})\Theta(\ell_{ij}^{hk}-\cos\chi)$$
$$\times\frac{(g_{ij}^{hk})^2\left\{g\,g_{ij}^{hk}(1+\cos^2\chi)-\cos\chi\left[g^2+(g_{ij}^{hk})^2\right]\right\}}{\left[\left(g-g_{ij}^{hk}\right)^2+2g(1-\cos\chi)g_{ij}^{hk}\right]^2} \tag{39}$$

for (i,j,h,k) belonging to the set (5), and g_{ij}^{hk} given in (8).

Now, it is easy to check that $B_{12}^{34}(g,\chi)$ and $B_{34}^{12}(g,\chi)$ satisfy the relation

$$g\,B_{12}^{34}(g,\Omega\cdot\Omega')=\frac{\tilde{\sigma}_{12}^2}{\tilde{\sigma}_{34}^2}g_{12}^{34}\,B_{34}^{12}(g_{12}^{34},\Omega\cdot\Omega') \tag{40}$$

for $g^2>\delta_{12}^{34}$. Thus, the scattering kernels (31) and (37) obey the microreversibility conditions (10) if the following relation between the *reactive* mean diameters and reduced masses is satisfied:

$$\tilde{\sigma}_{12}\mu_{12}=\tilde{\sigma}_{34}\mu_{34}. \tag{41}$$

We note that condition (41) is a natural generalization of the two assumptions used in the original SRS model: no net mass and no hard sphere diameter changes in the reactions.

The scattering kernels given in (39), together with the property (41), provide the first, physically plausible, realization of the reactive kinetic theory[(4)].

We point out that although the microreversibility conditions (10) do not appear explicitly in the original SRS model, it can be traced back to the equality

$$\beta_{12}\sigma_{12}^2 = \beta_{34}\sigma_{34}^2. \tag{42}$$

The equality (42) holds for the SRS kinetic model and, at the same time, it can be considered as a weaker form of the conditions $\sigma_{12} = \sigma_{34}$ and $\beta_{12} = \beta_{34}$. Indeed, the condition (42) together with the equality of reduced masses before and after reaction ($\mu_{12} = \mu_{34}$), guarantees the existence of an H-function (see, Proposition 3.1 in ref. 13) in the SRS model.

Finally, the expressions for the elastic kernels of the Rossani–Spiga model can be obtained from (39) when $\Delta E = 0$ (no reactions) and $\tilde{\sigma}_{ij}$ is replaced by $\bar{\sigma}_{ij}$, where $\bar{\sigma}_{ij}$ are proper elastic mean diameters. We have

$$B_{ij}(g, \chi) = B_{ij}^{ij}(g, \chi) = g\,\bar{\sigma}_{ij}^2/4 \tag{43}$$

for $i, j = 1, \ldots, 4$, where Ω' becomes now the direction ω of the outgoing relative velocity for the elastic scattering (see Fig. 1).

The scattering kernels (32) and (38), together with (43), reproduce the reactive and elastic scattering kernels for the SRS model in the Rossani–Spiga formalism.

An interesting consistency result can be found by computing the total (angle integrated) reactive cross sections for both models, that for the Rossani–Spiga model reads as

$$\widehat{I}_{ij}^{hk}(g) = \int_{\mathbb{S}^2} I_{ij}^{hk}(g, \Omega\cdot\Omega')\,\mathrm{d}\Omega', \tag{44}$$

where $I_{ij}^{hk}(g, \Omega\cdot\Omega')$ is the differential cross section given in (39), whereas for the original SRS model, the total cross sections are given by

$$\beta_{ij}\sigma_{ij}^2 \frac{1}{g}\int_{\mathbb{S}^2} \Theta\left(\langle \mathsf{n}, v-w\rangle - \Gamma_{ij}\right)\langle \mathsf{n}, v-w\rangle\,\mathsf{dn}. \tag{45}$$

The integral in the right-hand side of (44) reduces to the integration of a rational function, indeed, the substitution $\cos\chi = \mu$ yields

$$\widehat{I}_{ij}^{hk}(g) = 2\pi\tilde{\sigma}_{ij}^2 (g_{ij}^{hk})^2 \Theta(g^2 - \delta_{ij}^{hk}) \int_{-1}^{\ell_{ij}^{hk}} \frac{g g_{ij}^{hk} - [g^2 + (g_{ij}^{hk})^2]\mu + g g_{ij}^{hk}\mu^2}{[(g + g_{ij}^{hk})^2 - 2g g_{ij}^{hk}\mu]^2}\mathrm{d}\mu \tag{46}$$

(with ℓ_{ij}^{hk} given in (29) and (36)) which, upon setting $\alpha = \frac{g^2+(g_{ij}^{hk})^2}{2gg_{ij}^{hk}} > 1$, gives

$$\begin{aligned}\widehat{I}_{ij}^{hk}(g) &= \frac{\pi}{2}\,\tilde{\sigma}_{ij}^2\Theta(g^2-\delta_{ij}^{hk})\frac{g_{ij}^{hk}}{g}\int_{-1}^{\ell_{ij}^{hk}}\left[1-\frac{\alpha^2-1}{(\mu-\alpha)^2}\right]\mathrm{d}\mu \\ &= \frac{\pi}{2}\,\tilde{\sigma}_{ij}^2\Theta(g^2-\delta_{ij}^{hk})\frac{g_{ij}^{hk}}{g}\,\frac{1-(\ell_{ij}^{hk})^2}{\alpha-\ell_{ij}^{hk}}.\end{aligned} \tag{47}$$

The result depends thus on whether $g_{ij}^{hk} < g$ or $g_{ij}^{hk} > g$, and reads as

$$\widehat{I}_{ij}^{hk}(g) = \begin{cases}\pi\tilde{\sigma}_{ij}^2\Theta(g^2-\delta_{ij}^{hk})\left(\frac{g_{ij}^{hk}}{g}\right)^2 & \text{for} \quad g_{ij}^{hk} < g, \\ \pi\tilde{\sigma}_{ij}^2\Theta(g^2-\delta_{ij}^{hk}) & \text{for} \quad g_{ij}^{hk} > g.\end{cases} \tag{48}$$

In the SRS case, in particular, for the endothermic reaction $A_1 + A_2 \rightarrow A_3 + A_4$ we have always $g_{12}^{34} = \sqrt{g^2 - 2\Delta E/\mu_{12}} < g$ and then

$$\widehat{I}_{12}^{34}(g) = \pi\tilde{\sigma}_{12}^2\Theta(g^2 - 2\Delta E/\mu_{12})\left(\frac{\sqrt{g^2-2\Delta E/\mu_{12}}}{g}\right)^2, \tag{49}$$

whereas for the exothermic reaction $A_3 + A_4 \rightarrow A_1 + A_2$ we have $g_{34}^{12} = \sqrt{g^2 + 2/\Delta E/\mu_{34}} > g$ and then

$$\widehat{I}_{34}^{12}(g) = \tilde{\sigma}_{34}^2\pi. \tag{50}$$

It is easy to check that the equivalent conclusion for the original SRS model (with $\gamma_{12} = \Delta E$) is obtained from (45), which uses n instead of Ω' as integration variable. Indeed the final expressions coincide with (49) and (50) only with $\beta_{ij}\sigma_{ij}^2$ replacing $\tilde{\sigma}_{ij}^2$.

These results for the SRS model (in both representations) have a clear physical interpretation since, for the endothermic reaction, the total geometrical sectional area $\pi\tilde{\sigma}_{12}^2$ is not entirely available to chemical reaction. In fact, the almost grazing collisions are forbidden due to the energy threshold on the normal component of the relative speed (in other words, there is like a shade on a ring close to the border). This does not apply to the exothermic case, since the previous threshold does not exist. Here the whole collision area is allowed and $\Omega \cdot \Omega'$ is restricted only because of the energy gain. In general then the angle integrated reactive cross sections for hard spheres depend on the relative speed, contrary to the elastic case, in which it is well known that it is a constant.

The Rossani–Spiga representation of the reactive interactions of the original SRS model, provided by the scattering kernels (32) and (38), establishes a link between the two kinetic theories. In order, however, for the model (2)–(3)–(11) to become the SRS kinetic system (21)–(22)–(23) (with $\gamma_{12} = \Delta E$ and $\gamma_{34} = 0$), the reactive scattering kernels $B_{12}^{34^{\mathrm{SRS}}}(g,\chi)$ and $B_{34}^{12^{\mathrm{SRS}}}(g,\chi)$, need to be appended by further relationships relating mean diameters and steric factors. In addition, the range of integration in the elastic collisional integrals (3) with the kernels B_{ij} given in (43) must exclude those pre-collisional states that are energetic enough to result in reaction (the second term of the elastic collisional term (22)). In the SRS kinetic model, the restriction on pre-collisional velocities of the elastic encounters eliminates situations in which certain pairs of particles can undergo simultaneously both reactive and elastic collisions. In the Rossani–Spiga model, a superposition of two independent, elastic and reactive, interaction potentials is employed, with no apparent restrictions imposed on pre-collisional velocities of the elastic encounters. Thus, the SRS model suggests a new variant of the reactive kinetic theory, where some of the elastic collisional contributions are introduced differently in order to account for situations in which certain pairs of particles can undergo simultaneously both reactive and elastic collisions. Such modified elastic and reactive collisional terms have the form

$$J_i^{Em} = \sum_{j=1}^{4} \iint_{\mathbb{R}^3\times\mathbb{S}^2} B_{ij}(g,\Omega\cdot\Omega') \times\Big[f_i(t,x,v_{ij}^{ij})f_j(t,x,w_{ij}^{ij}) - f_i(t,x,v)f_j(t,x,w)\Big]\,\mathrm{d}w\,\mathrm{d}\Omega' \tag{51}$$

$$-\beta_{ij}\iint_{\mathbb{R}^3\times\mathbb{S}^2} \Theta(g^2-\delta_{ij}^{hk})B_{ij}(g,\Omega\cdot\Omega') \times\Big[f_i(t,x,v_{ij}^{ij})f_j(t,x,w_{ij}^{ij}) - f_i(t,x,v)f_j(t,x,w)\Big]\,\mathrm{d}w\,\mathrm{d}\Omega' \tag{52}$$

and

$$J_i^{Rm} = \beta_{ij}\iint_{\mathbb{R}^3\times\mathbb{S}^2} \Theta(g^2-\delta_{ij}^{hk})B_{ij}^{hk}(g,\Omega\cdot\Omega') \times\left[\left(\frac{\mu_{ij}}{\mu_{hk}}\right)^3 f_h(v_{ij}^{hk})f_k(w_{ij}^{hk}) - f_i(v)f_j(w)\right]\mathrm{d}w\,\mathrm{d}\Omega', \tag{53}$$

where the scattering kernels satisfy the symmetry (9) and the microreversibility (10) conditions. The coefficient $0 \leqslant \beta_{ij} = \beta_{ji} \leqslant 1$ indicates the fraction of energetic enough pre-collisional pairs that actually undergo the reactions. The steric coefficient β_{ij} can depend on the threshold energy and on the macroscopic temperature $T(t,x)$. Also, the pre-collisional (i, j) and post-collisional (h,k) indices in (52) are associated with the set of indices (i, j, h, k) given in (5). As in the SRS model, term (52) removes those pre-collisional configurations that are energetic enough to result in reaction. Furthermore, the above model reduces itself to the original SRS kinetic theory (with $\gamma_{12} = \Delta E$ and $\gamma_{34} = 0$), when B_{ij} are given by (43), $B_{12}^{34} = B_{12}^{34^{\rm SRS}}$ and $B_{34}^{12} = B_{34}^{12^{\rm SRS}}$ are given by (32) and (38), respectively, and the corresponding mean diameters are replaced by the geometrical ones.

We note that due to the fact that for the elastic encounters the moduli of the pre-collisional and post-collisional relative velocities are identical ($g = g_{ij}^{ij}$), the above variant of the reactive kinetic theory enjoys the same basic properties as the original (2)–(3)–(11) system, i.e., the following (slightly modified) Theorem 5.1, the H-function (76), and Theorem 5.2.

We observe further that by changing slightly the meaning of the kernels B_{ij} and B_{ij}^{hk} in (3) and (11), respectively, the modified collisional terms (51)–(52)–(53) can be easily accommodated in the original Rossani–Spiga framework. This would require a proper definition of the (fictitious) diameters $\tilde{\sigma}_{ij}$ and $\bar{\sigma}_{ij}$. Nonetheless, an additional analysis is needed to clarify consistency and correctness of the above arguments with the particle system dynamics and/or the macroscopic equations and the corresponding transport coefficients.

Indeed, while the SRS model can be derived from the Liouville equation (see, refs. 8 and 12), or from the corresponding BBGKY hierarchy equations, it is not known at this time whether the original Rossani–Spiga kinetic theory, or its variant (51)–(52)–(53), have their origins in particle system equations.

5. PROPERTIES OF THE ROSSANI–SPIGA KINETIC THEORY

In this section we derive the properties of the system (2)–(3)–(4) that play crucial role in the existence results and approach to equilibrium. Throughout this section, the scattering kernels B_{ij} and B_{ij}^{hk} satisfy the following bound

$$\max_{0\leqslant\lambda<2.} \left\{ \sup_{\Omega\in\mathbb{S}^2} \int_{\mathbb{S}^2} B_{ij}(g, \Omega\cdot\Omega')\, \mathrm{d}\Omega',\ \sup_{\Omega\in\mathbb{S}^2} \int_{\mathbb{S}^2} B_{ij}^{hk}(g, \Omega\cdot\Omega')\, \mathrm{d}\Omega' \right\} \leqslant \text{constant}\cdot g^{\lambda},\ 0\leqslant\lambda<2. \qquad (54)$$

Assuming the usual angular cutoff hypothesis [17], the inequality (54) is satisfied for all inverse power potentials $V(r)=r^{-s}$ with $s>2$. The hard-sphere potential ($s=\infty$) corresponds to $\lambda=1$.

We recall that the gas mixture is confined to $D\subseteq\mathbb{R}^3$ with $D=\mathbb{R}^3$ or D being a three-dimensional torus $[0,L]^3$, $L>0$. The latter choice corresponds to case of the periodic boundary conditions on $[0,L]^3$.

The conservation of mass, momentum and total energy yield the following crucial property of the Rossani–Spiga system (2)–(3)–(4):

Theorem 5.1. For Φ_i measurable on $D\times\mathbb{R}^3$ and $f_i(t,\cdot)\in C_0(D\times\mathbb{R}^3)$, $i=1,\dots,4$,

$$\sum_{i=1}^{4}\int_{\mathbb{R}^3}\Phi_i J_i^E\,\mathrm{d}v=\frac{1}{4}\sum_{i=1}^{4}\sum_{j=1}^{4}\iiint_{\mathbb{R}^3\times\mathbb{R}^3\times\mathbb{S}^2}\left[\Phi_i(v)+\Phi_j(w)-\Phi_i(v_{ij}^{ij})-\Phi_j(w_{ij}^{ij})\right]$$
$$\times B_{ij}(g,\Omega\cdot\Omega')\left\{f_i(v)+f_j(w)-f_i(v_{ij}^{ij})-f_j(w_{ij}^{ij})\right\}\mathrm{d}v\,\mathrm{d}w\,\mathrm{d}\Omega', \tag{55}$$

$$\sum_{i=1}^{4}\int_{\mathbb{R}^3}\Phi_i J_i^R\,\mathrm{d}v=\iiint_{\mathbb{R}^3\times\mathbb{R}^3\times\mathbb{S}^2}\Theta(g^2-\delta_{12}^{34})\Big[\Phi_1(v)+\Phi_2(w)-\Phi_3(v_{12}^{34})-\Phi_4(w_{12}^{34})\Big]$$
$$\times\left\{\frac{\mu_{12}}{\mu_{34}}\frac{g_{12}^{34}}{g}B_{34}^{12}(g_{12}^{34},\Omega\cdot\Omega')f_3(v_{12}^{34})f_4(w_{12}^{34})\right.$$
$$\left.-B_{12}^{34}(g,\Omega\cdot\Omega')f_1(v)f_2(w)\right\}\mathrm{d}v\,\mathrm{d}w\,\mathrm{d}\Omega', \tag{56}$$

and

$$\sum_{i=1}^{4}\int_{\mathbb{R}^3}\Phi_i J_i^R\,dv=\iiint_{\mathbb{R}^3\times\mathbb{R}^3\times\mathbb{S}^2}\Big[\Phi_3(v)+\Phi_4(w)-\Phi_1(v_{34}^{12})-\Phi_2(w_{34}^{12})\Big]$$
$$\times\left\{\frac{\mu_{34}}{\mu_{12}}\frac{g_{34}^{12}}{g}B_{12}^{34}(g_{34}^{12},\Omega\cdot\Omega')f_1(v_{34}^{12})f_2(w_{34}^{12})\right.$$
$$\left.-B_{34}^{12}(g,\Omega\cdot\Omega')f_3(v)f_4(w)\right\}\mathrm{d}v\,\mathrm{d}w\,\mathrm{d}\Omega'. \tag{57}$$

Proof. The identity (55) is a standard result from inert mixtures (see, for example, ref. 16). For the proof of (56) and (57) we need the following lemma.

Lemma 5.1. The Jacobian of the transformation $(v, w, \Omega') \mapsto \left(v_{ij}^{hk}, w_{ij}^{hk}, \Omega\right)$ has the form

$$\left|\frac{\partial\left(v_{ij}^{hk}, w_{ij}^{hk}, \Omega\right)}{\partial(v, w, \Omega')}\right| = \frac{\mu_{ij}}{\mu_{hk}} \frac{g_{ij}^{hk}}{g}, \tag{58}$$

where v_{ij}^{hk}, w_{ij}^{hk}, and g_{ij}^{hk} are given in (7) and (8), respectively. Here, the pre-reactive pairs (i, j) and the post-reactive pairs (h, k) are associated with the following set of indices (i, j, k, l)

$$(1, 2, 3, 4), \quad (2, 1, 4, 3), \quad (3, 4, 1, 2), \quad (4, 3, 2, 1),$$

corresponding to all possible reactions $A_i + A_j \rightleftharpoons A_h + A_k$.

Proof of Lemma 5.1. First we note that the domain of the transformation $(v, w, \Omega') \mapsto \left(v_{ij}^{hk}, w_{ij}^{hk}, \Omega\right)$ is defined by the conditions $g^2 \geqslant \delta_{ij}^{hk}$ corresponding to the threshold energies for the endothermic reactions. This fact will be used in the proof of Theorem 5.1.

Now, if

$$G_{rs} = \frac{\mu_{rs}}{m_s} v + \frac{\mu_{rs}}{m_r} w$$

denotes the velocity of the center-of-mass, (invariant throughout the reaction, i.e., $G_{ij} = G_{hk}$), $V = v - w$, and $V_{ij}^{hk} = v_{ij}^{hk} - w_{ij}^{hk}$ are the relative velocities before and after collision, respectively, then the following equality holds

$$\frac{\partial\left(v_{ij}^{hk}, w_{ij}^{hk}, \Omega\right)}{\partial(v, w, \Omega')} = \frac{\partial\left(G_{hk}, V_{ij}^{hk}, \Omega\right)}{\partial\left(G_{ij}, V, \Omega'\right)} = \frac{\partial\left(V_{ij}^{hk}, \Omega\right)}{\partial(V, \Omega')}. \tag{59}$$

The use of polar coordinates together with $V_{ij}^{hk} = g_{ij}^{hk} \Omega'$,

$$\mathrm{d}V_{ij}^{hk}\, \mathrm{d}\Omega = \left(g_{ij}^{hk}\right)^2 dg_{ij}^{hk}\, \mathrm{d}\Omega'\, \mathrm{d}\Omega = g_{ij}^{hk} \frac{\mu_{ij}}{\mu_{hk}} g\, dg\, \mathrm{d}\Omega\, \mathrm{d}\Omega' = \frac{g_{ij}^{hk}}{g} \frac{\mu_{ij}}{\mu_{hk}} \mathrm{d}V\, \mathrm{d}\Omega', \tag{60}$$

proves the lemma.

For the proof of Theorem 5.1 we consider the first two integrals ($i = 1, 2$) appearing on the left-hand side of (56),

$$\int_{\mathbb{R}^3} \Phi_1(v) J_1^R \,\mathrm{d}v = \int\int\int_{\mathbb{R}^3\times\mathbb{R}^3\times\mathbb{S}^2} \Theta(g^2 - \delta_{12}^{34}) \times \left[\frac{\mu_{12}}{\mu_{34}} \frac{g_{12}^{34}}{g} B_{34}^{12}(g_{12}^{34}, \Omega\cdot\Omega') f_3(v_{12}^{34}) f_4(w_{12}^{34}) - B_{12}^{34}(g, \Omega\cdot\Omega') f_1(v) f_2(w) \right] \times \Phi_1(v) \,\mathrm{d}v \,\mathrm{d}w \,\mathrm{d}\Omega', \tag{61}$$

$$\int_{\mathbb{R}^3} \Phi_2(v) J_2^R \,dv = \int\int\int_{\mathbb{R}^3\times\mathbb{R}^3\times\mathbb{S}^2} \Theta(g^2 - \delta_{21}^{43}) \times \left[\frac{\mu_{21}}{\mu_{43}} \frac{g_{21}^{43}}{g} B_{43}^{21}(g_{21}^{43}, \Omega\cdot\Omega') f_4(v_{21}^{43}) f_3(w_{21}^{43}) - B_{21}^{43}(g, \Omega\cdot\Omega') f_2(v) f_1(w) \right] \times \Phi_2(v) \,\mathrm{d}v \,\mathrm{d}w \,\mathrm{d}\Omega'. \tag{62}$$

After the change of variables $(v, w, \Omega') \mapsto (w, v, -\Omega')$ and the symmetry property (9), the right-hand side of (62) becomes

$$\int_{\mathbb{R}^3} \Phi_2(v) J_2^R \,\mathrm{d}v = \int\int\int_{\mathbb{R}^3\times\mathbb{R}^3\times\mathbb{S}^2} \Theta(g^2 - \delta_{12}^{34}) \times \left[\frac{\mu_{12}}{\mu_{34}} \frac{g_{12}^{34}}{g} B_{34}^{12}(g_{12}^{34}, \Omega\cdot\Omega') f_3(v_{12}^{34}) f_4(w_{12}^{34}) - B_{12}^{34}(g, \Omega\cdot\Omega') f_1(v) f_2(w) \right] \times \Phi_2(w) \,\mathrm{d}v \,\mathrm{d}w \,\mathrm{d}\Omega'. \tag{63}$$

In the third integral ($i = 3$) on the left-hand side of (56),

$$\int_{\mathbb{R}^3} \Phi_3(v) J_3^R \,\mathrm{d}v = \int\int\int_{\mathbb{R}^3\times\mathbb{R}^3\times\mathbb{S}^2} \times \left[\frac{\mu_{34}}{\mu_{12}} \frac{g_{34}^{12}}{g} B_{12}^{34}(g_{34}^{12}, \Omega\cdot\Omega') f_1(v_{34}^{12}) f_2(w_{34}^{12}) - B_{34}^{12}(g, \Omega\cdot\Omega') f_3(v) f_4(w) \right] \times \Phi_3(v) \,\mathrm{d}v \,\mathrm{d}w \,\mathrm{d}\Omega', \tag{64}$$

we change the variables $\big(v_{34}^{12}, w_{34}^{12}, \Omega\big) \mapsto (\tilde{v}, \tilde{w}, \tilde{\Omega}')$, This amounts to reversing the reaction, when g_{34}^{12} becomes $\tilde{g}$, g becomes $\tilde{g}_{12}^{34}$ and the triplet of variables (v, w, Ω') becomes $\big(\tilde{v}_{12}^{34}, \tilde{w}_{12}^{34}, \tilde{\Omega}\big)$. Now, using Lemma 5.1 together with the fact that $\tilde{g} \geqslant \delta_{12}^{34}$, and after dropping all tildes, we obtain,

$$\int_{\mathbb{R}^3} \Phi_3(v) J_3^R \, \mathrm{d}v = \iiint_{\mathbb{R}^3\times\mathbb{R}^3\times\mathbb{S}^2} \Big[\frac{\mu_{34}}{\mu_{12}} \frac{g}{g_{12}^{34}} B_{12}^{34}(g, \Omega\cdot\Omega') f_1(v) f_2(w) - B_{34}^{12}(g_{12}^{34}, \Omega\cdot\Omega') f_3(v_{12}^{34}) f_4(w_{12}^{34})\Big] \times \Phi_3(v_{12}^{34}) \frac{\mu_{12}}{\mu_{34}} \Theta(g^2 - \delta_{12}^{34}) \frac{g_{12}^{34}}{g} \, \mathrm{d}v \, \mathrm{d}w \, \mathrm{d}\Omega = - \iiint_{\mathbb{R}^3\times\mathbb{R}^3\times\mathbb{S}^2} \Theta(g^2 - \delta_{12}^{34}) \times \left[\frac{\mu_{12}}{\mu_{34}} \frac{g_{12}^{34}}{g} B_{34}^{12}(g_{12}^{34}, \Omega\cdot\Omega') f_3(v_{12}^{34}) f_4(w_{12}^{34}) - B_{12}^{34}(g, \Omega\cdot\Omega') f_1(v) f_2(w) \right] \times \Phi_3(v_{12}^{34}) \, \mathrm{d}v \, \mathrm{d}w \, \mathrm{d}\Omega. \tag{65}$$

In the fourth integral ($i=4$) on the left-hand side of (56),

$$\int_{\mathbb{R}^3} \Phi_4(v) J_4^R \, \mathrm{d}v = \iiint_{\mathbb{R}^3\times\mathbb{R}^3\times\mathbb{S}^2} \left[\frac{\mu_{43}}{\mu_{21}} \frac{g_{43}^{21}}{g} B_{21}^{43}(g_{43}^{21}, \Omega\cdot\Omega') f_2(v_{43}^{21}) f_1(w_{43}^{21}) - B_{43}^{21}(g, \Omega\cdot\Omega') f_4(v) f_3(w) \right] \times \Phi_4(v) \, \mathrm{d}v \, \mathrm{d}w \, \mathrm{d}\Omega', \tag{66}$$

we perform the same changes that have led to (63) and (65). The result is

$$\int_{\mathbb{R}^3} \Phi_4(v) J_4^R \, \mathrm{d}v = - \iiint_{\mathbb{R}^3\times\mathbb{R}^3\times\mathbb{S}^2} \Theta(g^2 - \delta_{12}^{34}) \Big[\frac{\mu_{12}}{\mu_{34}} \frac{g_{12}^{34}}{g} B_{34}^{12}(g_{12}^{34}, \Omega\cdot\Omega') f_3(v_{12}^{34}) f_4(w_{12}^{34}) - B_{12}^{34}(g, \Omega\cdot\Omega') f_1(v) f_2(w) \Big] \Phi_4(v_{12}^{34}) \, \mathrm{d}v \, \mathrm{d}w \, \mathrm{d}\Omega'. \tag{67}$$

Finally, we sum up the right-hand sides of (61), (63), (65), and (67) to obtain the identity (56).

For the proof of (57) we follow the same line of arguments as above. This time, however, the third integral ($i=3$) on the left-hand side of (57), (or equivalently the integral on right-hand side of (64)) is taken as the reference point. In this process, the variables of integration in the right-hand side of (61) and (62) are changed from $\left(v_{12}^{34}, w_{12}^{34}, \Omega\right)$ and $\left(v_{21}^{43}, w_{21}^{43}, \Omega\right)$ to $(\tilde{v}, \tilde{w}, \tilde{\Omega}')$, and then the integration variables (v, w, Ω') become $(\tilde{v}_{34}^{12}, \tilde{w}_{34}^{12}, \tilde{\Omega})$ and $(\tilde{v}_{43}^{21}, \tilde{w}_{43}^{21}, \tilde{\Omega})$.

Remark 5.1. In view of (54), the assumption that $f_i(t,\cdot)\in C_0(D\times\mathbb{R}^3)$, for $i=1,\dots,4$, is needed to make sure that all integrals exist and are finite.

Theorem 5.1 yields the following implication,

$$\forall \Phi_i(v) = a\,m_i + m_i\langle b, v\rangle + c\left(\frac{m_i v^2}{2} + E_i\right),\quad a, c\in\mathbb{R}, b\in\mathbb{R}^3$$
$$\Longrightarrow \begin{cases} \sum_{i=1}^4 \int_{\mathbb{R}^3} \Phi_i J_i^E \,\mathrm{d}v = 0. \\ \sum_{i=1}^4 \int_{\mathbb{R}^3} \Phi_i J_i^R \,\mathrm{d}v = 0. \end{cases} \tag{68}$$

In other words, if f_i is a nonnegative smooth solution of (2)–(3)–(4) on $[0, T_0]$, $T_0 > 0$, then at least formally, we have the usual conservation laws of total mass, momentum and total energy, for $t\in[0, T_0]$. Indeed, they follow from multiplication of the system (2) by the corresponding $\Phi_i = m_i$, $\Phi_i = m_i\langle v, e_k\rangle$ (e_k, the basis in $\mathbb{R}^3$), and $\Phi_i = m_i v^2/2 + E_i$, $i = 1,\dots,4$, integrating with respect to $(t, v, x)\in[0, T_0]\times D\times\mathbb{R}^3$, and summing over i. The result is

$$\sum_{i=1}^4 \iint_{D\times\mathbb{R}^3} m_i f_i(t,x,v)\,\mathrm{d}v\,\mathrm{d}x = \sum_{i=1}^4 \iint_{D\times\mathbb{R}^3} m_i f_{i0}(x,v)\,\mathrm{d}v\,\mathrm{d}x, \tag{69}$$

$$\sum_{i=1}^4 \iint_{D\times\mathbb{R}^3} m_i\,\langle v, e_k\rangle f_i(t,x,v)\,\mathrm{d}v\,\mathrm{d}x = \sum_{i=1}^4 \iint_{D\times\mathbb{R}^3} m_i\,\langle v, e_k\rangle f_{i0}(x,v)\,\mathrm{d}v\,\mathrm{d}x, \tag{70}$$

$$\sum_{i=1}^4 \iint_{D\times\mathbb{R}^3} \left(m_i v^2/2 + E_i\right) f_i(t,x,v)\,\mathrm{d}v\,\mathrm{d}x$$
$$= \sum_{i=1}^4 \iint_{D\times\mathbb{R}^3} \left(m_i v^2/2 + E_i\right) f_{i0}(x,v)\,\mathrm{d}v\,\mathrm{d}x. \tag{71}$$

Remark 5.2. It has been furthermore shown (see ref. 9), the collision invariants Φ_i form a seven-dimensional linear space; in addition to conservation of the total mass, there are also three independent partial sums of number densities that are conserved. This is related to the balance between reactants and products in the chemical reaction under consideration.

An additional conservation law (along the characteristics of the streaming operator) can be obtained by noticing that also $\Phi_i(x,v) = m_i(x-tv)^2/2 + E_i$ is a collision invariant for any $t\in[0, T_0]$ and $i=1,\dots,4$.

Then we have for $t \in [0, T_0]$

$$\sum_{i=1}^{4} \iint_{D\times\mathbb{R}^3} \left(\frac{m_i (x - tv)^2}{2} + E_i \right) f_i(t, x, v) \mathrm{d}v \, \mathrm{d}x = \sum_{i=1}^{4} \iint_{D\times\mathbb{R}^3} \left(\frac{m_i x^2}{2} + E_i \right) f_{i0}(x, v) \mathrm{d}v \, \mathrm{d}x. \tag{72}$$

The conservation laws (69)–(72) and non–negativity of f_i, f_{i0} yield the following estimation, which is useful when the spatial domain is equal to $D = \mathbb{R}^3$,

$$\sup_i \sup_{t\in[0,T_0]} \iint_{D\times\mathbb{R}^3} x^2 f_i(t, x, v) \mathrm{d}v \, \mathrm{d}x \leqslant C_1 \tag{73}$$

where $C_1 > 0$ depends only on T_0, on $\sup_i \iint_{D\times\mathbb{R}^3} x^2 f_i \, \mathrm{d}v \, \mathrm{d}x$, and on $\sup_i \iint_{D\times\mathbb{R}^3} (1 + v^2) f_i \, \mathrm{d}v \mathrm{d}x$.

Next, the existence of a Liapunov functional (H-function) follows from the Theorem 5.1 if the microreversibility conditions (10) are taken into account. After multiplying (2) by $1 + \log \hat{f}_i$, with $\hat{f}_i = f_i/(m_i^3)$ (a smooth nonnegative solution), integrating over D, summing up over $i = 1, \ldots, 4$, and using (55)–(57) (with $\Phi_i = 1, \log \hat{f}_i$) we obtain the following entropy identity

$$\begin{aligned}
0 = &\sum_{i=1}^{4} \frac{\mathrm{d}}{\mathrm{d}t} \iint_{D\times\mathbb{R}^3} f_i \log \hat{f}_i \, \mathrm{d}v \, \mathrm{d}x \\
&+ \frac{1}{4} \sum_{i,j=1}^{4} \iiiint_{D\times\mathbb{R}^3\times\mathbb{R}^3\times\mathbb{S}^2} B_{ij}(g, \Omega\cdot\Omega') \log \left(\frac{f_i(v) f_j(w)}{f_i(v_{ij}^{ij}) f_j(w_{ij}^{ij})} \right) \\
&\times \left[f_i(v_{ij}^{ij}) f_j(w_{ij}^{ij}) - f_i(v) f_j(w) \right] \mathrm{d}v \, \mathrm{d}w \, \mathrm{d}\Omega' \, \mathrm{d}x \\
&+ \iiiint_{D\times\mathbb{R}^3\times\mathbb{R}^3\times\mathbb{S}^2} \Theta(g^2 - \delta_{12}^{34}) \log \left(\frac{\hat{f}_1(v) \hat{f}_2(w)}{\hat{f}_3(v_{12}^{34}) \hat{f}_4(w_{12}^{34})} \right) \\
&\times \left[B_{12}^{34}(g, \Omega\cdot\Omega') f_1(v) f_2(w) - \frac{\mu_{12}}{\mu_{34}} \frac{g_{12}^{34}}{g} B_{34}^{12}(g_{12}^{34}, \Omega\cdot\Omega') f_3(v_{12}^{34}) f_4(w_{12}^{34}) \right] \\
&\times \mathrm{d}v \mathrm{d}w \, \mathrm{d}\Omega' \, \mathrm{d}x.
\end{aligned} \tag{74}$$

The second term in the right-hand side of (74) is nonnegative since the integrands are of the form $(x-1)\log x$, which is a nonnegative convex function for $x>0$. On the other hand, the integrand appearing in the third term of (74) is not necessarily nonnegative, however, if we use the microversibility conditions (10), it becomes

$$\Theta(g^2-\delta_{12}^{34})B_{12}^{34}(g,\Omega\cdot\Omega')(m_1m_2)^3\log\left(\frac{\hat{f}_1(v)\hat{f}_2(w)}{\hat{f}_3(v_{12}^{34})\hat{f}_4(w_{12}^{34})}\right)$$
$$\left[\hat{f}_1(v)\hat{f}_2(w)-\hat{f}_3(v_{12}^{34})\hat{f}_4(w_{12}^{34})\right]\geqslant 0. \tag{75}$$

Thus, for a nonnegative solution f_i of (2), the function $H(t)$ defined by

$$H(t)=\sum_{i=1}^{4}\iint_{D\times\mathbb{R}^3} f_i\log\hat{f}_i\,\mathrm{d}v\,\mathrm{d}x \tag{76}$$

is nonincreasing in t.

The H-function (76), satisfying the identity (74), guarantees that solutions of the Rossani–Spiga model (2)–(3)–(11) tend to equilibrium solutions. Parameters of the equilibrium solutions are the macroscopic quantities: the number densities $n_i(t,x)$, the macroscopic velocity $u(t,x)$, and the macroscopic temperature $T(t,x)$. They are given by the following standard expressions:

$$n_i(t,x)=\int_{\mathbb{R}^3} f_i(t,x,v)\,\mathrm{d}v,\qquad n(t,x)=\sum_{i=1}^{4}n_i(t,x), \tag{77}$$

$$u(t,x)=\frac{\sum_{i=1}^{4}m_in_i(t,x)u_i(t,x)}{\sum_{i=1}^{4}m_in_i(t,x)},\qquad u_i(t,x)=\frac{\int_{\mathbb{R}^3}vf_i(t,x,v)\,\mathrm{d}v}{n_i(t,x)}, \tag{78}$$

$$3kn(t,x)T(t,x)=\sum_{i=1}^{4}m_i\int_{\mathbb{R}^3}[v-u(t,x)]^2 f_i(t,x,v)\,\mathrm{d}v, \tag{79}$$

where k is the Boltzmann constant. As in ref. 4 (see also Proposition 3.2 in ref. 13), the equilibrium solutions are Maxwellians,

$$f_i=n_i\left(\frac{m_i}{2\pi kT}\right)^{3/2}\exp\left(-\frac{m_i(v-u)^2}{2kT}\right),\quad i=1,\dots,4, \tag{80}$$

with n_i, u, and T given in (77), (78), and (79), respectively. Furthermore, in the case of the Rossani–Spiga model, the mass action law has the form

$$\frac{n_1 n_2}{n_3 n_4} = \left(\frac{m_1 m_2}{m_3 m_4}\right)^{3/2} \exp\left(\frac{\Delta E}{kT}\right). \tag{81}$$

We observe that the elastic collisional terms (3) are responsible for the equilibrium solutions to be Maxwellian distributions. Indeed, non-negativity of both the second term in (74) and term (75) guarantee that, at equilibrium,

$$f_i(v_{ij}^{ij}) f_j(w_{ij}^{ij}) = f_i(v) f_j(w), \quad i, j = 1, 2, 3, 4, \tag{82}$$

for all (v, w) for which $B_{ij} > 0$, and

$$\hat{f}_3(v_{12}^{34}) \hat{f}_4(w_{12}^{34}) = \hat{f}_1(v) \hat{f}_2(w) \tag{83}$$

for all (v, w) for which $B_{12}^{34} > 0$. Next, following Proposition 6.1 of ref. 18, the identities,

$$f_k(v_{kl}^{kl}) f_l(w_{kl}^{kl}) = f_k(v) f_l(w), \qquad f_l(v_{kl}^{kl}) f_k(w_{kl}^{kl}) = f_l(v) f_k(w) \tag{84}$$

for fixed k and l, guarantee that the distributions f_k and f_l are the local Maxwellians with common macroscopic velocity $u(t, x)$ and common macroscopic temperature $T(t, x)$. Thus, the presence of certain terms J_{ij}^E in the elastic collisional integrals (3) appears to be necessary for the equilibrium solutions f_1, f_2, f_3, and f_4 to be local Maxwellians, with common velocity $u(t, x)$ and temperature $T(t, x)$. One such example is provided by $J_1^E = J_{13}^E + J_{14}^E$, $J_2^E = J_{24}^E$, $J_3^E = J_{31}^E$, and $J_4^E = J_{41}^E + J_{42}^E$. Finally, we note that identity (83) yields the mass action law (81).

We end this section by stating a global (in time) existence result for the Rossani–Spiga system (2)–(3)–(11). The idea of the proof is based on the L^1-weak compactness argument and the notion of the renormalized solutions developed by DiPerna and Lions[(19)] in the context of the single specie and nonreactive Boltzmann equation. The conservation of total mass (69), momentum (70), and total energy (71), together with the entropy identity (74) and (75), imply that nonnegative, smooth solutions of the system (2)–(3)–(11) satisfy the bound

$$\sup_i \sup_{t \in [0, T_0]} \iint_{D \times \mathbb{R}^3} \left(1 + x^2 + v^2 + \log^+ f_i\right) f_i \, \mathrm{d}v \, \mathrm{d}x = C_{T_0} < \infty \tag{85}$$

if the following inequality is satisfied,

$$\sup_i \iint_{D\times\mathbb{R}^3} \left(1+x^2+v^2+\log^+ f_{i0}\right) f_{i0}\,\mathrm{d}v\mathrm{d}x = C_0 < \infty \tag{86}$$

for nonnegative initial distributions f_{i0}. As in the case of the Boltzmann equation (see also ref. 13 for the SRS model), the inequality (85) implies that the family of solutions $\{f_i(t): 0 \leqslant t \leqslant T_0\}$ is relatively weakly compact in $L^1(D\times\mathbb{R}^3)$. Furthermore, there can be no infinite concentration of densities in the system described by (2)–(3)–(11).

Definition 5.1. Nonnegative $f_i \in L^1_{loc}((0,T_0)\times D\times\mathbb{R}^3)$ $(i=1,2,3,4)$ are renormalized solutions of (2)–(3)–(11) if

$$\frac{1}{1+f_i} J_i^{E\pm} \in L^1_{loc}((0,T)\times D\times\mathbb{R}^3), \qquad \frac{1}{1+f_i} J_i^{R\pm} \in L^1_{loc}((0,T)\times D\times\mathbb{R}^3) \tag{87}$$

and

$$\frac{\partial}{\partial t}\log(1+f_i) + v\frac{\partial}{\partial x}\log(1+f_i) = \frac{1}{1+f_i}\left[J_i^E + J_i^R\right] \tag{88}$$

in $\mathcal{D}'((0,T)\times D\times\mathbb{R}^3)$, where

$$J_i^E = J_i^{E+} - J_i^{E-}, \qquad J_i^R = J_i^{R+} - J_i^{R-} \tag{89}$$

with $J_i^{E\pm}$ and $J_i^{R\pm}$ are given in (3) and (11), respectively.

The following global existence result is true:

Theorem 5.2. Assume that the scattering kernels B_{ij} and B_{hk}^{ij} satisfy the conditions (54). If for $i=1,2,3,4$, $f_{i0}\geqslant 0$ satisfy condition (86) then there exists a nonnegative renormalized solution f_i of (2)–(3)–(11) with $f_i \in C([0,T_0]; L^1(D\times\mathbb{R}^3))$ satisfying (85), and such that $f_i(t)\big|_{t=0} = f_{i0}$ for $i=1,2,3,4$.

Proof of Theorem 5.2. It follows similar arguments as in ref. 13. The main idea is to find suitable approximations J_{in}^E and J_{in}^R of J_i^E and J_i^R, respectively, for which the system,

$$\begin{aligned} \frac{\partial f_i^n}{\partial t} + v\cdot\frac{\partial f_i^n}{\partial x} &= J_{in}^E + J_{in}^R, \qquad f_i^n(0,x,v) = f_{i0}^n(x,v),\\ i &= 1,\ldots,4, \qquad (x,v)\in D\times\mathbb{R}^3, \end{aligned} \tag{90}$$

is easily solvable by known methods for $n = 1, 2, \ldots$. Next, one shows that the weak limits $f_i^n \to f_i$ are renormalized solutions of (2)–(3)–(11). The crucial passage to the limit is based on the DiPerna-Lions arguments found in ref. 19. For completeness, we provide, below, an example of suitable approximations of the collisional terms that allow for this passage to the limit to take place:

$$J_{in}^E = \left(\frac{1}{1 + \frac{1}{n} \sum_{i=1}^4 \int_{\mathbb{R}^3} f_i^n \, \mathrm{d}v} \right) \sum_{j=1}^4 \iint_{\mathbb{R}^3 \times \mathbb{S}^2} B_{ij}^n(g, \Omega \cdot \Omega') \times \left[f_i^n(t, x, v_{ij}^{ij}) f_j^n(t, x, w_{ij}^{ij}) - f_i^n(t, x, v) f_j^n(t, x, w) \right] \mathrm{d}w \, \mathrm{d}\Omega' \quad (91)$$

and

$$J_{in}^R = \left(\frac{1}{1 + \frac{1}{n} \sum_{i=1}^4 \int_{\mathbb{R}^3} f_i^n \, \mathrm{d}v} \right) \iint_{\mathbb{R}^3 \times \mathbb{S}^2} \Theta(g^2 - \delta_{ij}^{hk}) (B_{ij}^{hk})^n (g, \Omega \cdot \Omega') \times \left[\left(\frac{\mu_{ij}}{\mu_{hk}} \right)^3 f_h^n(v_{ij}^{hk}) f_k^n(w_{ij}^{hk}) - f_i^n(v) f_j^n(w) \right] \mathrm{d}w \, \mathrm{d}\Omega', \quad (92)$$

where

$$B_{ij}^n(g, \Omega \cdot \Omega') = \begin{cases} B_{ij}(g, \Omega \cdot \Omega') & \text{if } v^2 + w^2 \leqslant n, \\ 0, & \text{otherwise} \end{cases} \quad (93)$$

for $i = 1, 2, 3, 4$,

$$(B_{34}^{12})^n(g, \Omega \cdot \Omega') = \begin{cases} B_{34}^{12}(g, \Omega \cdot \Omega') & \text{if } v^2 + w^2 \leqslant n, \\ 0 & \text{otherwise} \end{cases} \quad (94)$$

and

$$(B_{12}^{34})^n(g, \Omega \cdot \Omega') = \left(\frac{g_{12}^{34}}{g} \right) \left(\frac{\mu_{34}}{\mu_{12}} \right)^2 (B_{34}^{12})^n (g_{12}^{34}, \Omega \cdot \Omega') \quad (95)$$

with $(B_{21}^{43})^n = (B_{12}^{34})^n$ and $(B_{43}^{21})^n = (B_{34}^{12})^n$. It is easy to check that the above approximated kernels B_{ij}^n and $(B_{ij}^{hk})^n$ are bounded and converge pointwise to B_{ij} and B_{ij}^{hk}, respectively, as $n \to \infty$. Furthermore, they satisfy the symmetry relations (9), while the reactive approximated kernels satisfy the microreversibility conditions (10). Thus, Theorem 5.1 holds for the approximated system (90) and the function $H(t)$ defined in (76) is its H-function. From now on the proof follows very similar arguments as in refs. 13 and 19.

It is an open problem whether the system (2)–(3)–(4) possesses a solution. As in the case of the nonreactive spatially inhomogeneous Boltzmann equation, the weak compactness argument in L^1, followed from existence of an H-function, is used to obtain a renormalized solution for the system (2)–(3)–(11). Without the microreversibility conditions (10), it is not known whether the system (2)–(3)–(4) possesses an H-function, and thus the question of existence cannot be settled at present time.

In ref. 20, Mischler and Wennberg shown that for any initial data with finite mass and energy, there exists a unique (global in time) solution to the nonreactive spatially homogeneous Boltzmann equation (for one specie) for which these two quantities are conserved in time. Whether these techniques work for the spatially homogeneous version of the system (2)–(3)–(4) is currently under investigation.

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