On the kinetic systems for simple reacting spheres: modeling and linearized equations

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Abstract In this work we present some results on the kinetic theory of chemically reacting gases, concerning the model of *simple reacting spheres* (SRS) for a gaseous mixture undergoing a chemical reaction of type $A_1 + A_2 \rightleftharpoons A_3 + A_4$. Starting from the approach developed in paper [11], we provide properties of the SRS system needed in the mathematical and physical analysis of the model. Our main result in this proceedings provides basic properties of the SRS system linearized around the equilibrium, including the explicit representations of the kernels of the linearized SRS operators.

1 Introduction

The problem of polyatomic reactive mixtures, within kinetic theory, was first investigated by Prigogine and Xhrouet [13] in 1949. They treated the reactive contributions as perturbations of the elastic terms. This approach is only valid if the reactive cross sections are much smaller than the elastic cross sections. In 1959, Present gave another important contribution to this problem [12]. Although, in some aspects different from the work by Prigogine and Xhrouet, the Present's theory is also based on the assumption that the reactive terms are small perturbations of the elastic terms. Ross and Mazur, in 1961, as well as Shizgal and Karplus, in 1970, see papers [14, 15] respectively, used the Chapman-Enskog method in the spatial homogeneous case with the aim of investigating the non-equilibrium effects induced by the chemical reactions and deducing, in particular, the explicit expression of the reaction rate specifying the chemical production of each constituent of the mixture. The works of

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Moreau [9], in 1975, and Xystris and Dahler [17], in 1978, used the method of Grad in both spatial homogeneous and inhomogeneous cases with the aim of deducing, again, explicit expressions for the reaction rate.

The kinetic theory of the simple reacting spheres was first proposed by Marron in 1970, see [8], and then developed by Xystris and Dahler in 1978, see [18]. Within this theory, both elastic and reactive collisions are of hard-sphere type. This feature reduces the micro-reversibility principle to a simpler condition.

In 2000, Polewczak proved, in his work [10], the existence of global in time, spatially inhomogeneous, and L^1-renormalized solution for the model of simple re-acting spheres, under the assumption of finite initial mass, momentum and energy. The existence result refers to a four component mixture with a chemical bimolecu-lar reaction in which there was neither mass nor diameters exchange. In this paper we consider a more general situation where the mass and the diameter exchange is allowed. In the dilute-gas limit, this constitutes an interesting kinetic model of chemical reactions that has not yet been studied in detail.

The paper is organized as follows. First, in Section 2, we present the mathemat-ical aspects of the kinetic modeling within the SRS theory. In Sections 3 and 4 we introduce the relevant properties of the collisional operators that are essential to as-sure the mathematical and physical consistency of the model, and study the tendency of the mixture to approach the equilibrium. In section 5 we define the macroscopic variables and derive the connection of the SRS model to the macroscopic frame-work in terms of hydrodynamic equations. In Sections 6 and 7 we introduce the linearized SRS system, state its main properties and provide explicit representations for the kernels of the linearized integral operators. Finally, in Section 8 we include a brief discussion about our ongoing research in progress.

2 Kinetic modeling

We consider a gas mixture with four constituents, say $A_1, ..., A_4$, with masses $m_1, ..., m_4$ and formation energies $E_1, ..., E_4$, respectively. We restrict our analysis to particles without internal degrees of freedom, which can interact through binary elastic collisions and reactive collisions obeying to the reversible chemical law

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

The mass is conserved during the chemical reaction, so that $m_1 + m_2 = m_3 + m_4$. The constituents' indexes are chosen in such a way that the reaction heat, defined by $Q_R = E_3 + E_4 - E_1 - E_2$, verifies the condition $Q_R > 0$. This means that the reverse chemical reaction, $A_3 + A_4 \rightharpoonup A_1 + A_2$, is exothermic.

Elastic collisions. An elastic collision between particles A_i and A_s with velocities c_i and c_s, respectively, results in a change of velocities of both constituents, $(c_i, c_s) \rightarrow (c_i', c_s')$, with $i, s = 1, \ldots, 4$. The conservation laws of linear momentum and kinetic energy of the colliding particles are specified by

$$m_i c_i + m_s c_s = m_i c_i' + m_s c_s', \qquad m_i c_i^2 + m_s c_s^2 = m_i c_i'^2 + m_s c_s'^2. \tag{2}$$

In our model we consider elastic cross sections of hard-spheres type, given by

$$\sigma_{is}^2 = \frac{1}{4}(d_i + d_s)^2, \tag{3}$$

where d_i and d_s denote the diameters of the particle constituents A_i and A_s, respectively. This model of cross sections is one of the most important and frequently used model, mainly due to its simplicity. Conditions (2), together with assumption (3), imply that the elastic post-collisional velocities corresponding to the pre-collisional velocities c_i and c_s are given by

$$c_i' = c_i - 2\frac{\mu_{is}}{m_i}\varepsilon\langle\varepsilon, c_i - c_s\rangle \qquad \text{and} \qquad c_s' = c_s + 2\frac{\mu_{is}}{m_s}\varepsilon\langle\varepsilon, c_i - c_s\rangle. \tag{4}$$

Reactive collisions. A reactive collision between particles A_i and A_j with velocities c_i and c_j, respectively, results in a transition of the reactants A_i and A_j into products A_k and A_l and a consequent change of velocities to c_k^* and c_l^*, with $(i, j, k, l) \in \{(1,2,3,4), (2,1,4,3), (3,4,1,2), (4,3,2,1)\}$. In addition, a reactive collision results in a rearrangement of masses and a redistribution of formation energies. Besides the mass conservation, also the linear momentum and total energy of the colliding particles are preserved, so that the following conditions hold

$$m_i c_i + m_j c_j = m_k c_k^* + m_l c_l^*, \tag{5}$$

$$E_i + \frac{1}{2}m_i c_i^2 + E_j + \frac{1}{2}m_j c_j^2 = E_k + \frac{1}{2}m_k c_k^{*2} + E_l + \frac{1}{2}m_l c_l^{*2}. \tag{6}$$

In what follows, we use the following notation for the relative velocities of the colliding particles participating in reactive collisions, $\xi_1 = \xi_2 = \xi = c_1 - c_2$, $\xi_3 = \xi_4 = \xi' = c_3 - c_4$. In the SRS model, reactive collisions are treated as hard-spheres like collisions, with the particularity that a reactive collision between particles A_i and A_j occurs if the kinetic energy associated with the relative motion along the line of centers exceeds the activation energy. Accordingly, reactive cross sections are assumed in the form

$$\sigma_{12}^{*2} = \begin{cases} \beta_{12}\sigma_{12}^2, & \langle\varepsilon, c_1 - c_2\rangle \geq \Gamma_{12}, \\ 0, & \langle\varepsilon, c_1 - c_2\rangle < \Gamma_{12}, \end{cases} \qquad \sigma_{34}^{*2} = \begin{cases} \beta_{34}\sigma_{34}^2, & \langle\varepsilon, c_3 - c_4\rangle \geq \Gamma_{34}, \\ 0, & \langle\varepsilon, c_3 - c_4\rangle < \Gamma_{34}, \end{cases} \tag{7}$$

for the direct and reverse chemical reaction, respectively. Above, β_{ij} is the steric factor for the collision between constituents A_i and A_j, with $0 \leq \beta_{ij} \leq 1$. Moreover, Γ_{ij} is a threshold velocity given by $\Gamma_{ij} = \sqrt{2\gamma_i/\mu_{ij}}$, where γ_i is the activation energy for the constituent A_i, and $\mu_{ij} = \frac{m_i m_j}{m_i + m_j}$ is a reduced mass. The notation $\langle\cdot,\cdot\rangle$ is used for the inner product in $\mathbb{R}^3$ and ε is the unit vector along the line passing through the centers of the spheres at the moment of impact,

$$\varepsilon \in \left\{\varepsilon \in \mathbb{R}^3 : |\varepsilon| = 1 \wedge \langle\varepsilon, c_i - c_j\rangle \geq 0\right\} \equiv \mathbb{S}_+^2.$$

Notice that, for the chemical reaction defined in Eq. (1), the activation energies verify the conditions $\gamma_2 = \gamma_1$, $\gamma_3 = \gamma_1 - Q_R$, $\gamma_4 = \gamma_3$ and the steric factors are such that $\beta_{ij} = 0$, for $(i,j) \notin \{(1,2),(2,1),(3,4),(4,3)\}$. Furthermore, since the reaction heat Q_R is positive, we must have $\gamma_1 > Q_R$.

In our SRS model, the post-collisional velocities for the direct chemical reaction are given by

$$c_3^* = \frac{1}{M}\left[m_1 c_1 + m_2 c_2 + m_4 \sqrt{\frac{\mu_{12}}{\mu_{34}}}\left\{\xi - \varepsilon\langle\varepsilon,\xi\rangle + \varepsilon\alpha^-\right\}\right], \tag{8}$$

$$c_4^* = \frac{1}{M}\left[m_1 c_1 + m_2 c_2 - m_3 \sqrt{\frac{\mu_{12}}{\mu_{34}}}\left\{\xi - \varepsilon\langle\varepsilon,\xi\rangle + \varepsilon\alpha^-\right\}\right], \tag{9}$$

whereas, the post-collisional velocities for the reverse chemical reaction are

$$c_1^* = \frac{1}{M}\left[m_3 c_3 + m_4 c_4 + m_2 \sqrt{\frac{\mu_{34}}{\mu_{12}}}\left\{\xi' - \varepsilon\langle\varepsilon,\xi'\rangle + \varepsilon\alpha^+\right\}\right] \tag{10}$$

$$c_2^* = \frac{1}{M}\left[m_3 c_3 + m_4 c_4 - m_1 \sqrt{\frac{\mu_{34}}{\mu_{12}}}\left\{\xi' - \varepsilon\langle\varepsilon,\xi'\rangle + \varepsilon\alpha^+\right\}\right]. \tag{11}$$

where $\alpha^- = \sqrt{(\langle\varepsilon,\xi\rangle)^2 - 2Q_R/\mu_{12}}$ and $\alpha^+ = \sqrt{(\langle\varepsilon,\xi'\rangle)^2 + 2Q_R/\mu_{34}}$. Velocities c_i, c_j, c_k^*, c_l^*, with $(i,j,k,l) \in \{(1,2,3,4),(2,1,4,3),(3,4,1,2),(4,3,2,1)\}$ and c_k^*, c_l^* given by expressions (8-11), verify the conservation laws expressed in Eqs. (5-6).

Kinetic equations. In the absence of external forces, the kinetic equations, describing the time-space evolution of the one-particle distribution functions $f_i(x,c_i,t)$, $i = 1,\ldots,4$, can be written in the form

$$\frac{\partial f_i}{\partial t} + \sum_{l=1}^3 c_l^i \frac{\partial f_i}{\partial x_l} = \mathcal{Q}_i^E + \mathcal{Q}_i^R, \quad i = 1,\ldots,4, \tag{12}$$

where $\mathcal{Q}_i^E$ and $\mathcal{Q}_i^R$ represent the elastic and reactive collisional operators. Following paper [11], the collisional operators have the form

$$\mathcal{Q}_i^E = \sum_{s=1}^4 \left\{\sigma_{is}^2 \int_{\mathbb{R}^3}\int_{\mathbb{S}_+^2} \left[f_i' f_s' - f_i f_s\right]\langle\varepsilon, c_i - c_s\rangle d\varepsilon dc_s\right\} \tag{13}$$

$$-\beta_{ij}\sigma_{ij}^2 \int_{\mathbb{R}^3}\int_{\mathbb{S}_+^2} \left[f_i' f_j' - f_i f_j\right]\Theta(\langle\varepsilon,\xi_i\rangle - \Gamma_{ij})\langle\varepsilon,\xi_i\rangle d\varepsilon dc_j,$$

where Θ is the Heaviside step function and $(i,j) \in \{(1,2),(2,1),(3,4),(4,3)\}$, and

$$\mathcal{Q}_i^R = \beta_{ij}\sigma_{ij}^2 \int_{\mathbb{R}^3}\int_{\mathbb{S}_+^2} \left[\left(\frac{\mu_{ij}}{\mu_{kl}}\right)^2 f_k^* f_l^* - f_i f_j\right]\Theta(\langle\varepsilon,\xi_i\rangle - \Gamma_{ij})\langle\varepsilon,\xi_i\rangle d\varepsilon dc_j, \tag{14}$$

where $(i,j,k,l) \in \{(1,2,3,4),(2,1,4,3),(3,4,1,2),(4,3,2,1)\}$, and $f_k^* = f_k(x,c_k^*,t)$, $f_l^* = f_l(x,c_l^*,t)$. As explained in papers [11, 18], the second term in the expression of $\mathscr{Q}_i^E$ is a correction term for the occurrence of reactive collisions and prevent a double counting of the contributions in the collisional operators. In fact, those encounters between A_i and A_j particles which are sufficiently energetic in the sense that $\langle \varepsilon, \xi_i \rangle \geq \Gamma_{ij}$ result in chemical reaction and should not be counted as elastic encounters.

3 Properties of the collisional operators

The consistency of the model is assured when the collisional operators have some important properties. We begin with the following fundamental results, concerning the elastic and reactive operators.

Proposition 1 *If we assume that $\beta_{ij} = \beta_{ji}$ then, for ψ_i measurable on $\mathbb{R}^3$ and $f_i \in C_0(\mathbb{R}^3)$, $i = 1,\ldots,4$, we have*

$$\int_{\mathbb{R}^3} \psi_i \mathscr{Q}_i^E dc_i = \frac{1}{4} \sum_{s=1}^{4} \left\{ \sigma_{is}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} \left[\psi_i + \psi_s - \psi_i' - \psi_s' \right] \left[f_i' f_s' - f_i f_s \right] \langle \varepsilon, c_i - c_s \rangle d\varepsilon dc_s dc_i \right\}$$

$$- \frac{1}{4} \beta_{ij} \sigma_{ij}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} \left[\psi_i + \psi_j - \psi_i' - \psi_j' \right] \left[f_i' f_j' - f_i f_j \right]$$

$$\times \Theta(\langle \varepsilon, \xi_i \rangle - \Gamma_{ij}) \langle \varepsilon, \xi_i \rangle d\varepsilon dc_j dc_i.$$

Proposition 2 *If $\beta_{ij} = \beta_{ji}$ and $\beta_{12} \sigma_{12}^2 = \beta_{34} \sigma_{34}^2$, then we have*

$$\sum_{i=1}^{4} \int_{\mathbb{R}^3} \psi_i \mathscr{Q}_i^R dc_i = \beta_{12} \sigma_{12}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} \left[\psi_1 + \psi_2 - \psi_3^* - \psi_4^* \right]$$

$$\times \left[\left(\frac{\mu_{12}}{\mu_{34}} \right)^2 f_3^* f_4^* - f_1 f_2 \right] \Theta(\langle \varepsilon, \xi \rangle - \Gamma_{12}) \langle \varepsilon, \xi \rangle d\varepsilon dc_2 dc_1$$

$$= \beta_{34} \sigma_{34}^2 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} \left[\psi_3 + \psi_4 - \psi_1^* - \psi_2^* \right]$$

$$\times \left[\left(\frac{\mu_{34}}{\mu_{12}} \right)^2 f_1^* f_2^* - f_3 f_4 \right] \Theta(\langle \varepsilon, \xi' \rangle - \Gamma_{34}) \langle \varepsilon, \xi' \rangle d\varepsilon dc_4 dc_3.$$

Propositions 1 and 2 can be proven considering the symmetry properties of the collisional operators, and constitute the basis of the proof of the following results.

Proposition 3 *The elastic collisional operators are such that*

$$\int_{\mathbb{R}^3} \mathscr{Q}_i^E dc_i = 0, \qquad i = 1,\ldots,4. \tag{15}$$

Proposition 3 states that elastic encounters do not change the number of particles of each constituent.

Proposition 4 *The reactive collisional operators satisfy the following properties*

$$\int_{\mathbb{R}^3} \mathcal{Q}_1^R dc_1 = \int_{\mathbb{R}^3} \mathcal{Q}_2^R dc_2 = -\int_{\mathbb{R}^3} \mathcal{Q}_3^R dc_3 = -\int_{\mathbb{R}^3} \mathcal{Q}_4^R dc_4. \qquad (16)$$

Proposition 4 states that the variation of the number of particles of constituent A_1 is the same as that of constituent A_2 and symmetric to the variation of constituents A_3 and A_4. It assures the correct chemical exchange rates of the constituents predicted by the reaction mechanism.

Definition 1 *A function $\psi = (\psi_1, \psi_2, \psi_3, \psi_4)$ is a collisional invariant in the velocity space, for the SRS model, if*

$$\sum_{i=1}^{4} \int_{\mathbb{R}^3} \psi_i \left(\mathcal{Q}_i^E + \mathcal{Q}_i^R \right) dc_i = 0. \qquad (17)$$

The following Proposition 5 presents the collisional invariants of model and establishes the consistency of the model from the physical point of view.

Proposition 5 *Functions $\psi = (1,0,1,0)$, $\psi = (1,0,0,1)$, $\psi = (0,1,1,0)$, and functions $\psi = (\psi_1, \psi_2, \psi_3, \psi_4)$ defined by $\psi_i = m_i c_1^i$, $\psi_i = m_i c_2^i$, $\psi_i = m_i c_3^i$ and $\psi_i = E_i + \frac{1}{2} c_i^2 m_i$ are collisional invariants.*

The first three invariants assure the conservation of the partial number density of a pair of constituents, one reactant and one product of the chemical reaction, namely A_1 and A_3, A_1 and A_4, and A_2 and A_3, respectively. They also assure the conservation of the total number density of the reactive mixture. The next three invariants assure the conservation of the linear momentum components of the mixture, whereas the last invariant assures the conservation of the total energy of the reactive mixture.

4 Equilibrium distributions and the Boltzmann H-theorem

When the gas reaches the equilibrium the elastic and reactive collisions do not stop, they become balanced. This means that, when the mixture is at equilibrium conditions, the collisional process does not modify the one-particle distibutions f_i. In particular, the number of particles that enter a volume element in the phase space per unit time is the same as the number of particles that leave the volume element in the phase space per unit time.

Definition 2 *The gas mixture is in thermodynamical equilibrium when the elastic and reactive collisional operators are such that*

$$\mathcal{Q}_i^E + \mathcal{Q}_i^R = 0, \qquad i = 1, \dots, 4. \qquad (18)$$

In particular, in our model, condition (18) implies the vanishing of the elastic collisional operators,

$$\mathcal{Q}_i^E = 0, \qquad i = 1, \dots, 4. \qquad (19)$$

Condition (19), in absence of reactive terms, is usually called a state of *mechanical equilibrium*.

The following Proposition 6 is well known in the case on one-single component gas and a formal proof can be found in many books, see for example [3].

Proposition 6 *If all constituents are at the same temperature, the only distribution function that assures the mechanical equilibrium is the Maxwellian distribution*

$$f_i^M(x,c_i,t) = n_i \left(\frac{m_i}{2\pi kT} \right)^{\frac{3}{2}} \exp\left[-\frac{m_i(c_i-v)^2}{2kT} \right], \quad i=1,\ldots,4, \tag{20}$$

where n_i, T *and* v *are the number density of constituent* A_i, *temperature and mean velocity of the whole mixture, respectively, and* k *is the Boltzmann constant.*

The above Maxwellian distributions (20) do not assure, in general, the vanishing of the reactive collisional operators and thus do not define a state of thermodynamical equilibrium for the reactive mixture.

Proposition 7 *If all constituents are at the same temperature, the only distribution function that assures the thermodynamical equilibrium is the thermodynamical Maxwellian distribution given by*

$$M_i(x,c_i,t) = n_i \left(\frac{m_i}{2\pi kT} \right)^{3/2} \exp\left[-\frac{m_i(c_i-v)^2}{2kT} \right], \quad i=1,\ldots,4, \tag{21}$$

with the number densities n_i *constrained to the condition*

$$n_1 n_2 = n_3 n_4 \sqrt{\frac{\mu_{12}}{\mu_{34}}} \exp\left(\frac{Q_R}{kT} \right). \tag{22}$$

Equation (22) represents the law of mass action for the SRS model.

The important physical feature of trend to equilibrium is now presented in the specific case of spatial domain $\Omega = \mathbb{R}^3$, proving the existence of an H-function (Liapunov functional) of the SRS system (12), (13) and (14).

Proposition 8 *($\mathscr{H}$-theorem) If the steric factors* β_{ij} *and cross sections* σ_{ij} *are such that* $\beta_{ij} = \beta_{ji}$ *and* $\beta_{12}\sigma_{12}^2 = \beta_{34}\sigma_{34}^2$, *the convex function* $H(t)$, *defined by*

$$H(t) = \sum_{i=1}^{4} \int_\Omega \int_{\mathbb{R}^3} f_i \log\left(\frac{f_i}{\mu_{ij}} \right) dc_i dx, \tag{23}$$

where $(i,j) \in \{(1,2),(2,1),(3,4),(4,3)\}$ *and* $f_i \in L^1(\Omega \times \mathbb{R}^3)$ *for all* $i=1,\ldots,4$, *is an H-function (Liapunov functional) for the SRS system (12), (13) and (14), that is*

$$\frac{dH}{dt}(t) \leq 0 \quad \text{for all} \quad t \geq 0, \quad \text{and}$$

$$\frac{dH}{dt}(t) = 0 \quad \text{if and only if} \quad f_i = M_i \quad \text{for all} \quad i=1,\ldots,4.$$

In the case of a spatial homogeneous evolution, the domain Ω is irrelevant for the behavior of the corresponding H-function, $\mathscr{H}(t) = \sum_{i=1}^{4} \int_{\mathbb{R}^3} f_i \log\left(\frac{f_i}{\mu_{ij}}\right) dc_i$. In the general case considered in Proposition 8, there exists a limited range of known situations for which the result is still valid. Some of them correspond to consider Ω as a box with boundary conditions of periodic type or boundary conditions of specular reflection at the walls, see for instance Refs. [3, 16].

The result expressed in Proposition 8 states that the reactive mixture evolves to a thermodynamical equilibrium state. In particular, in the proof of this proposition one shows that both elastic and reactive collisions contribute, independently, to this tendency to equilibrium. The spatial homogeneous version of an $\mathscr{H}$-theorem, similar to Proposition 8, is proven in paper [7], for a kinetic model for a quaternary reactive mixture undergoing a reversible bimolecular reaction. In comparison to the SRS model studied in our paper, the kinetic model considered in paper [7] has two major differences. First, the reactive cross sections of paper [7] follow the line-of-centers model, in contrast to those considered in our paper which are of hard-sphere type. Second, contrarily to the SRS system, the model of paper [7] does not consider any correction term in the collisional operators for preventing a double counting of the contributions. See the explanations at the end of Section 2.

In paper [7], the authors use their $\mathscr{H}$-theorem to prove the strong convergence in L^1-sense of the solution of their kinetic system to a Maxwellian distribution of thermodynamical equilibrium, under the assumption of uniformly boundedness and equicontinuity of the distribution functions for the spatial homogeneous case. Thus, in our opinion, Proposition 8 should constitute a central result in the convergence analysis of the solution of the kinetic equations (12) to a thermodynamical Maxwellian distribution.

5 Macroscopic framework

It is well known that the Boltzmann equation constitutes a fundamental model in the kinetic theory of gases, that describes the dynamics of the gas particles. At the same time, in the hydrodynamic limit, it leads to a description in terms of physically meaningful macroscopic quantities and related balance equations. The same happens with the SRS model studied in this paper. The mathematical and physical properties of the collisional operators, stating the consistency of the SRS system, are fundamental for the validity of the model as well as for the passage to the hydrodynamic limit. From a formal point of view, the connection between the microscopic variables and the macroscopic framework is based on the idea that all measurable macroscopic quantities can be expressed in terms of microscopic averages of the distribution functions. We now define the macroscopic quantities of the SRS model and provide the evolution equations for the most relevant macroscopic quantities.

Macroscopic variables. As usual, we define the macroscopic variables as suitable moments of the distribution functions f_i. We use the index i for those quantities

associated to the constituent A_i, $i = 1, \dots, 4$, and denote with plain symbols the macroscopic variables referred to the whole mixture. Moreover, indexes l and j are used to represent spatial components of vectorial quantities in $\mathbb{R}^3$.

Number density
$$n_i = \int_{\mathbb{R}^3} f_i d\mathbf{c}_i \quad \text{and} \quad n = \sum_{i=1}^{4} n_i$$

Mass density
$$\rho_i = \int_{\mathbb{R}^3} m_i f_i d\mathbf{c}_i \quad \text{and} \quad \rho = \sum_{i=1}^{4} \rho_i$$

Momentum density
$$\rho_i v_i = \int_{\mathbb{R}^3} m_i c_i f_i d\mathbf{c}_i \quad \text{and} \quad \rho v = \sum_{i=1}^{4} \rho_i v_i$$

Diffusion velocity
$$u_i = \frac{1}{\rho_i} \int_{\mathbb{R}^3} m_i \zeta_i f_i d\mathbf{c}_i$$

Pressure
$$p_i = \frac{1}{3} \int_{\mathbb{R}^3} m_i \zeta_i^2 f_i d\mathbf{c}_i \quad \text{and} \quad p = \sum_{i=1}^{4} p_i$$

Pressure tensor components
$$p_{lj}^i = \int_{\mathbb{R}^3} m_i \zeta_l^i \zeta_j^i f_i d\mathbf{c}_i \quad \text{and} \quad p_{lj} = \sum_{i=1}^{4} p_{lj}^i$$

Temperature
$$T_i = \frac{p_i}{n_i k} \quad \text{and} \quad T = \sum_{i=1}^{4} \frac{n_i}{n} T_i = \frac{p}{nk}$$

Heat flux components
$$q_l^i = \int_{\mathbb{R}^3} \frac{1}{2} m_i \zeta_i^2 \zeta_l^i f_i dc_i \quad \text{and} \quad q_l = \sum_{i=1}^{4} \left(q_l^i + n_i E_i u_l^i \right)$$

where $\zeta_i = c_i - v$ is the peculiar velocity, and ζ_l^i or ζ_j^i represent its spatial components. Moreover, the term $n_i E_i u_l^i$ in the definition of q_l refers to the formation energy transfer of the constituent A_i due to diffusion.

Balance equations. By multiplying the SRS equations (12) by suitable functions ψ_i, and then integrating over $c_i \in \mathbb{R}^3$, one can derive the balance equations for each constituent A_i. Omitting here the details, the balance equations for the number density, linear momentum components and total energy of each constituent A_i, $i = 1, \dots, 4$, have the form

$$\frac{\partial n_i}{\partial t} + \sum_{l=1}^{3} \frac{\partial}{\partial x_l} \left(n_i u_l^i + n_i v_l \right) = \int_{\mathbb{R}^3} \left(\mathscr{Q}_i^E + \mathscr{Q}_i^R \right) d\mathbf{c}_i, \tag{24}$$

$$\frac{\partial}{\partial t} \left(\rho_i v_l^i \right) + \sum_{r=1}^{3} \frac{\partial}{\partial x_r} \left(p_{lr}^i + \rho_i u_l^i v_r + \rho_i u_r^i v_l + p_i \right) = \int_{\mathbb{R}^3} m_i c_l^i \left(\mathscr{Q}_i^E + \mathscr{Q}_i^R \right) d\mathbf{c}_i, \tag{25}$$

$$\frac{\partial}{\partial t} \left[\frac{3}{2} p_i + n_i E_i + \rho_i u_l^i v_l + \frac{1}{2} \rho_i v^2 \right] + \sum_{l=1}^{3} \frac{\partial}{\partial x_l} \left[q_l^i + p_{lr}^i v_r + n_i E_i u_l^i + \frac{1}{2} \rho_i u_l^i v^2 \right.$$
$$\left. + \left(\frac{3}{2} p_i + n_i E_i + \rho_i u_l^i v_l + \frac{1}{2} \rho_i v^2 \right) v_i \right] \tag{26}$$
$$= \int_{\mathbb{R}^3} \left(\frac{1}{2} m_i c_i^2 + E_i \right) \left(\mathscr{Q}_i^E + \mathscr{Q}_i^R \right) d\mathbf{c}_i.$$

In particular, Eq. (24) constitutes the *reaction rate equation* of the SRS system and specifies the production rate of each constituent of the gas mixture.

Conservation laws. The conservation equations for partial number densities are obtained from the balance equations (24) by summing over one reactant ($i = 1, 2$) and one product ($i = 3, 4$) of the chemical reaction. Moreover, the conservation equations for mass density, linear momentum components and total energy of the whole mixture are obtained from the balance equations (24-26) by summing over all constituents. They can be written in the form

$$\frac{\partial}{\partial t}(n_i + n_j) + \sum_{l=1}^{3} \frac{\partial}{\partial x_l} \left[n_i u_l^i + n_j u_l^j + (n_i + n_j) v_l^i \right] = 0, \quad i = 1, 2, \ j = 3, 4, \quad (27)$$

$$\frac{\partial \rho}{\partial t} + \sum_{l=1}^{3} \frac{\partial}{\partial x_l}(\rho v_l) = 0, \tag{28}$$

$$\frac{\partial}{\partial t}(\rho v_l) + \sum_{k=1}^{3} \frac{\partial}{\partial x_k}(p_{lk} + \rho v_l v_k) = 0, \qquad l = 1, 2, 3, \tag{29}$$

$$\frac{\partial}{\partial t} \left(\frac{3}{2} nkT + \sum_{i=1}^{4} n_i E_i + \frac{1}{2} \rho v^2 \right) + \sum_{l=1}^{3} \frac{\partial}{\partial x_l} \left[q_l + \sum_{l=1}^{3} p_{lk} v_k \right. \tag{30}$$
$$\left. + \left(\frac{3}{2} nkT + \sum_{i=1}^{4} n_i E_i + \frac{1}{2} \rho v^2 \right) v_l \right] = 0.$$

6 Linearized SRS system

The linearized formulation of the SRS system around thermodynamical equilibrium arises as a simplification of the full system, which is valid when the reactive mixture is close to the thermodynamical equilibrium. In this section we construct the linearized SRS kinetic system and state its fundamental properties.

Linearized SRS system. To obtain the linearized equations, first the distribution function f_i is expanded around the thermodynamical Maxwellian distribution M_i with zero drifting velocity ($v = 0$), in the form

$$f_i(x, c_i, t) = M_i(x, c_i, t) \left[1 + h_i(x, c_i, t) \right], \qquad i = 1, \ldots, 4, \tag{31}$$

where h_i represents the deviation of the distribution function from the equilibrium. Then, expansions (31) are inserted into the SRS system (12-14) and the conservation laws (2) and (5-6) associated to elastic and reactive collisions, respectively, are used, together with the law of mass action (22). In the sequel we introduce the notation $\underline{w} = (w_1, w_2, w_3, w_4)^T$.

Proposition 9 *If we neglect quadratic and higher order terms in the deviations h_i, the linearized SRS system takes the form*

$$\frac{\partial h_i}{\partial t} + \sum_{l=1}^{3} c_l^i \frac{\partial h_i}{\partial x_l} = \mathscr{L}_i^E(\underline{h}) + \mathscr{L}_i^R(\underline{h}) \equiv \mathscr{L}_i(\underline{h}), \qquad i = 1,\ldots,4, \tag{32}$$

with

$$\mathscr{L}_i^E(\underline{h}) = \sum_{s=1}^{4} \sigma_{is}^2 \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} M_s \left[h_i' + h_s' - h_i - h_s \right] \langle \varepsilon, c_i - c_s \rangle \, d\varepsilon \, dc_s \tag{33}$$

$$- \beta_{ij} \sigma_{ij}^2 \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} M_j \left[h_i' + h_j' - h_i - h_j \right] \Theta(\langle \varepsilon, \xi_i \rangle - \Gamma_{ij}) \langle \varepsilon, \xi_i \rangle \, d\varepsilon \, dc_j,$$

for $(i,j) \in \{(1,2),(2,1),(3,4),(4,3)\}$, *and*

$$\mathscr{L}_i^R(\underline{h}) = \beta_{ij} \sigma_{ij}^2 \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} M_j \left[h_k^* + h_l^* - h_i - h_j \right] \Theta(\langle \varepsilon, \xi_i \rangle - \Gamma_{ij}) \langle \varepsilon, \xi_i \rangle \, d\varepsilon \, dc_j, \tag{34}$$

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

Properties of the linearized SRS system. Some important mathematical properties of the linearized SRS system (32-34) will be presented in the sequel. In order to easily compare our results with previous ones existing in literature for inert gases, we consider the following weighted distribution function and weighted operator,

$$\widehat{f_i} = M_i^{1/2} f_i \qquad \text{and} \qquad \widehat{\mathscr{L}_i}(\hat{\underline{h}}) = M_i^{1/2} \mathscr{L}_i(\underline{h}), \qquad i = 1,\ldots,4. \tag{35}$$

We can easily verify that h_i defines a solution of the linearized SRS system (32-34) if and only if $\hat{h}_i$ defines a solution of the following weighted linearized system

$$\frac{\partial \hat{h}_i}{\partial t} + \sum_{l=1}^{3} c_l^i \frac{\partial \hat{h}_i}{\partial x_l} = \widehat{\mathscr{L}_i}(\hat{\underline{h}}), \qquad i = 1,\ldots,4, \tag{36}$$

where the weighted linearized operator $\widehat{\mathscr{L}_i}(\hat{\underline{h}})$ can be split in its elastic and reactive parts, given by

$$\widehat{\mathscr{L}}_i^E(\hat{\underline{h}}) = M_i^{1/2} \mathscr{L}_i^E(h) \quad \text{and} \quad \widehat{\mathscr{L}}_i^R(\hat{\underline{h}}) = M_i^{1/2} \mathscr{L}_i^R(h). \tag{37}$$

Moreover, we introduce the space $Y = L^2(\mathbb{R}^3 \times \mathbb{R}^3)$ and consider the Maxwellian weighted velocity L^2-space, Y^4, endowed with the inner product defined by

$$\langle \underline{F}, \underline{G} \rangle = \sum_{i=1}^{4} \int_{\mathbb{R}^3} F_i(c_i) G_i(c_i) dc_i. \tag{38}$$

The weighted linearized collisional operator satisfies the following property.

Proposition 10 *If the steric factors β_{ij} and cross sections σ_{ij} are such that $\beta_{ij} = \beta_{ji}$ and $\beta_{12}\sigma_{12}^2 = \beta_{34}\sigma_{34}^2$, the weighted linearized collisional operator $\widehat{\mathscr{L}}$ is symmetric and non-positive semi-definite, that is*

(a) $\langle \hat{\underline{g}}, \widehat{\mathscr{L}}(\hat{\underline{h}}) \rangle = \langle \hat{\underline{h}}, \widehat{\mathscr{L}}(\hat{\underline{g}}) \rangle$, for all $\underline{g}, \underline{h} \in Y^4$;

(b) $\langle \hat{\underline{h}}, \widehat{\mathscr{L}}(\hat{\underline{h}}) \rangle \leq 0$, for all $\underline{h} \in Y^4$, and $\langle \hat{\underline{h}}, \widehat{\mathscr{L}}(\hat{\underline{h}}) \rangle = 0$ if and only if $\underline{h}$ is a colli-
sional invariant.

7 Kernels of the linearized integral operators

For a one component inert gas, the explicit expression of the kernel of the linearized
collisional operator, as well as the techniques used to compute the kernel, are de-
tailed in many works, in particular in paper [4]. However, this is not the case for a
reactive gas mixture. In fact, the computations for the case of a reactive gas mixture
are long and very technical. Concerning, in particular, the SRS system, we were able
to obtain the explicit representation of the kernels of the linearized elastic and reac-
tive operators, in the general case of arbitrary molecular masses. The computations
have been done by the first author of the present work and are part of his PhD thesis,
see [1]. See also Ref. [2] for the details about the computations of the kernels.

Kernels of the linearized elastic operators. The operator $\widehat{\mathscr{L}}_i^E(\hat{\underline{h}})$ can be split into
several contributions as follows

$$\widehat{\mathscr{L}}_i^E(\hat{\underline{h}}) = -v_i \hat{h}_i - Q_i^{(1)}(\hat{\underline{h}}) + Q_i^{(2)}(\hat{\underline{h}}) + Q_i^{(3)}(\hat{\underline{h}}), \tag{39}$$

where

$$v_i \hat{h}_i = \hat{h}_i \sum_{s=1}^{4} \sigma_{is}^2 \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} M_s \langle \varepsilon, c_i - c_s \rangle \, d\varepsilon \, dc_s, \tag{40}$$

$$Q_i^{(1)}(\hat{\underline{h}}) = \sum_{s=1}^{4} \sigma_{is}^2 \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} M_i^{1/2} M_s^{1/2} \hat{h}_s \langle \varepsilon, c_i - c_s \rangle \, d\varepsilon \, dc_s, \tag{41}$$

$$Q_i^{(2)}(\hat{\underline{h}}) = \sum_{s=1}^{4} \sigma_{is}^2 \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} M_i^{1/2} M_s M_i'^{-1/2} \hat{h}_i' \langle \varepsilon, c_i - c_s \rangle \, d\varepsilon \, dc_s, \tag{42}$$

$$Q_i^{(3)}(\hat{\underline{h}}) = \sum_{s=1}^{4} \sigma_{is}^2 \int_{\mathbb{R}^3} \int_{\mathbb{S}_+^2} M_i^{1/2} M_s M_s'^{-1/2} \hat{h}_s' \langle \varepsilon, c_i - c_s \rangle \, d\varepsilon \, dc_s. \tag{43}$$

The multiplication operator v_i defined in (40) can be identified as a mean collision
frequency. Concerning the integral operators (41-43), the full representation of the
kernels, in the general case of arbitrary molecular masses, is omitted here due to
space limitations. In fact, some of the expressions are very long. We only include
the expressions of the kernels in the particular case of a reactive mixture with equal
molecular masses. They are given by the following expressions, for $i = 1, 2, 3, 4$,

$$N(Q_i^{(1)})(u, w) = \pi \sigma_{is}^2 \|u - w\| \sqrt{n_i n_s} \left(\frac{m}{2\pi kT} \right)^{3/2} \exp\left(-\frac{m(u^2 + w^2)}{4kT} \right), \tag{44}$$

$$N(Q_i^{(2)})(u, w) = \sigma_{is}^2 n_s \left(\frac{m}{2\pi kT} \right)^{1/2} \frac{1}{\|u - w\|} \tag{45}$$

$$\times \exp\left[-\frac{m}{8kT}\frac{(u^2-w^2)^2}{\|u-w\|^2}-\frac{m}{8kT}(u-w)^2\right],$$

$$N(Q_i^{(3)})(u,w)=\sigma_{is}^2\sqrt{n_i n_s}\left(\frac{m}{2\pi kT}\right)^{1/2}\frac{1}{\|u-w\|} \tag{46}$$

$$\times \exp\left[-\frac{m}{8kT}\frac{(u^2-w^2)^2}{\|u-w\|^2}-\frac{m}{8kT}(u-w)^2\right].$$

Note that, in the case of one component gas, expressions (44-46) reduce to those presented by Grad in paper [5], for the intermolecular potential of hard-sphere type.

Kernels of the linearized reactive operators. The procedure adopted to obtain the representation of the kernels of the reactive operators is similar to the one used for the elastic operators. The starting point is the decomposition of the operator $\widehat{\mathscr{L}}_i^R(\underline{\hat{h}})$ into several contributions, in the form

$$\widehat{\mathscr{L}}_i^R(\underline{\hat{h}}) = -\nu_i^R(u)\hat{h}_i(u) - \mathscr{R}_i^{(1)}(\underline{\hat{h}}) + \mathscr{R}_i^{(2)}(\underline{\hat{h}}) + \mathscr{R}_i^{(3)}(\underline{\hat{h}}),$$

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

$$\nu_i^R(u)\hat{h}_i(u) = \hat{h}_i\beta_{ij}\sigma_{ij}^2\int_{\mathbb{R}^3}\int_{\mathbb{S}_+^2}M_j\Theta(\langle\varepsilon,\xi_i\rangle-\Gamma_{ij})\langle\varepsilon,\xi_i\rangle\,d\varepsilon\,dc_j, \tag{47}$$

$$\mathscr{R}_i^{(1)}(\underline{\hat{h}}) = \beta_{ij}\sigma_{ij}^2\int_{\mathbb{R}^3}\int_{\mathbb{S}_+^2}M_i^{1/2}M_j\hat{h}_j\Theta(\langle\varepsilon,\xi_i\rangle-\Gamma_{ij})\langle\varepsilon,\xi_i\rangle\,d\varepsilon\,dc_j, \tag{48}$$

$$\mathscr{R}_i^{(2)}(\underline{\hat{h}}) = \beta_{ij}\sigma_{ij}^2\int_{\mathbb{R}^3}\int_{\mathbb{S}_+^2}M_j^{1/2}M_l^{*1/2}\hat{h}_k^*\Theta(\langle\varepsilon,\xi_i\rangle-\Gamma_{ij})\langle\varepsilon,\xi_i\rangle\,d\varepsilon\,dc_j, \tag{49}$$

$$\mathscr{R}_i^{(3)}(\underline{\hat{h}}) = \beta_{ij}\sigma_{ij}^2\int_{\mathbb{R}^3}\int_{\mathbb{S}_+^2}M_j^{1/2}M_k^{*1/2}\hat{h}_l^*\Theta(\langle\varepsilon,\xi_i\rangle-\Gamma_{ij})\langle\varepsilon,\xi_i\rangle\,d\varepsilon\,dc_j. \tag{50}$$

Again, the multiplication operator ν_i^R defined in (47) can be identified as a mean reactive collision frequency. Concerning the integral operators (48-50), the full representation of their kernels, for the general case of arbitrary molecular masses, is omitted here due to space limitations. The reader is addressed to Refs. [1, 2] for the details. Here we present the particular case of equal molecular masses, and only present the kernels of the operators $\mathscr{R}_i^{(1)}(\hat{h})$, for $i=1,2,3,4$, and $\mathscr{R}_1^{(2)}(\hat{h})$, $\mathscr{R}_1^{(3)}(\hat{h})$,

$$N(\mathscr{R}_i^{(1)})(u,w) = \frac{1}{2}\,\beta_{ij}\sigma_{ij}^2\sqrt{n_i n_j}\left(\frac{m}{2\pi kT}\right)^{3/2}\frac{\|u-w\|^2-\Gamma_{ij}^2}{\|u-w\|} \tag{51}$$

$$\times \exp\left(-\frac{m(u^2+w^2)}{4kT}\right), \quad i=1,2,3,4,$$

$$N(\mathscr{R}_1^{(2)})(u,w) = \frac{1}{2} \, \beta_{12} \, \sigma_{12}^2 \sqrt{n_2 n_4} \left(\frac{m}{2\pi kT} \right)^{3/2} \tag{52}$$

$$\times \frac{||u-w||^2}{\left(||u-w|| + \frac{Q_R}{m||u-w||} \right)^3} \; \Theta \left(||u-w|| + \frac{Q_R}{m||u-w||} - \Gamma_{12} \right)$$

$$\times \left[\frac{2Q_R}{m \left(||u-w|| + \frac{Q_R}{m||u-w||} \right)^2 \sqrt{1 - \frac{4Q_R}{m \left(||u-w|| + \frac{Q_R}{m||u-w||} \right)^2}}} - \frac{||u-w||}{||u-w|| + \frac{Q_R}{m||u-w||}} \right]$$

$$\times \int_{L \perp (w-u)} \exp \left\{ -\frac{m}{4kT} \left[\left(u - L + \frac{2(w-u)}{1 - \sqrt{1 - \frac{4Q_R}{m \left(||u-w|| + \frac{Q_R}{m||u-w||} \right)^2}}} \right)^2 \right. \right.$$

$$\left. \left. + \left(2u - L - w + \frac{2(w-u)}{1 - \sqrt{1 - \frac{4Q_R}{m \left(||u-w|| + \frac{Q_R}{m||u-w||} \right)^2}}} \right)^2 \right] \right\} dL,$$

$$N(\mathscr{R}_1^{(3)})(u,w) = \beta_{12} \, \sigma_{12}^2 \sqrt{n_2 n_3} \left(\frac{m}{2\pi kT} \right)^{3/2} \int_{D_L} \exp \left\{ -\frac{m}{4kT} \left[\right. \right. \tag{53}$$

$$\times \left(u + \frac{1}{2} \left(-1 + \sqrt{1 - \frac{4Q_R}{mL^2}} \right) L \right)^2 + \left(w + \frac{1}{2} \left(-1 + \sqrt{1 - \frac{4Q_R}{mL^2}} \right) L \right)^2 \right] \right\}$$

$$\times \Theta \left(||L|| - \Gamma_{12} \right) \frac{1}{||w - u - \frac{1}{2} \left(1 + \sqrt{1 - \frac{4Q_R}{mL^2}} \right) L||} \; dL,$$

where the integration domain D_L is defined by

$$D_L = \left\{ L \in \mathbb{R}^3 : \; \langle L, v - w \rangle = \frac{1}{2} \left(1 + \sqrt{1 - \frac{4Q_R}{mL^2}} \right) L^2 \right\}.$$

8 Final remarks

The content of this paper is the first part of a work in progress on the SRS model for a quaternary mixture with no restriction on the molecular masses of the constituents. The properties of the linearized SRS system presented here, and especially the explicit representations of its kernels, are essential in obtaining detailed spectral analysis of the system. This in turn provides the asymptotic behavior of its evolution operator that is used in existence and stability of close to equilibrium solutions for

the SRS system and the rigorous treatment of the hydrodynamical limits at the Euler and Navier-Stokes level.

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