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ORIGINAL RESEARCH ARTICLE

Transport Coefficients for the Simple Reacting Spheres Kinetic Model II: Thermal Conductivity, Diffusion, Thermal-Diffusion Ratio

Jacek Polewczak[1] · Adriano W. Silva[2] · Ana Jacinta Soares[3]

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Abstract

We investigate the transport coefficients for a dilute reactive mixture of four constituents undergoing a chemical reaction of type $A + B \rightleftharpoons C + D$, which is described by the Simple Reacting Spheres (SRS) kinetic model. The dynamics of the SRS model is very interesting and relatively simple. Both reactive and inert collisions obey to the hard spheres potential and the collisional operator incorporates a "correction" term that singles out those pre-collisional pairs of particles having enough energy to react chemically. Starting from this setting, we consider the mixture in a chemical regime for which both elastic and reactive collisions occur with comparable characteristic times and use the Chapman–Enskog method to determine the first-order approximation of the non-equilibrium solution to the SRS system. In a preceding paper (part I), the focus was on the coefficients associated to reaction rate and shear viscosity and in the present work we are interested on the coefficients associated to thermal conductivity, diffusion, and thermal-diffusion ratio. These coefficients are analysed numerically for both exothermic and endothermic reactions. The analysis allows to investigate the influence of the chemical reaction and the impact of the "correction" term proper of the SRS model on the transport coefficients.

Keywords Boltzmann equation · Chemical reactions · Enskog expansion · Transport coefficients

✉ Ana Jacinta Soares
ajsoares@math.uminho.pt

Jacek Polewczak
jacek.polewczak@csun.edu

Adriano W. Silva
adriano.silva@ifpr.edu.br

1 Department of Mathematics, California State University, Northridge, CA, USA

2 Instituto Federal de Educação, Ciência e Tecnologia do Paraná, Curitiba, Brazil

3 Centro de Matemática, Universidade do Minho, Braga, Portugal

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1 Introduction

Transport properties of multicomponent reactive mixtures have several applications in chemical engineering, combustion technology and many industrial processes. The description of the chemical kinetics involved in the reaction mechanism is an important part of the process, which can be obtained with the contributions coming from the mathematical models, and computational simulations. When the models are based on the kinetic theory, many explicit results can be obtained instead of resorting to some empirical laws [13, 17, 19, 24, 26].

The main objective in this paper is precisely the application of the kinetic theory tools to investigate the transport properties of a chemically reactive mixture.

This work is a continuation of the previous paper [6], and both are devoted to the determination of the transport coefficients for a dilute reactive mixture of four constituents undergoing a chemical reaction of type $A + B \rightleftharpoons C + D$, described by the Simple Reacting Spheres (SRS) kinetic model. The focus of the present work is on the coefficients associated to thermal conductivity, diffusion and thermal-diffusion ratio, whereas that of the previous paper was on the coefficients associated to reaction rate and shear viscosity.

Besides the study of the transport properties of the mixture, another aim of the present paper is connected with a particular term proper of the SRS model. We study here the impact of this term on the transport coefficients which means, in practice, to evaluate the transport coefficients when this term is considered in the dynamics and when it is not taken into account. This choice leads to the question of studying a variant of the original SRS model, that allows for this turning on and turning off the referred term.

Having these aims in mind, we have organized our work as follows. In Sect. 2, we revisit the SRS kinetic system and briefly describe its properties focusing on the molecular and chemical properties of the mixture and on the kinetic system with the correction term proper of the SRS model. Then, in Sect. 3, we develop one "variant" of the SRS kinetic model by expanding the system to encompass a broader range of scenarios. The new model allows to turn off the chemical reaction and establish a coherent model for non-reactive mixtures. Furthermore, it enables to explore different situations, in which the chemical reaction exhibits varying degrees of significance in the evolution of the system. The main properties of the extended system are stated. In Sect. 4, we study the transport properties of the SRS system in its extended formulation. We determine the asymptotic solution of the kinetic system and use this approximate solution to deduce the constitutive equations and obtain the transport coefficients of diffusion, thermal conductivity and thermal diffusion ratio. In Sect. 5, we develop a comparative analysis between the transport coefficients for the SRS model of Sect. 2 and those of the extended model of Sect. 3. We perform some numerical simulations in order to investigate the influence of some key parameters on the behaviour of the transport coefficients, and to investigate the impact of the correction term incorporated

in our SRS model on the transport coefficients. Finally, in Sect. 6, we summarise and comment our results. We also discuss possible scenarios for future work.

2 The SRS Kinetic Model Revisited

In this section we introduce the SRS kinetic model for a dilute reactive mixture and briefly describe its main aspects and properties. For a detailed description, see, for example, [5, 21, 22] and the references cited therein. Our exposition of the SRS model is limited to the characterization of the equilibrium states, presentation of the linearized kinetic equations, introduction of the macroscopic field equations and brief description of both the zero-order and first-order approximations of the non-equilibrium solution to the SRS kinetic system.

2.1 The Reactive Mixture

We consider a mixture of four constituents, A, B, C and D, whose particles behave as if they were single mass points. Internal degrees of freedom for the gas particles, such as vibrational and rotational energies, are not taken into account. We use the indices 1, 2, 3, 4 for the constituents A, B, C, D, respectively. For each constituent $i = 1, \ldots, 4$, we denote by m_i, d_i and E_i the molecular mass, the molecular diameter and the chemical binding energy of each i-constituent.

Besides elastic collisions, particles of the mixture undergo reactive encounters according to the reversible chemical reaction

$$A + B \rightleftharpoons C + D. \tag{1}$$

Reactive collisions occur when the particles are separated by a distance $\sigma_{12} = \frac{1}{2}(d_1 + d_2)$ or $\sigma_{34} = \frac{1}{2}(d_3 + d_4)$, and result in a redistribution of masses and in a rearrangement of energies among the colliding particles. In particular, conservation of mass implies that

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

and conservation of the total energy, kinetic and binding, leads to the definition of the reaction heat as $E_{abs} = E_3 + E_4 - E_1 - E_2$. Thus, $E_{abs} > 0$ means that the forward reaction $A + B \to C + D$ is endothermic and E_{abs} represents the absorbed heat energy, whereas $E_{abs} < 0$ means that the forward reaction is exothermic and E_{abs} represents the energy released in the form of heat. We also introduce $\gamma_1 = \gamma_2$ and $\gamma_3 = \gamma_4$ representing the activation energy of the forward and backward reactions, respectively, and we have $E_{abs} = \gamma_1 - \gamma_3$.

2.2 The SRS Kinetic System

The time–space evolution of the one-particle distribution functions $f_i(t, x, v)$, for $i = 1, \ldots, 4$, is given by the kinetic equations

$$\frac{\partial f_i}{\partial t} + v \cdot \nabla_x f_i = J_i^E + J_i^{E*} + J_i^R, \qquad i = 1, \ldots, 4, \tag{3}$$

where J_i^E is the elastic collision term, J_i^{E*} is the *correction* term, proper of the SRS model [22] and J_i^R is the reactive collision term, given by

$$J_i^E = \sum_{j=1}^{4} \left\{ \sigma_{ij}^2 \iint_{\mathbb{R}^3 \times \mathbb{S}_+^2} \left[f_i(t, x, v') f_j(t, x, w') - f_i(t, x, v) f_j(t, x, w) \right] \langle \epsilon, v - w \rangle \, \mathrm{d}\epsilon \mathrm{d}w \right\} \tag{4}$$

$$\begin{aligned} J_i^{E*} = & -\beta_{ij} \sigma_{ij}^2 \iint_{\mathbb{R}^3 \times \mathbb{S}_+^2} \left[f_i(t, x, v') f_j(t, x, w') - f_i(t, x, v) f_j(t, x, w) \right] \\ & \times \Theta\left(\langle \epsilon, v - w \rangle - \Gamma_{ij} \right) \langle \epsilon, v - w \rangle \mathrm{d}\epsilon \mathrm{d}w, \end{aligned} \tag{5}$$

$$\begin{aligned} J_i^R = & \beta_{ij} \sigma_{ij}^2 \iint_{\mathbb{R}^3 \times \mathbb{S}_+^2} \left[\left(\frac{\mu_{ij}}{\mu_{kl}} \right)^2 f_k(t, x, v_{ij}^{\odot}) f_l(t, x, w_{ij}^{\odot}) - f_i(t, x, v) f_j(t, x, w) \right] \\ & \times \Theta\left(\langle \epsilon, v - w \rangle - \Gamma_{ij} \right) \langle \epsilon, v - w \rangle \mathrm{d}\epsilon \mathrm{d}w. \end{aligned} \tag{6}$$

In the above expressions of operators J_i^{E*} and J_i^R, the indexes i, j, k, l are associated to the reactive species, in agreement with the chemical law (1), and are such that

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

Here, v, w are pre-collisional velocities of particles from species i and j, and v', w' are elastic post-collisional velocities given by

$$v' = v - 2\frac{\mu_{ij}}{m_i} \epsilon \langle \epsilon, v - w \rangle, \quad w' = w + 2\frac{\mu_{ij}}{m_j} \epsilon \langle \epsilon, v - w \rangle, \tag{7}$$

where $\langle \cdot, \cdot \rangle$ is the inner product in $\mathbb{R}^3$, ϵ is a vector along the line passing through the centers of the spheres at the moment of impact, i.e., $\epsilon \in \mathbb{S}_+^2$, with $\mathbb{S}_+^2 = \{\epsilon \in \mathbb{R}^3 : |\epsilon| = 1, \langle \epsilon, v - w \rangle \geq 0\}$, and $\mu_{ij} = m_i m_j / (m_i + m_j)$ is the reduced mass of the colliding pair, Θ is the Heaviside step function, and $\Gamma_{ij} = \sqrt{2\gamma_i / \mu_{ij}}$ represents a threshold velocity of the colliding pair.

Moreover, the pairs of post-reactive velocities associated to the endothermic forward reaction are $(v_{ij}^{\odot}, w_{ij}^{\odot}) = (v^{\ddagger}, w^{\ddagger})$ for $i, j = 1, 2$, given by

$$v^{\ddagger} = \frac{1}{M}\left[m_1 v + m_2 w + m_4\sqrt{\frac{\mu_{12}}{\mu_{34}}}\left\{(v-w) - \epsilon\langle\epsilon, v-w\rangle + \epsilon\alpha^{-}\right\}\right], \tag{8a}$$

$$w^{\ddagger} = \frac{1}{M}\left[m_1 v + m_2 w - m_3\sqrt{\frac{\mu_{12}}{\mu_{34}}}\left\{(v-w) - \epsilon\langle\epsilon, v-w\rangle + \epsilon\alpha^{-}\right\}\right], \tag{8b}$$

with $\alpha^{-} = \sqrt{\left(\langle\epsilon, v-w\rangle\right)^2 - 2E_{abs}/\mu_{12}}$. The post-reactive velocities associated to the exothermic backward reaction are $(v_{ij}^{\odot}, w_{ij}^{\odot}) = (v^{\dagger}, w^{\dagger})$ for $i, j = 3, 4$, given by

$$v^{\dagger} = \frac{1}{M}\left[m_3 v + m_4 w + m_2\sqrt{\frac{\mu_{34}}{\mu_{12}}}\left\{(v-w) - \epsilon\langle\epsilon, v-w\rangle + \epsilon\alpha^{+}\right\}\right], \tag{9a}$$

$$w^{\dagger} = \frac{1}{M}\left[m_3 v + m_4 w - m_1\sqrt{\frac{\mu_{34}}{\mu_{12}}}\left\{(v-w) - \epsilon\langle\epsilon, v-w\rangle + \epsilon\alpha^{+}\right\}\right], \tag{9b}$$

with $\alpha^{+} = \sqrt{\left(\langle\epsilon, v-w\rangle\right)^2 + 2E_{abs}/\mu_{34}}$.

Post and pre-collisional velocities of the reactive pairs satisfy momentum conservation and total energy conservation, that is

$$m_1 v + m_2 w = m_3 v^{\ddagger} + m_4 w^{\ddagger}, \qquad m_3 v + m_4 w = m_1 v^{\dagger} + m_2 w^{\dagger}, \tag{10}$$

$$m_1 v^2 + m_2 w^2 = m_3 v^{\ddagger 2} + m_4 w^{\ddagger 2} + 2E_{abs},$$

$$m_3 v^2 + m_4 w^2 = m_1 v^{\dagger 2} + m_2 w^{\dagger 2} - 2E_{abs}. \tag{11}$$

A relevant property of the SRS model is the inclusion of the correction term (5), which removes, from the elastic operator (4), the contributions that correspond to reactive encounters and are considered in the reactive operator (6). In fact, the encounters between particles A and B or between particles C and D that are sufficiently energetic, in the sense that $\langle\epsilon, v-w\rangle \geq \Gamma_{ij}$, are counted twice, since they are considered both as reactive and appear in J_i^R and as elastic and appear in J_i^E. The double counting is corrected precisely because J_i^{E*} is part of the collision operator.

In Eq. (5), the coefficients β_{ij}, with $0 \leq \beta_{ij} \leq 1$, appearing in the expression of J_i^{E*}, indicate that only a fraction β_{ij} of collisions with high energy result in a chemical reaction. It is important to mention that the SRS system (3) reduces to the Boltzmann system for an inert mixture with hard-spheres potential, when the chemical reaction is turned off and coefficients β_{ij} are taken equal to zero, for all $i, j = 1, \ldots, 4$. On the other hand, if the coefficients β_{ij} are taken equal to one, for all $i, j = 1, \ldots, 4$, the resulting SRS kinetic system (3) corresponds to the situation in which all collisions with sufficient amount of energy result in the chemical reactions.

The model introduced in this section has been studied by the authors and different problems have been investigated in some previous papers, see for example [5, 6, 21, 22].

In the present work, when studying the transport coefficients, we put the emphasis on the role of the correction term J_i^{E*} given in (5), and therefore we will refer to the model that results from the SRS model by removing the correction term. This motivates the introduction of a generalized SRS model, as described in the next section.

3 Generalized SRS Kinetic Model

In this section, we study one "variant" of the SRS kinetic system described in Sect. 2. In simple terms, this variant provides an interesting kinetic model for the reactive mixture introduced in Subsection 2.1, that is obtained from the SRS equations (3) by introducing a scalar parameter that allows to *turn off* or to *turn on* the correction term J_i^{E*} given in (5). We call this variant as the *generalized SRS model*.

3.1 Generalized SRS System

Starting from the SRS system (3), let us consider the following kinetic system

$$\frac{\partial f_i}{\partial t} + v \cdot \nabla_x f_i = J_i^E + \alpha J_i^{E*} + J_i^R, \qquad i = 1, \ldots, 4, \tag{12}$$

where the collision operators J_i^E, J_i^{E*} and J_i^R are given in (4), (5) and (6), respectively, and $\alpha \in \{0, 1\}$ is a scalar parameter. In other words, if $\alpha = 1$, then Eq. (12) coincide with the SRS system (3), whereas if $\alpha = 0$ Eq. (12) reduce to the standard hard-sphere kinetic system without correction term. Equations (12) constitute the generalized SRS system.

3.2 Properties of the Generalized Collision Operators

The weak form of the collision operators is characterized in the following properties.

Proposition 3.1 *If we assume that $\beta_{ij} = \beta_{ji}$ then, for ψ_i measurable functions on $\mathbb{R}^3$ and $f_i \in C_0(\mathbb{R}^3)$, for $i = 1, \ldots, 4$, we have that*

$$\begin{aligned}
\int_{\mathbb{R}^3} \psi_i J_i^E \mathrm{d}v = \frac{1}{4} \sum_{j=1}^{4} \Bigg\{ \sigma_{ij}^2 \iiint_{\mathbb{R}^3 \times \mathbb{R}^3 \times \mathbb{S}_+^2} & \\
\times \Big(\psi_i + \psi_j - \psi_i' - \psi_j' \Big) \Big(f_i' f_j' - f_i f_j \Big) \langle \epsilon, v - w \rangle \mathrm{d}\epsilon \mathrm{d}w \mathrm{d}v \Bigg\}, & \\
\int_{\mathbb{R}^3} \psi_i J_i^{E*} \mathrm{d}v = -\frac{1}{4} \alpha \beta_{ij} \sigma_{ij}^2 \iiint_{\mathbb{R}^3 \times \mathbb{R}^3 \times \mathbb{S}_+^2} & \Big(\psi_i + \psi_j - \psi_i' - \psi_j' \Big) \Big(f_i' f_j' - f_i f_j \Big) \\
\times \Theta(\langle \epsilon, v - w \rangle - \Gamma_{ij}) \langle \epsilon, v - w \rangle \, \mathrm{d}\epsilon \mathrm{d}w \mathrm{d}v. &
\end{aligned}$$

Proposition 3.2 *If we assume that $\beta_{ij} = \beta_{ji}$ and $\beta_{12}\sigma_{12}^2 = \beta_{34}\sigma_{34}^2$, then, for ψ_i measurable functions on $\mathbb{R}^3$ and $f_i \in C_0(\mathbb{R}^3)$, for $i = 1, \ldots, 4$, we have that*

$$\begin{aligned}\sum_{i=1}^{4} \int_{\mathbb{R}^3} \psi_i J_i^R \mathrm{d}v &= \beta_{12}\sigma_{12}^2 \iiint\limits_{\mathbb{R}^3\times\mathbb{R}^3\times\mathbb{S}_+^2} \left(\psi_1 + \psi_2 - \psi_3^{\odot} - \psi_4^{\odot}\right) \\ &\quad \times \left[\left(\frac{\mu_{12}}{\mu_{34}}\right)^2 f_3^{\odot} f_4^{\odot} - f_1 f_2\right] \Theta(\langle \epsilon, v - w\rangle - \Gamma_{12}) \\ &\quad \langle \epsilon, v - w\rangle \mathrm{d}\epsilon \mathrm{d}w \mathrm{d}v \\ &= \beta_{34}\sigma_{34}^2 \iiint\limits_{\mathbb{R}^3\times\mathbb{R}^3\times\mathbb{S}_+^2} \left(\psi_3 + \psi_4 - \psi_1^{\odot} - \psi_2^{\odot}\right) \\ &\quad \times \left[\left(\frac{\mu_{34}}{\mu_{12}}\right)^2 f_1^{\odot} f_2^{\odot} - f_3 f_4\right] \Theta(\langle \epsilon, v - w\rangle - \Gamma_{34}) \\ &\quad \langle \epsilon, v - w\rangle \mathrm{d}w \mathrm{d}v.\end{aligned}$$

Propositions 3.1 and 3.2 can be proven by considering the symmetry properties of the collisional operators, see [3], and are essential to derive the conservation laws and to prove the H-Theorem.

Definition 3.1 A measurable function $\psi = (\psi_1, \psi_2, \psi_3, \psi_4)$, defined almost everywhere in $\mathbb{R}^3$, is a collisional invariant for the SRS model if

$$\sum_{i=1}^{4} \int_{\mathbb{R}^3} \psi_i \left(J_i^E + \alpha J_i^{E*} + J_i^R\right) \mathrm{d}v = 0. \tag{13}$$

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

Proposition 3.3 *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 their components $\psi_i = m_i v_{x_1}$, $\psi_i = m_i v_{x_2}$, $\psi_i = m_i v_{x_3}$ and $\psi_i = E_i + \frac{1}{2}v^2 m_i$ are collisional invariants for the SRS model.*

The first three invariants considered in Proposition 3.3 assure the conservation of the partial number density of a pair of 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. As a consequence, they also assure the conservation of the total number density of the mixture. The following three invariants assure the conservation of the momentum components of the mixture. Finally, the last invariant assures the conservation of the total energy of the mixture.

3.3 Equilibrium of the Generalized SRS System

The thermodynamical equilibrium solutions for the generalized SRS kinetic system (12) are characterized by the vanishing of the collision operators, as usual, namely

$$J_i^E = 0, \quad J_i^{E*} = 0 \quad \text{and} \quad J_i^R = 0, \qquad \text{for } \ i = 1, \ldots, 4. \tag{14}$$

The first two conditions above lead to Maxwellian distributions centered at the mixture rest frame [4], characterizing the so called mechanical equilibrium, given by

$$f_i = n_i \left(\frac{m_i}{2\pi kT}\right)^{3/2} \exp\left[-\frac{m_i(v-u)^2}{2kT}\right], \quad i = 1, \ldots, 4, \tag{15}$$

where k is the Boltzmann constant, n_i the number density of the i-constituent, T and u the temperature and mean velocity of the mixture. The mechanical equilibrium corresponds to a state in which all constituents share a common temperature and mean velocity, which are those of the whole mixture.

If the mixture is in mechanical equilibrium, the last condition in (14) establishes an additional constraint to be imposed to the Maxwellian distributions given in (15). This constraint will result in the chemical equilibrium condition for the reactive mixture. The main result is stated in the following proposition.

Proposition 3.4 *The thermodynamical equilibrium is determined by distribution functions given by* (15) *constrained to the mass action law*

$$\frac{n_1 n_2}{n_3 n_4} = \left(\frac{\mu_{12}}{\mu_{34}}\right)^{1/2} \exp\left(\frac{E_{abs}}{kT}\right). \tag{16}$$

We adopt the notation F_i^M to indicate thermodynamical equilibrium distributions defined as in (15) with n_i and T constrained to (16). Similarly, the notation f_i^M is adopted for mechanical equilibrium distributions defined as in (15) with n_i and T not constrained by (16). Distributions F_i^M and f_i^M satisfy the following properties that will be useful in the sequel.

Proposition 3.5 *Conservation of the kinetic energy during elastic collisions implies that Maxwellians f_i^M satisfy the relation*

$$f_i^M(v')f_j^M(w') = f_i^M(v)f_j^M(w), \qquad \textit{for} \ \ i, j = 1, \ldots, 4, \tag{17}$$

and equilibrium distributions F_i^M satisfy the relation

$$\begin{aligned}
&\left(\frac{\mu_{ij}}{\mu_{kl}}\right)^2 F_k^M(v_{ij}^{\odot})F_l^M(w_{ij}^{\odot}) - F_i^M(v)F_j^M(w) \\
&= F_i^M(v)F_j^M(w)\left[\left(\frac{\mu_{ij}}{\mu_{kl}}\right)^2 \frac{F_k^M(v_{ij}^{\odot})F_l^M(w_{ij}^{\odot})}{F_i^M(v)F_j^M(w)} - 1\right]
\end{aligned}$$

$$= F_i^M(v)F_j^M(w)\left[\left(\frac{\mu_{ij}}{\mu_{kl}}\right)^{1/2}\exp\left(\frac{E_{abs}}{kT}\right)\frac{n_k n_l}{n_i n_j} - 1\right], \tag{18}$$

The stability of the equilibrium in the specific case of spatial domain $\Omega = \mathbb{R}^3$, is stated in the following proposition.

Proposition 3.6 *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 $\mathsf{H}(t)$, defined by*

$$\mathsf{H}(t) = \sum_{i=1}^{4}\int_\Omega\int_{\mathbb{R}^3} f_i \log\left(\frac{f_i}{\mu_{ij}}\right)\mathrm{d}v\mathrm{d}x, \tag{19}$$

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 a Liapunov functional for the SRS system (3), that is

$$\frac{\mathrm{d}\mathsf{H}}{\mathrm{d}t}(t) \le 0, \quad \textit{for all} \quad t \ge 0, \quad \textit{and}$$

$$\frac{\mathrm{d}\mathsf{H}}{\mathrm{d}t}(t) = 0, \quad \textit{if and only if} \quad f_i = F_i^M, \quad \textit{for all} \quad i = 1, \ldots, 4.$$

Proposition 3.6 states that the reactive mixture, when evolving according to the SRS system (3), approaches the 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 deviation of the reactive mixture from thermodynamical equilibrium can be measured by a chemical force, see Ref. [17], defined as follows.

Definition 3.2 The affinity of the forward chemical reaction is defined by

$$\mathcal{A} = kT\ln\left(\frac{n_1 n_2\, n_3^{\mathrm{eq}} n_4^{\mathrm{eq}}}{n_3 n_4\, n_1^{\mathrm{eq}} n_2^{\mathrm{eq}}}\right), \tag{20}$$

where n_i^{eq} denotes the number density of each constituent in thermodynamical equilibrium conditions, i.e. verifying the mass action law (16).

Observe that the affinity vanishes at thermodynamical equilibrium conditions and tends to $-\infty$ in the exceptional conditions that the mixture reduces to the products of the forward reaction i.e., $n_1 = n_2 = 0$.

Moreover, the affinity $\mathcal{A}$ represents the main thermodynamical force of the reactive mixture and will be crucial for the evaluation of the transport coefficients. The non-equilibrium distribution obtained with the Chapman–Enskog method will be expressed, besides other thermodynamical forces, in terms of the affinity, and the following expression, that follows from the mass action law (16), will be used in the

sequel,

$$\exp\left(-\frac{\mathcal{A}}{kT}\right) = \left(\frac{\mu_{12}}{\mu_{34}}\right)^{1/2} \exp\left(\frac{E_{abs}}{kT}\right) \frac{n_3 n_4}{n_1 n_2}. \tag{21}$$

3.4 Linearized Form of the Generalized SRS Equations

We consider a first-order expansion of the distribution functions f_i around the thermodynamical equilibrium of the form

$$f_i(t,x,v) = F_i^M(t,x,v)\Big[1 + h_i(t,x,v)\Big], \qquad i = 1,\dots,4, \tag{22}$$

where $F_i^M(t,x,v)$ are equilibrium distributions given as in (15) and (16). Introducing expansions (22) into the kinetic equations (3) and neglecting quadratic terms on the deviations h_i, we obtain

$$\frac{\partial h_i}{\partial t} + v\frac{\partial h_i}{\partial x} = \sum_{j=1}^{4} \mathscr{L}_{ij}^E(\underline{h}) + \mathscr{L}_i^{E*}(\underline{h}) + \mathscr{L}_i^R(\underline{h}), \qquad i = 1,\dots,4, \tag{23}$$

where

$$\mathscr{L}_{ij}^E(\underline{h}) = \sigma_{ij}^2 \iint_{\mathbb{R}^3\times\mathbb{S}_+^2} F_j^M(w)\big[h_i(v') + h_j(w') - h_i(v) - h_j(w)\big]\langle\epsilon, v-w\rangle \,\mathrm{d}\epsilon\mathrm{d}w \tag{24}$$

$$\begin{aligned}\mathscr{L}_i^{E*}(\underline{h}) = -\alpha\beta_{ij}\sigma_{ij}^2 &\iint_{\mathbb{R}^3\times\mathbb{S}_+^2} F_j^M(w)\big[h_i(v') + h_j(w') - h_i(v) - h_j(w)\big] \\ &\times\Theta(\langle\epsilon, v-w\rangle - \Gamma_{ij})\langle\epsilon, v-w\rangle \,\mathrm{d}\epsilon\mathrm{d}w,\end{aligned} \tag{25}$$

$$\begin{aligned}\mathscr{L}_i^R(\underline{h}) = \beta_{ij}\sigma_{ij}^2 &\iint_{\mathbb{R}^3\times\mathbb{S}_+^2} F_j^M(w)\big[h_k(v_{ij}^{\odot}) + h_l(w_{ij}^{\odot}) - h_i(v) - h_j(w)\big] \\ &\times\Theta(\langle\epsilon, v-w\rangle - \Gamma_{ij})\langle\epsilon, v-w\rangle \,\mathrm{d}\epsilon\mathrm{d}w.\end{aligned} \tag{26}$$

The linearized operators given in (24), (25) and (26) are crucial for the determination of the transport coefficients by the Chapman–Enskog expansion method.

3.5 Macroscopic Equations

Formally, we can derive macroscopic field equations from the SRS kinetic system (3), defining first measurable macroscopic quantities in terms of averages of the distribution functions, and then deriving evolution equations for the macroscopic observables.

If we consider n_i, for $i = 1,\dots,4$, u, and T as the hydrodynamic fields describing the reactive mixture, the evolution equations for such fields can be formally derived

from Eq. (3) in the form, see [22] for details,

$$\frac{\partial n_i}{\partial t} + \sum_{s=1}^{3} \frac{\partial}{\partial x_s}\left(n_i \overline{u}_i^{(s)} + n_i u^{(s)}\right) = \tau_i, \quad \text{with} \quad \tau_i = \int_{\mathbb{R}^3} J_i^R \mathrm{d}v, \quad \text{for} \quad i = 1, \ldots, 4, \tag{27}$$

$$\frac{\partial}{\partial t}\left(\varrho u^{(r)}\right) + \sum_{s=1}^{3} \frac{\partial}{\partial x_s}\left[p^{(rs)} + \varrho u^{(r)} u^{(s)}\right] = 0, \qquad \text{for} \quad r = 1, 2, 3, \tag{28}$$

$$\frac{\partial}{\partial t}\left(\frac{3nkT}{2} + \sum_{i=1}^{4} n_i E_i + \frac{\varrho u^2}{2}\right) + \sum_{r=1}^{3} \frac{\partial}{\partial x_r}\left[q^{(r)} + \sum_{s=1}^{3} p^{(rs)} u^{(s)} + \left(\frac{3nkT}{2} + \sum_{i=1}^{4} n_i E_i + \frac{\varrho u^2}{2}\right) u^{(r)}\right] = 0. \tag{29}$$

Equation (27) is the *chemical rate equation* of both the generalized SRS model and the SRS model. This equation specifies the balance of the number density of each i-th component of the mixture and emphasizes that the changes on n_i result exclusively from the chemical reaction, as expected, since elastic collisions do not change the concentration of each constituent. Furthermore, Eqs. (28) and (29) are the *conservation laws* for the momentum components and total energy of the mixture, respectively.

In the above equations, the production term τ_i on the right-hand side of (27) represents the *reaction rate* for the i-th component of the mixture. Moreover, $\overline{u}_i$ denotes the diffusion velocity of the i-th component of the mixture, whereas n, ϱ, u, $p^{(rs)}$, T and q represent, respectively, the number density, mass density, mean velocity, pressure tensor components, temperature and heat flux of the mixture. The upper indices r and s indicate spatial directions in a given orthogonal reference system.

In particular, the reaction rate τ_i is given by

$$\begin{aligned}\tau_i(t,x) = -\nu_i \beta_{12} \sigma_{12}^2 \iiint_{\mathbb{R}^3 \times \mathbb{R}^3 \times \mathbb{S}_+^2} & \\ \times \left[\left(\frac{\mu_{12}}{\mu_{34}}\right)^2 f_3(t,x,v_{12}^{\odot}) f_4(t,x,w_{12}^{\odot}) - f_1(t,x,v) f_2(t,x,w)\right] & \\ \times \Theta\left(\langle \epsilon, v-w\rangle - \Gamma_{12}\right) \langle \epsilon, v-w\rangle \mathrm{d}\epsilon \mathrm{d}w \mathrm{d}v, \quad i = 1, \ldots, 4, & \end{aligned} \tag{30}$$

where the coefficients ν_i are the stoichiometric coefficients associated to the chemical reaction (1), with $\nu_1 = \nu_2 = -1$, $\nu_3 = \nu_4 = 1$. The diffusion velocities $\overline{u}_i$, are given by

$$\overline{u}_i(t,x) = \frac{1}{\varrho_i(t,x)} \int_{\mathbb{R}^3} m_i\big(v - u(t,x)\big) f_i(t,x,v) \mathrm{d}v, \text{ with } \sum_{i=1}^{4} \varrho_i(t,x) \overline{u}_i(t,x) = 0, \tag{31}$$

whereas the components of the pressure tensor, $p^{(rs)}$, and heat flux q are given as follows

$$p^{(rs)}(t,x) = \sum_{i=1}^{4} \int_{\mathbb{R}^3} m_i \Big(v_r - u_r(t,x)\Big)\Big(v_s - u_s(t,x)\Big) f_i(t,x,v)\mathrm{d}v, \quad r,s = 1,2,3, \tag{32}$$

and

$$q(t,x) = \sum_{i=1}^{4} \Big(q_i(t,x) + E_i n_i(t,x)\overline{u}_i(t,x)\Big), \tag{33}$$

with

$$q_i(t,x) = \frac{1}{2}\int_{\mathbb{R}^3} m_i |v - u(t,x)|^2 \big(v - u(t,x)\big) f_i(t,x,v)\mathrm{d}v. \tag{34}$$

We do not give here the explicit expressions of the other quantities, see the paper [22].

As usual, Eqs. (27), (28) and (29) do not constitute a closed set, because they involve the above unknown fields. The system can be closed at the first-order level of the asymptotic Chapman–Enskog method and this will be the object of the next section.

4 Transport Properties of the SRS Kinetic Systems

In this section we study the transport properties of the SRS system in its formulation expressed by Eq. (12) with $\alpha = 1$, corresponding to the full SRS system (3), and $\alpha = 0$, corresponding to the SRS system without the correction term J_i^{E*}.

The analysis developed here is a continuation of our previous paper [6], where we have focused on both the reaction rate coefficients and shear viscosity, for the full SRS system (3). Here, the focus will be the analysis of the transport coefficients of thermal conductivity, diffusion and thermal-diffusion ratio, and also on the comparison of those coefficients when evaluated for both full system (3) and the corresponding reduced system (3) with $\alpha = 0$.

The details about the Chapman–Enskog procedure, for what concerns the transport algorithm, the zero-order approximation and the evaluation of the reaction rate coefficients and shear viscosity, can be seen in paper [6].

4.1 Asymptotic Solution of the Generalized SRS System

We assume that both elastic and reactive collisions occur with comparable characteristic times and start with the scaled full SRS system written as, see [6],

$$\frac{\partial f_i}{\partial t} + v \cdot \nabla_x f_i = \frac{1}{\delta}\Big(J_i^E + J_i^{E*} + J_i^R\Big), \qquad i = 1, \ldots, 4, \tag{35}$$

where δ is a formal expansion parameter. We consider a first-order expansion of functions f_i of the form

$$f_i = f_i^{(0)}\big(1 + \delta\phi_i\big), \quad i = 1, \ldots, 4, \tag{36}$$

where $\phi_i = \phi_i(t, x, v)$ represents a small perturbation function.

Since the Chapman–Enskog method requires that f_i and $f_i^{(0)}$ yield the same moments associated to the collision invariants of the reactive mixture, we conclude that the perturbations ϕ_i satisfy the following orthogonality conditions that will be essential in the sequel,

$$\begin{aligned} &\sum_{i=1}^{4} \int_{\mathbb{R}^3} f_i^{(0)} \phi_i \, \mathrm{d}v = 0, \quad \sum_{i=1}^{4} \int_{\mathbb{R}^3} m_i v f_i^{(0)} \phi_i \, \mathrm{d}v = 0, \\ &\sum_{i=1}^{4} \int_{\mathbb{R}^3} \left(m_i \frac{v^2}{2} + E_i\right) f_i^{(0)} \phi_i \, \mathrm{d}v = 0. \end{aligned} \tag{37}$$

Introducing expansions (36) into Eq. (35) and equating the terms of the same order in δ, we easily obtain that the zero-order approximation $f_i^{(0)}$ is such that

$$J_i^E(\{f_i^{(0)}\}) + J_i^{E*}(\{f_i^{(0)}\}) + J_i^R(\{f_i^{(0)}\}) = 0, \quad i = 1, \ldots, 4, \tag{38}$$

where the notation used signifies that the collision operators only depend on $f_1^{(0)}, f_2^{(0)}, f_3^{(0)}, f_4^{(0)}$. As a consequence of condition (38), the zero-order approximations $f_i^{(0)}$ are the equilibrium Maxwellian (15) constrained to the mass action law (16), i.e.

$$f_i^{(0)} = F_i^M, \quad i = 1, \ldots, 4. \tag{39}$$

Equating the terms of the order $\mathcal{O}(1)$ in Eq. (35), we obtain, as in [6], the following linear integral equations for the perturbation terms ϕ_i,

$$\begin{aligned} &f_i^{(0)} \Bigg\{ \frac{m_i}{kT} \sum_{r,s}^{3} (v_r - u_r)(v_s - u_s) \left(\frac{\partial u_s}{\partial x_r} - \frac{1}{3}\left(\sum_{\ell}^{3} \frac{\partial u_\ell}{\partial x_\ell} \right) \delta_{rs} \right) \\ &+ \sum_{r=1}^{3} \frac{1}{T}(v_r - u_r)\left(\frac{m_i}{2kT}(v-u)^2 - \frac{5}{2} \right) \frac{\partial T}{\partial x_r} + \frac{n}{n_i} \sum_{r=1}^{3} (v_r - u_r) d_r^i \\ &+ \frac{\nu_i}{n_i} \tau_f^{(0)} \frac{\mathcal{A}}{kT} - \frac{2\nu_i}{3n} \tau_f^{(0)} \frac{E_{abs}}{kT} \left(\frac{3}{2} - \frac{m_i}{2kT}(v-u)^2 \right) \frac{\mathcal{A}}{kT} \end{aligned}$$

$$+\beta_{ij}\sigma_{ij}^2\left(\iint\limits_{\mathbb{R}^3\times\mathbb{S}_+^2} f_j^{(0)}(w)\Theta\left(\langle\epsilon, v-w\rangle-\Gamma_{ij}\right)\langle\epsilon, v-w\rangle \mathrm{d}\epsilon\mathrm{d}w\right)\frac{\mathcal{A}}{kT}\Bigg\}$$

$$=\sum_{j=1}^{4}\mathscr{L}_{ij}^{E}(\{\phi_i\})+\mathscr{L}_i^{E*}(\{\phi_i\})+\mathscr{L}_i^{R}(\{\phi_i\}),\quad \text{for}\quad i=1,\ldots,4, \tag{40}$$

where $\tau_f^{(0)}$ represents the forward reaction rate at the zero-order level, given by

$$\tau_f^{(0)}=\beta_{12}\sigma_{12}^2\sqrt{\frac{8\pi kT}{\mu_{12}}}\exp\left(-\frac{\gamma_1}{kT}\right)n_1^{(0)}n_2^{(0)}, \tag{41}$$

with $n_i^{(0)}$ being the zero-order approximation of the constituent number density, and d_r^i represents spatial r-components of generalized diffusion forces of the i-constituent, given by

$$d_r^i=\frac{1}{p}\frac{\partial p_i}{\partial x_r}-\frac{\rho_i}{\rho\, p}\frac{\partial p}{\partial x_r},\quad i=1,\ldots,4,\quad r=1,2,3, \tag{42}$$

such that

$$\sum_{i=1}^{4}d_r^i=0,\quad r=1,2,3.$$

In Eq. (42), p_i represents the pressure of the i-constituent and p the pressure of the mixture. Moreover, $\mathscr{L}_{ij}^{E}$, $\mathscr{L}_i^{E*}$ and $\mathscr{L}_i^{R}$ are the linearized operators defined in (24), (25) and (26), respectively

As explained in paper [6], we assume a trial form for the perturbation ϕ_i which is a linear combination of the thermodynamic forces appearing on the left-hand side of (40),

$$\phi_i=-A_i\sum_{r=1}^{3}(v_r-u_r)\frac{\partial T}{\partial x_r}-B_i\sum_{r,s}^{3}(v_r-u_r)(v_s-u_s)\left(\frac{\partial u_s}{\partial x_r}-\frac{1}{3}\left(\sum_{\ell}^{3}\frac{\partial u_\ell}{\partial x_\ell}\right)\delta_{rs}\right)$$
$$-\sum_{j=1}^{4}H_{ij}\sum_{r=1}^{3}(v_r-u_r)d_r^j-G_i\frac{\mathcal{A}}{kT},\qquad i=1,\ldots,4, \tag{43}$$

where the coefficients A_i, B_i, H_{ij} and G_i are scalar quantities depending on the number densities n_i, scalar velocity $|v-u|^2$, and mixture temperature T. Therefore, the problem of determining the perturbations ϕ_i becomes the one of determining such coefficients. Since these thermodynamic forces are linearly independent, system (40) decouples into four subsystems, and for our convenience, we introduce the following components of ϕ_i,

$$\phi_i^{(A)} = A_i \sum_{r=1}^{3} (v_r - u_r) \frac{\partial T}{\partial x_r},$$
$$\phi_i^{(B)} = B_i \sum_{r,s}^{3} (v_r - u_r)(v_s - u_s) \left(\frac{\partial u_s}{\partial x_r} - \frac{1}{3} \left(\sum_{\ell}^{3} \frac{\partial u_\ell}{\partial x_\ell} \right) \delta_{rs} \right),$$
$$\phi_i^{(H)} = \sum_{j=1}^{4} H_{ij} \sum_{r=1}^{3} (v_r - u_r) d_r^j, \phi_i^{(G)} = G_i \frac{\mathcal{A}}{kT}, \qquad i = 1, \ldots, 4. \tag{44}$$

Each subsystem involves one component of ϕ_i and determines the corresponding coefficients. The resulting subsystems are solved separately assuming appropriate expansions for the coefficients A_i, B_i, H_{ij} and G_i. A standard assumption is to consider that such coefficients are expanded in terms of specific Sonine polynomials of the dimensionless quantity,

$$C_i^2 = m_i \frac{(v-u)^2}{2kT}.$$

The reaction rate coefficients and the shear viscosity have been determined in paper [6] solving the subsystems for $\phi_i^{(G)}$ and $\phi_i^{(B)}$, respectively. In the present paper, we solve the subsystems for $\phi_i^{(H)}$ and $\phi_i^{(A)}$ and determine the diffusion coefficients as well as the thermal conductivity and the thermal diffusion ratio.

4.2 Transport Coefficients

We use now the procedure briefly explained above to determine the components $\phi_i^{(A)}$ and $\phi_i^{(H)}$ of the perturbation of the equilibrium distribution functions. We will omit the computational details that are explained in paper [6] and in references quoted therein, in particular in papers [8, 12, 17, 19].

4.2.1 Fick Law and Diffusion Coefficients

The diffusion coefficients are obtained through several steps that will be explained in the sequel.

(i) Subsystem for $\phi_i^{(H)}$ We start with the subsystem for the perturbation component $\phi_i^{(H)}$, namely

$$f_i^{(0)} \left\{ \sum_{r=1}^{3} \frac{1}{T} (v_r - u_r) \left(\frac{m_i}{2kT} (v-u)^2 - \frac{5}{2} \right) \frac{\partial T}{\partial x_r} + \frac{n}{n_i} \sum_{r=1}^{3} (v_r - u_r) d_r^i \right\}$$
$$= \sum_{j=1}^{4} \mathscr{L}_{ij}^E(\{\phi_i^{(H)}\}) + \mathscr{L}_i^{E*}(\{\phi_i^{(H)}\}) + \mathscr{L}_i^R(\{\phi_i^{(H)}\}), \quad \text{for} \quad i = 1, \ldots, 4, \tag{45}$$

where $\phi_i^{(H)}$ is given in (44) in terms of the coefficients H_{ij}.

(ii) Coefficients H_{ij} Following the Chapman–Enskog method, we assume that each coefficient H_{ij} is expanded in terms of Sonine polynomials of index 3/2, and we take the first two terms of the expansion. Thus we start with

$$H_{ij} = h_{ij}^{(0)} S_{3/2}^{(0)}(C_i^2) + h_{ij}^{(1)} S_{3/2}^{(1)}(C_i^2),$$

that is

$$H_{ij} = h_{ij}^{(0)} + h_{ij}^{(1)} \left(\frac{5}{2} - \frac{m_i}{2kT}(v-u)^2 \right), \quad i = 1, 2, 3, 4, \tag{46}$$

where $h_{ij}^{(0)}$ and $h_{ij}^{(1)}$ are scalar constants to be determined. We multiply Eq. (45) by $S_{3/2}^{(1)}(C_i^2) \sum_{r=1}^{3}(v_r - u_r)$, integrate first over $v \in \mathbb{R}^3$ and then over $\mathbb{S}_+^2$ by using spherical coordinates, and finally we compute the sixfold integral over $\mathbb{R}^3 \times \mathbb{R}^3$ by transforming to the center of mass reference frame.

The resulting equations for the scalars $h_{ij}^{(0)}$ and $h_{ij}^{(1)}$ constitute an algebraic system that can be solved using any computer algebra system. We have used the computational software Maple system, version 2018.

Then the solution obtained for $h_{ij}^{(0)}$ and $h_{ij}^{(1)}$ determines the perturbation component $\phi_i^{(H)}$ through Eqs. (44) and (46).

(iii) Generalized Fick law The Fick law is associated to the first-order correction to the diffusion velocities $\overline{u}_i$.

The Fick law is derived by inserting the distribution function corrected by its H-component, $f_i^{(0)}(1 + \phi_i^{(H)})$, into expression (31) of the diffusion velocities. Performing the integration over the velocity v and neglecting the non-linear terms in the perturbations, we obtain the *generalized Fick law*, formally written as

$$\overline{u}_r^{\,i} = -\sum_{j=1}^{4} \Delta_{ij} d_r^j - D_T^i \frac{\partial}{\partial x_r} \ln T, \quad i = 1, \ldots, 4, \quad r = 1, 2, 3, \tag{47}$$

where Δ_{ij} is a generalized diffusion coefficient and D_T^i is the thermal diffusion coefficient. The Fick law (47) can be equivalently written as

$$\overline{u}_r^{\,i} = -\sum_{j=1}^{4} \Delta_{ij} \left(d_r^j + RT_j \frac{\partial}{\partial x_r} \ln T \right), \quad i = 1, \ldots, 4, \quad r = 1, 2, 3, \tag{48}$$

where RT_i are thermal-diffusion ratios such that

$$D_T^i = \sum_{j=1}^{4} \Delta_{ij} RT_j, \quad \text{for } i = 1, \ldots, 4, \quad \text{with } \sum_{j=1}^{4} RT_j = 0. \tag{49}$$

Note that the above constraint on RT_j results from condition (31) and from the fact that the thermodynamical forces d_r^i and $\frac{\partial T}{\partial x_r}$ are linearly independent. Therefore,

$$\sum_{i=1}^{4}\left(d_r^i + RT_i\,\frac{\partial}{\partial x_r}\ln T\right) = 0, \quad r = 1, 2, 3. \tag{50}$$

Using Eq. (50) together with (48), we can express the diffusion forces in terms of the diffusion velocities in the form

$$d_r^i = -RT_i\,\frac{\partial}{\partial x_r}\ln T - \frac{1}{n^2}\sum_{j=1}^{4}\frac{n_i n_j}{D_{ij}}\,(\overline{u}_r^{\,i} - \overline{u}_r^{\,j}), \quad i = 1, \ldots, 4, \quad r = 1, 2, 3, \tag{51}$$

where D_{ij} are the diffusion coefficients depending implicitly on $h_{ij}^{(0)}, h_{ij}^{(1)}$. For more details, see the book by Chapman and Cowling [8].
Equation (51) expresses the fact that the diffusion forces are supported by temperature gradients and diffusion velocities.

(iv) Diffusion coefficients We have to solve system (51) in order to determine the twelve independent diffusion coefficients D_{ij}. This is a cumbersome computation because the equations are rather intricate. We have used the computational software Maple system, version 2018.

4.2.2 Fourier Law, Thermal Conductivity and Thermal-Diffusion Ratio

The coefficients of thermal conductivity and thermal-diffusion ratio are obtained with a similar algorithm as the one utilized before for the diffusion coefficients.

(i) Subsystem for $\phi_i^{(A)}$
The subsystem for the perturbation component $\phi_i^{(A)}$ is given by

$$\begin{aligned} &f_i^{(0)}\left\{\sum_{r=1}^{3}\frac{1}{T}(v_r - u_r)\left(\frac{m_i}{2kT}(v-u)^2 - \frac{5}{2}\right)\frac{\partial T}{\partial x_r} + \frac{n}{n_i}\sum_{r=1}^{3}(v_r - u_r)d_r^i\right\} \\ &= \sum_{j=1}^{4}\mathscr{L}_{ij}^{E}(\{\phi_i^{(A)}\}) + \mathscr{L}_i^{E*}(\{\phi_i^{(A)}\}) + \mathscr{L}_i^{R}(\{\phi_i^{(A)}\}), \quad \text{for} \quad i = 1, \ldots, 4, \end{aligned} \tag{52}$$

where $\phi_i^{(A)}$ is given in (44) in terms of the coefficients A_i.

(ii) Coefficients A_i
We assume that each coefficient A_i is expanded in terms of Sonine polynomials of index $3/2$ and we take once more the first two terms of the expansion.

$$A_i = a_i^{(0)} S_{3/2}^{(0)}\big(C_i^2\big) + a_i^{(1)} S_{3/2}^{(1)}\big(C_i^2\big), \quad i = 1, \ldots, 4,$$

that is

$$A_i = a_i^{(0)} + a_i^{(1)}\left(\frac{5}{2} - \frac{m_i}{2kT}(v-u)^2\right), \quad i = 1, \ldots, 4, \tag{53}$$

where $a_i^{(0)}$ and $a_i^{(1)}$ are scalar constants to be determined. We then multiply Eq. (52) by $S_{3/2}^{(1)}\left(C_i^2\right)\sum_{r=1}^{3}(v_r - u_r)$, and perform the integration as explained before.

Then, we have used the software Maple to solve the resulting equations and determine $a_i^{(0)}$ and $a_i^{(1)}$. Finally, in turn, we have determined the perturbation component $\phi_i^{(A)}$ through Eqs. (44) and (53).

(iii) Generalized Fourier law

The Fourier law is associated to the first-order correction to the heat flux vector q. This law is derived by inserting the distribution function corrected by its A-component, $f_i^{(0)}\left(1 + \phi_i^{(A)}\right)$, into expression (33) of the heat flux vector, and it is formally given by

$$q_r = -\widetilde{\lambda}\frac{\partial T}{\partial x_r} - \sum_{j=1}^{4}\widetilde{D}_j d_r^j, \quad r = 1, 2, 3, \tag{54}$$

where $\widetilde{\lambda}$ and $\widetilde{D}_j$ are associated with thermal conductivity and diffusion thermal effects, respectively. They are given by

$$\widetilde{\lambda} = \sum_{j=1}^{4}\left[\frac{1}{6}\int_{\mathbb{R}^3} A_i m_i f_i^{(0)}(v-u)^4 \mathrm{d}v + \frac{n_i E_i}{T} D_T^i\right], \tag{55}$$

$$\widetilde{D}_j = \sum_{j=1}^{4}\left[\frac{1}{6}\int_{\mathbb{R}^3} H_{ij} m_i f_i^{(0)}(v-u)^4 \mathrm{d}v + n_i E_i \Delta_{ij}\right]. \tag{56}$$

(iv) The thermal conductivity and thermal diffusion ratio

The thermal conductivity is the coefficient of proportionality of the heat flux vector q with respect to the temperature gradient, when the diffusion is absent, that is when the diffusion velocities are equal to zero. Therefore, we substitute expression (51) with $\overline{u}_i = 0$ into Eq. (54), obtaining thermal conductivity given by

$$\lambda = \widetilde{\lambda} - \sum_{i=1}^{4}\widetilde{D}_i RT_i \tag{57}$$

where $\widetilde{\lambda}$ is given in (55) and RT_i is the thermal diffusion ratio appearing in (51), where $\widetilde{\lambda}$, $\widetilde{D}_i$ and RT_i depend implicitly on the coefficients A_i and H_{ij}. The computations result to be rather cumbersome, and, again, we have used the Maple system.

Table 1 Different reactive mixtures considered in our computations

Mixtures	m_1	m_2	m_3	m_4	μ_{12}	μ_{34}	x_1	x_2	x_3	x_4	$E_{abs}/(kT)$	
$\mathcal{M}_1$	2.2	1.8	3	1	0.99	0.75	0.10	0.10	0.40	0.40	−2.911	EXO
$\mathcal{M}_2$	2.2	1.8	3	1	0.99	0.75	0.40	0.40	0.10	0.10	2.634	ENDO
$\mathcal{M}_3$	2.2	1.8	3.8	0.2	0.99	0.19	0.10	0.10	0.40	0.40	−3.598	EXO
$\mathcal{M}_4$	2.2	1.8	3.8	0.2	0.99	0.19	0.40	0.40	0.10	0.10	1.947	ENDO

5 Comparative Study and Numerical Results

In this section we develop a comparative analysis between the transport coefficients for the full SRS model of Sect. 2, for $\alpha = 1$, and those of the variant version of the SRS model of Sect. 3, for $\alpha = 0$.

The numerical results refer to the transport coefficients of diffusion, thermal conductivity and thermal-diffusion ratio, and are obtained following the procedure described in Subsection 4.2.

Our aim is to analyse the influence of the chemical reaction in the behaviour of the above mentioned coefficients and to investigate the role of the elastic correction term proper of the SRS model in order to appreciate how it can affect the transport coefficients.

5.1 Parameters and Input Data

We consider four different reactive mixtures, $\mathcal{M}_1, \mathcal{M}_2, \mathcal{M}_3, \mathcal{M}_4$, characterized in terms of the molecular masses m_i and equilibrium concentrations x_i of the constituents, where $x_i = n_i/n$, for $i = 1, \ldots, 4$. See Table 1, where the last column indicates the values of the reaction heat in units of kT. Therefore, when $E_{abs} < 0$, the forward reaction is exothermic, and when $E_{abs} > 0$, it is endothermic.

The choice of the parameters and the equilibrium compositions of the reactive systems are presented below.

- We choose the molecular masses m_i varying in such a way that all constituents have disparate masses, more specifically the reduced mass of the products can be 75.8% or 19.2% of that of the reactants. Moreover, the mass conservation law imposes that $m_1 + m_2 = m_3 + m_4$.
- Among the four concentrations x_i, only two are independent, in general, since $\sum_{i=1}^{4} x_i = 1$ and the mass action law furnishes another constraint. Here, in agreement with our first paper [6], and other studies in [25, 26], we assume $x_2 = x_1$ and $x_4 = x_3$, and disregard the law of mass action for the determination of the concentrations. We obtain $x_3 = (1 - 2x_1)/2$
- The reaction heat E_{abs} is an important parameter when dealing with chemical reactions. Its sign determines when the forward reaction is endothermic, $E_{abs} > 0$, and when it is exothermic, $E_{abs} < 0$. In our simulations, this parameter is computed at equilibrium conditions from the mass action law (16), and thus from

the molecular masses and equilibrium concentrations, as

$$\frac{E_{abs}}{kT} = \ln\left(\sqrt{\frac{m_3 m_4}{m_1 m_2}}\,\frac{x_1 x_2}{x_3 x_4}\right). \tag{58}$$

- The molecular diameters are not relevant for chemical reactions in the dilute gas regime. For simplicity, we assume $d_i = 1$, $i = 1, \ldots, 4$, for all computations.
- The activation energies γ_1 and γ_3 are other important parameters when dealing with chemical reactions, since they represent the energy barriers that should be exceeded in order for the forward and backward chemical reactions to occur. They satisfy the relation $\gamma_3 = \gamma_1 - E_{abs}$, and therefore only one of the activation energies is an independent parameter. In our simulations, we choose γ_1 to be the independent one. We investigate the behaviour of the transport coefficients in terms of γ_1.
- Concerning the coefficients β_{ij}, $i, j = 1, \ldots, 4$, we choose $\beta_{ij} = \beta_{kl} = \beta$, consistently with the choice on the molecular diameters d_i. In our simulations, we consider $\beta = 1$ when investigating the impact of the correction term on the transport coefficients, whereas we take $\beta = 0.5, 0.75, 1$ when investigating the effects of such parameter on the behaviour of the transport coefficients.

5.2 Numerical Results

In this section we provide the results of our numerical simulations for different configurations of the SRS model described by different choices of the molecular masses m_i, equilibrium concentrations x_i, and parameter β.

Our aim is to analyse two problems. First, we want to understand how the parameters m_i, x_i, and also the corresponding exothermicity or endothermicity character of the chemical reaction, influence the behaviour of the transport coefficients. Second, we want to investigate the impact of the correction term incorporated in our SRS model on the transport coefficients.

5.2.1 Results for the Diffusion Coefficients

Figures 1 and 2 illustrate the behaviour of the diffusion coefficients D_{AB} and D_{CD} for mixtures $\mathcal{M}_1$ and $\mathcal{M}_2$, and how the coefficients vary depending on the dimensionless forward activation energy $\varepsilon = \gamma_1/(kT)$.

The left frames of Figs. 1 and 2 show the behaviour of the coefficients D_{AB}, D_{CD} for $\beta = 1$, when we consider the full SRS model with its correction terms (dashed lines), and when we remove the correction term from the SRS model (solid lines).

The right frames of the same figures show the impact of the parameter β on the coefficients D_{AB}, D_{CD}. All curves refer to the full SRS model with its correction term. In particular, the dotted lines correspond to $\beta = 1$ and is exactly the same one considered in left frames. Besides such curve, we also consider the curves for $\beta = 0.75$ (middle dashed lines) and $\beta = 0.5$ (solid lines).

We see that the non-equilibrium effects induced by the chemical reaction are more noticeable for small values of the activation energy, say ε, and start to be imperceptible

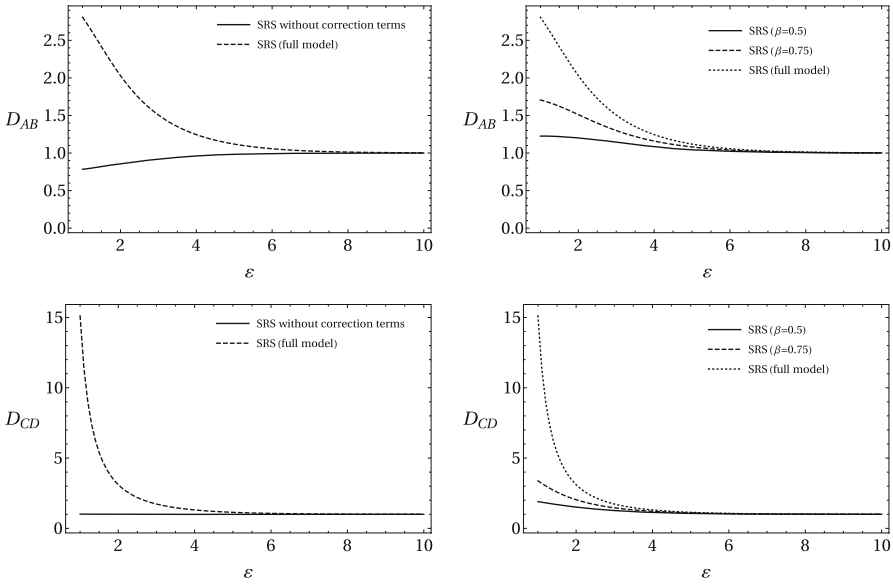

Fig. 1 Mixture $\mathcal{M}_1$ (exothermic forward reaction, $E_{abs} = -2.911$, $\mu_{34}/\mu_{12} = 0.758$). Diffusion coefficients D_{AB} and D_{CD} versus the forward activation energy ε. *Left frame:* Impact of the correction terms. Full SRS model, and SRS model without correction terms. *Right frame:* Effects of the parameter β. Full SRS model with $\beta = 1$, and with $\beta = 0.75$ and $\beta = 0.5$

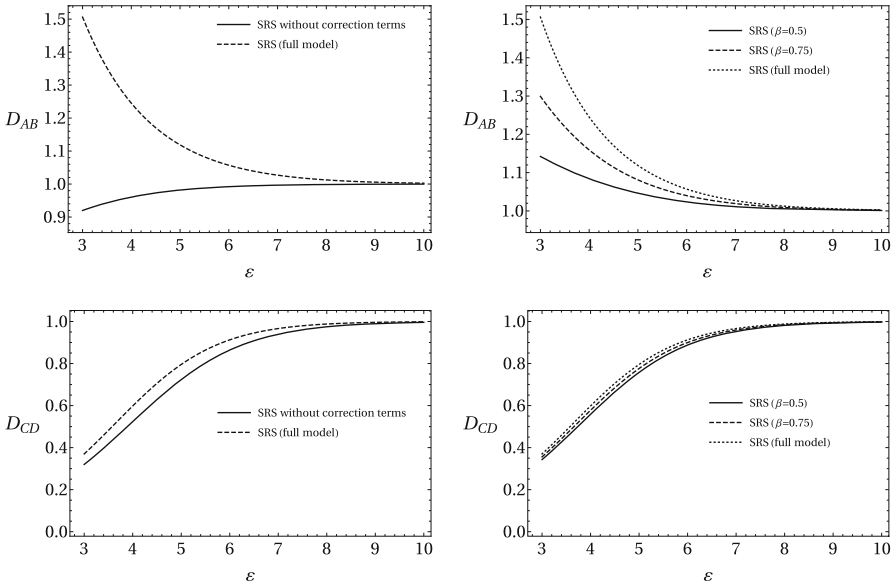

Fig. 2 Mixture $\mathcal{M}_2$ (endothermic forward reaction, $E_{abs} = 2.634$, $\mu_{34}/\mu_{12} = 0.758$). Diffusion coefficients D_{AB} and D_{CD} versus the forward activation energy ε. *Left frame:* Impact of the correction terms. Full SRS model, and SRS model without correction terms. *Right frame:* Effects of the parameter β. Full SRS model with $\beta = 1$, and with $\beta = 0.75$ and $\beta = 0.5$

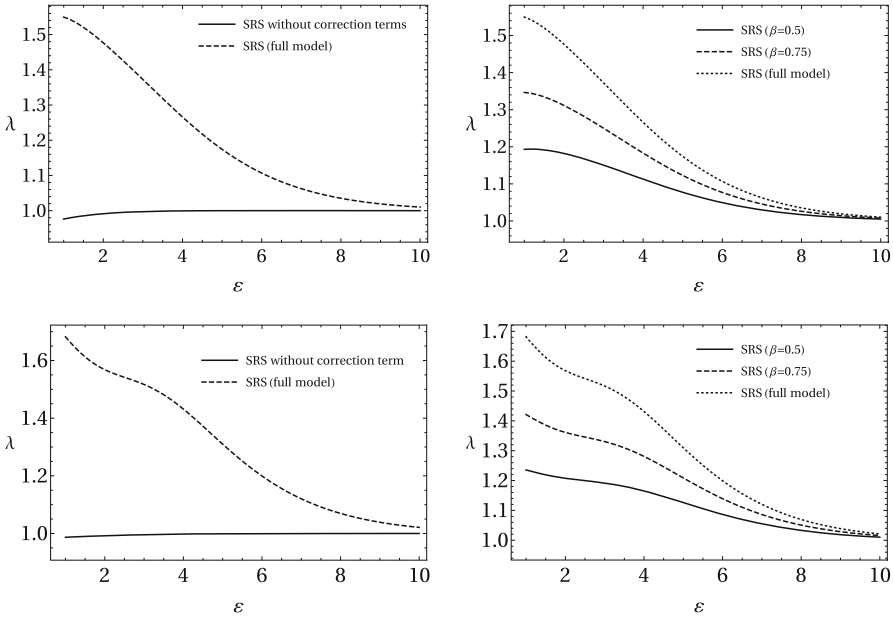

Fig. 3 Mixtures $\mathcal{M}_1$ in the top frames (exothermic forward reaction, $E_{abs} = -2.911$, $\mu_{34}/\mu_{12} = 0.758$) and $\mathcal{M}_3$ in the bottom frames (exothermic forward reaction, $E_{abs} = -3.598$, $\mu_{34}/\mu_{12} = 0.192$). Thermal conductivity λ versus the forward activation energy ε. *Left frames:* Impact of the correction terms. Full SRS model, and SRS model without correction terms. *Right frames:* Effects of the parameter β. Full SRS model with $\beta = 1$, and with $\beta = 0.75$ and $\beta = 0.5$

when γ_1 approaches the value 10. This is a consequence of the fact that a high value of the activation energy indicates that the threshold of the chemical reaction is so high that reactive collisions become very rare.

We also see that the correction terms contribute to the increase of the diffusion coefficients, meaning that the diffusion of the constituents is hidden when the correction terms are not included in the model. In other words, the presence of correction terms have the effect of restoring the diffusion among the constituents.

In both Figures, we can see that the effect on the diffusion coefficients is larger for the constituents that have a small concentration x_i.

Another interesting result highlighted in these figures is that, as expected, the effects of the correction terms are more pronounced in the diffusion coefficients of the products CD when the forward reaction is endothermic. Conversely, they are more pronounced for the reactants AB when the forward reaction is exothermic.

5.2.2 Results for the Thermal Conductivity

Figures 3 and 4 illustrate the behaviour of the thermal conductivity coefficient λ for mixtures $\mathcal{M}_1$, $\mathcal{M}_3$ and $\mathcal{M}_2$, $\mathcal{M}_4$ and how the coefficient varies depending on the dimensionless forward activation energy ε.

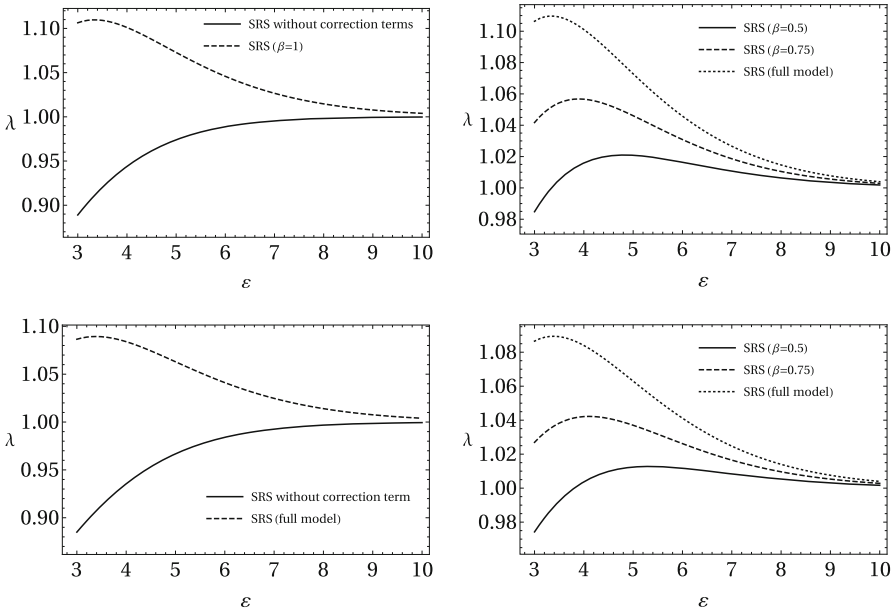

Fig. 4 Mixtures $\mathcal{M}_2$ in the top frames (endothermic forward reaction, $E_{abs} = 2.634$, $\mu_{34}/\mu_{12} = 0.758$) and $\mathcal{M}_4$ in the bottom frames (endothermic forward reaction, $E_{abs} = 1.947$, $\mu_{34}/\mu_{12} = 0.192$). Thermal conductivity λ versus the forward activation energy ε. *Left frames:* Impact of the correction terms. Full SRS model, and SRS model without correction terms. *Right frames:* Effects of the parameter β. Full SRS model with $\beta = 1$, and with $\beta = 0.75$ and $\beta = 0.5$

As before, the left frames of Figs. 3 and 4 show the behaviour of the thermal conductivity λ for $\beta = 1$, when we consider the full SRS model with its correction term (dotted lines), and when we remove the correction term from the SRS model (solid lines).

The right frames show how the coefficient λ is affected when we vary the parameter β and consider different proportions of reactive collisions. All curves refer to the full SRS model with its correction terms, with the dotted lines for $\beta = 1$, dashed lines for $\beta = 0.75$ and solid lines for $\beta = 0.5$.

The top and bottom frames of Fig. 3 are obtained for different values of the molecular masses m_3 and m_4, implying that bottom frames correspond to a chemical reaction with higher exothermicity character. The results of this figure show that the effect of increasing the absolute value of the reaction heat is not so relevant even if we can say that the thermal conductivity increases. Analogously, the top and bottom frames of Fig. 4 correspond to different values of m_3 and m_4, implying that top frames correspond to a chemical reaction with higher endothermicity character. Again, the results show that the impact of the reaction heat on the thermal conductivity is almost insignificant.

The coefficient of thermal conductivity is much affected by the chemical reaction, and therefore is also very much affected by the parameter β. From the analytical point of view, this is a direct consequence of the influence of the binding energies and reaction heat on the energy transport, as predicted by Eqs. (54)–(57).

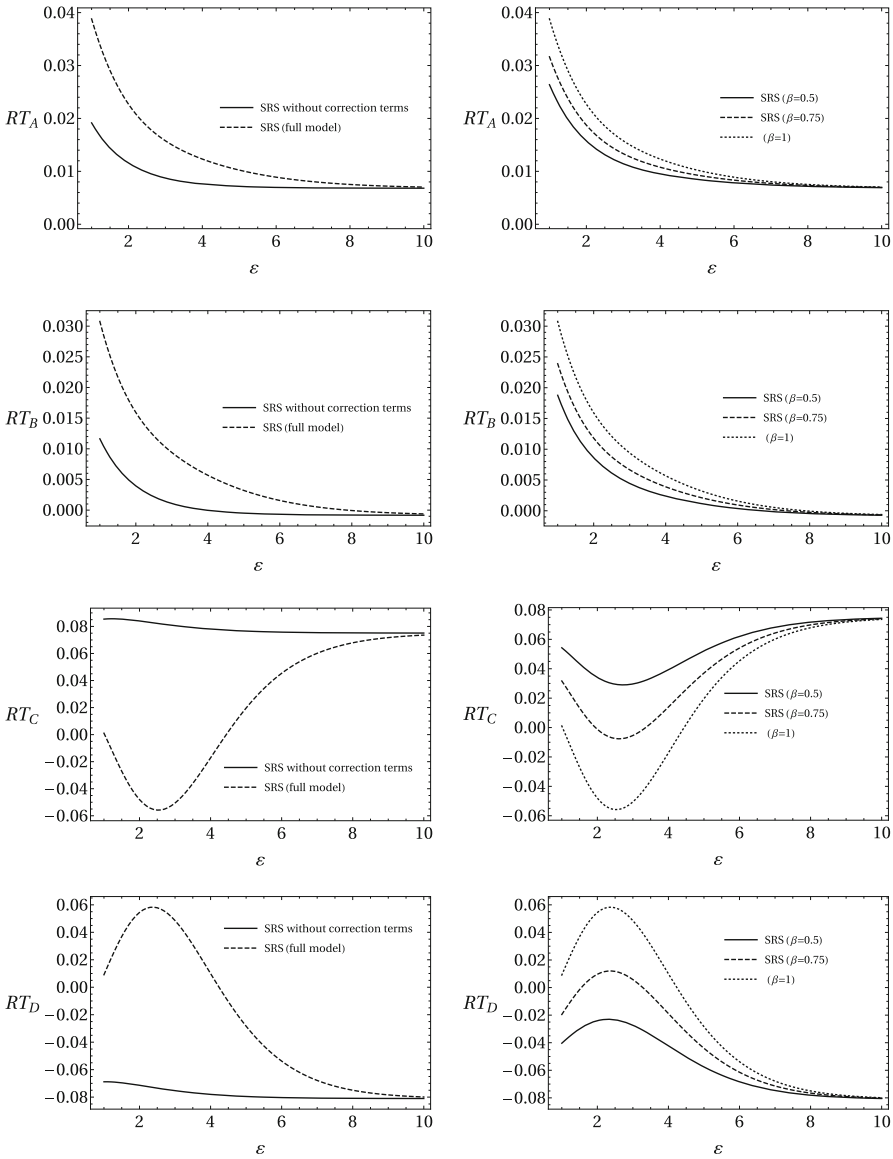

Fig. 5 Mixture $\mathcal{M}_1$ (exothermic forward reaction, $E_{abs} = -2.911, \mu_{34}/\mu_{12} = 0.758$). Thermal-diffusion ratio RT_A, RT_B, RT_C, RT_D versus the forward activation energy ε. *Left frames:* Impact of the correction terms. Full SRS model, and SRS model without correction terms. *Right frames:* Effects of the parameter β. Full SRS model with $\beta = 1$, and with $\beta = 0.75$ and $\beta = 0.5$

From the qualitative point of view, the results obtained for the thermal conductivity are similar to those obtained for the diffusion. It is clear that the correction terms contribute to increase the thermal conductivity λ, and, again, the effects are more noticeable for small values of the forward activation energy.

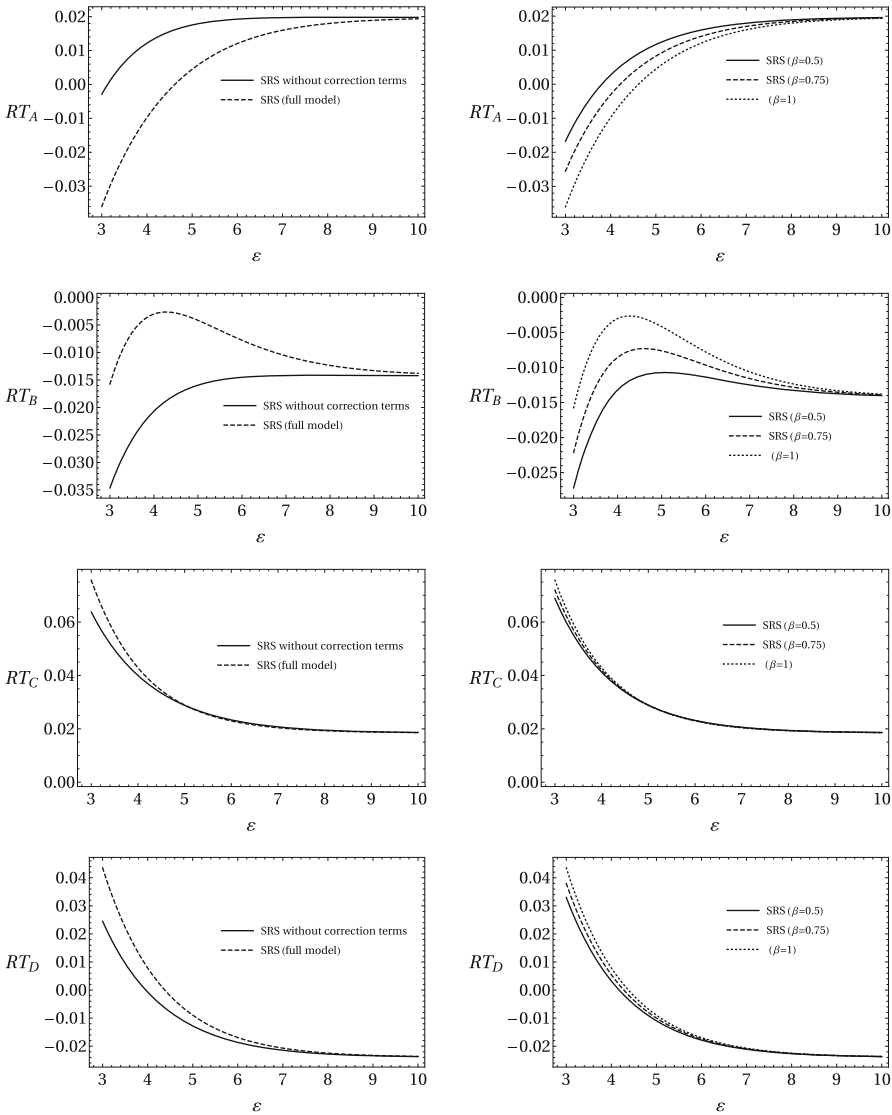

Fig. 6 Mixture $\mathcal{M}_2$ (endothermic forward reaction, $E_{abs} = 2.634$, $\mu_{34}/\mu_{12} = 0.758$). Thermal-diffusion ratio RT_A, RT_B, RT_C, RT_D versus the forward activation energy ε. *Left frames:* Impact of the correction terms. Full SRS model, and SRS model without correction terms. *Right frames:* Effects of the parameter β. Full SRS model with $\beta = 1$, and with $\beta = 0.75$ and $\beta = 0.5$

5.2.3 Results for the Thermal Diffusion Ratios

Figures 5 and 6 illustrate the behaviour of the thermal diffusion ratios RT_A, RT_B, RT_C, RT_D for mixtures $\mathcal{M}_1$ and $\mathcal{M}_2$ and how these coefficients vary in dependence of the dimensionless forward activation energy ε.

Once again, the left frames of Figs. 5 and 6 show the behaviour of the thermal diffusion ratio RT_i for $\beta = 1$, corresponding to the full SRS model with its correction term (dotted lines), and to the full SRS model without the correction term (solid lines). Moreover, the right frames show the impact of the parameter β on the coefficients RT_i

The thermal diffusion ratios are also very much affected by the chemical reaction, and therefore by the parameter β. This can be seen in Figs. 5 and 6 and also in Eqs. (54)–(57).

In Fig. 5, we can see that thermal diffusion ratio is positive for the reactants of the forward reaction, which are those with smaller concentrations, whereas it takes negative values for the products which have a great concentration. This seems to indicate that particles with smaller concentration tend to diffuse into cooler regions, whereas those with higher concentration diffuse to hot regions. A similar qualitative behaviour is observed in Fig. 6, exchanging the role among the reactants and products of the chemical reaction.

From the qualitative point of view, the results obtained for the thermal diffusion ratio are similar to those obtained for the thermal conductivity. It is clear that the correction terms contribute to increase the thermal diffusion ratio RT_i, and, again, the effects are more noticeable for small values of the forward activation energy.

6 Final Comments and Future Work

For all plots represented in the previous subsection, we can see that the transport coefficients studied here tend to their corresponding inert values when the forward activation energy increases, since the threshold of the chemical reaction becomes so high that reactive collisions become very rare.

Moreover, we also see that the influence of the chemical reaction is more evident in the coefficients of thermal conductivity and thermal-diffusion ratio. This can be explained by the fact that the impact of the reaction heat is grater on these last coefficients.

As an application of our study to be developed in the future, we plan to compute the transport coefficients with reference to the real reactive mixtures of Hydrogen-Chlorine and Hydrogen-Deuterium. Our objective is to compare our results with those obtained in paper [25] when real gases are considered.

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Data Availability Not applicable.

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