BGK-type models in strong reaction and kinetic chemical equilibrium regimes

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Abstract
A BGK-type procedure is applied to multi-component gases undergoing chemical reactions of bimolecular type. The relaxation process towards local Maxwellians, depending on mass and numerical densities of each species as well as common velocity and temperature, is investigated in two different cases with respect to chemical regimes. These cases are related to the *strong reaction regime* characterized by slow reactions, and to the *kinetic chemical equilibrium regime* where fast reactions take place. The consistency properties of both models are stated in detail. The trend to equilibrium is numerically tested and comparisons for the two regimes are performed within the hydrogen–air and carbon–oxygen reaction mechanism. In the spatial homogeneous case, it is also shown that the thermodynamical equilibrium of the models recovers satisfactorily the asymptotic equilibrium solutions to the reactive Euler equations.

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1. Introduction

Chemically reactive gas mixtures play a relevant role in many meaningful physical applications, as for instance combustion and plasma physics, for which kinetic models of the extended Boltzmann equation can be used to improve the knowledge of the involved macroscopic phenomena, starting from a description of the system at the mesoscopic scale.

The main objective of the present paper consists in the derivation, in the framework of kinetic theory, of simple models which at the same time are capable to provide a good description of reactive gas flows in unbounded domains for two different chemical regimes, and are easy to handle numerical simulations. More in detail, for a reactive mixture, a BGK-type procedure is proposed in order to replace the complex form of the collision operator by a

less detailed structure, based upon a simpler operator which retains the main properties of the true elastic and inelastic collision operator. Accordingly, two BGK-type models are proposed for strong and kinetic chemical equilibrium regimes, following a unified procedure.

The influence of chemical reactions in rarefied flows has been analysed since the fifties by Prigogine and Xhrouet [1] in the framework of the Boltzmann equation and more recently in the book by Bird [2] at the level of direct simulation methods. On the other hand, after the paper by Prigogine, a wide literature on this topic has been produced, as documented in the book [3], where the contribution to the generalization of the Boltzmann equation to reactive gas mixtures has been systematized. For a chemical mechanism with an arbitrary number of elementary reactions, the mathematical structure of chemistry source terms, conservation and equilibrium properties have been focused in paper [4], where different chemical regimes have also been analysed. In particular, the regimes corresponding to both slow and fast reactions, in a sense that will be better specified later on, are significant for the study of the present paper which refers to a gas mixture of four reactive species interacting through a bimolecular reaction. More in detail, consider the dimensionless extended Boltzmann equation for the one-particle distribution function f_i of species i,

$$\frac{\partial f_i}{\partial t} + \boldsymbol{v} \cdot \nabla f_i = \frac{1}{\epsilon} J_i[\underline{f}](\boldsymbol{v}) + \frac{1}{\epsilon^q} \mathcal{R}_i[\underline{f}](\boldsymbol{v}), \qquad i = 1, \ldots, 4, \tag{1}$$

where $[\underline{f}] = \{f_1, \ldots, f_4\}$ and the other symbols have the following meaning: the term J_i denotes the elastic collision operator including scattering contributions to the species i due to encounters with particles of any species; the term $\mathcal{R}_i$ denotes the reactive collision operator including the effects of the chemical production and loss mechanism due to inelastic collisions with chemical reactions. Moreover, ϵ represents a small parameter and q is an integer whose value allows us to define the chemical regimes. The case $q = 0$ characterizes the *strong reaction regime* in which a slow chemical reaction takes place. Accordingly, the ratio of characteristic times between reactive and inert collisions results to be of an order of magnitude greater than 1. The case $q = 1$ characterizes the *kinetic chemical equilibrium regime* [5] in which a fast chemical reaction occurs, so that the chemistry characteristic time is of the same order as the inert collisions time. Other regimes may be analysed as well but only these two will be considered in this paper.

Due to the mathematical complexity of the collision operators, a large piece of research works has been addressed to simplified kinetic models. A wide literature underlines the relevance of the BGK approach [6] and its reliability also for computing gas transport properties far from equilibrium, assuming relaxation of the distribution functions towards either a local Maxwellian or an anisotropic Gaussian [7–9]. Extensions of BGK-type models to multi-component systems can be found in [10], and more recently in [11] where a model satisfying the main properties of the true Boltzmann collision operator is presented. Both papers [10, 11] are concerned with mixtures of inert gases. Thus, a BGK approximation of the extended Boltzmann equation for chemically reacting gases seems to be a new interesting topic to deal with.

In the context of strong reaction regime, two recent BGK-type approaches [12, 13] are available for different choices of reference velocity distributions. Both BGK-type models assume relaxation towards distributions of Gaussian shape. More in detail, in paper [12] a first heuristic approach was based on relaxation towards Maxwellians depending on mass and number densities of each gas species, common velocity and temperature. Conversely, in [13], another approach was proposed assuming reference distributions depending on mass, number densities, velocity and temperature of each gas species.

The two approximate models of the present paper, derived in sections 3 and 4 for slow and fast reactions, respectively, can be formally written in non-dimensionless form as

$$\frac{\partial f_i}{\partial t} + \boldsymbol{v} \cdot \nabla f_i = \widetilde{J}_i[\underline{f}, \underline{\widetilde{f}}](\boldsymbol{v}) + \widetilde{\mathcal{R}}_i[\underline{f}, \underline{\widetilde{f}}](\boldsymbol{v}), \qquad i = 1, \ldots, 4, \tag{2}$$

where

$$\widetilde{f}_i(\boldsymbol{v}) = n_i \left(\frac{m_i}{2\pi k_{\mathrm{B}} T} \right)^{\frac{3}{2}} \exp\left(-\frac{m_i (\boldsymbol{v} - \boldsymbol{u})^2}{2 k_{\mathrm{B}} T} \right) \tag{3}$$

is the local Maxwellian distribution of species i depending on the masses m_i and number densities n_i of each i-species, common velocity $\boldsymbol{u}$ and temperature T. The terms $\widetilde{J}_i$ and $\widetilde{\mathcal{R}}_i$ approximate the true elastic and reactive operators, respectively. Two different expressions of them are examined. The former $J_i^{(1)}$ and $\mathcal{R}_i^{(1)}$ give rise to a BGK-type model in the strong reaction regime (hereinafter named *model* 1), and the latter $J_i^{(2)}$ and $\mathcal{R}_i^{(2)}$ determine a BGK-type model in the kinetic chemical equilibrium regime (*model* 2), according to the contents of sections 3 and 4, respectively.

Due to the assumptions on the characteristic times, in $\mathcal{R}_i^{(1)}$ the chemical gain terms involve mechanical equilibrium, whereas in $\mathcal{R}_i^{(2)}$ the chemical gains include both mechanical and chemical equilibrium. It is proven that both models verify indifferentiability principle, conservation of mass, momentum and total energy (kinetic plus chemical bond energy). The entropy inequality is assured, for the first model, under a suitable constraint on the distribution functions of the endothermic reaction products, and without any condition for the second model. All the preliminaries concerning the true Boltzmann equation for reactive gas mixtures, which are necessary to construct the approximate models and prove their fundamental properties, are based on the formulation of [14] and form the content of section 2.

At the end of the paper, in section 5, the behaviour of the models is tested with respect to their trend to equilibrium. At this scope, the explicit form of the kinetic equations is derived assuming elastic cross sections of Maxwellian molecules and isotropic pseudo-Maxwellian forms, temperature dependent, for the inelastic cross sections referred to the exothermic and endothermic reactions. Numerical experiments are given for the elementary reactions occurring in the hydrogen–air and carbon–oxygen reactive processes, which are typical in combustion applications [15]. At last, in the spatial homogeneous case, the thermodynamical equilibrium values of the models are compared with those proper for the reactive Euler equations formulated in the corresponding regimes of slow and fast chemical reactions. The comparisons reveal a satisfactory agreement with the asymptotic values of the Euler equations.

2. Exact kinetic equations for a reactive mixture

The microscopic state of the gaseous mixture, for which the chemical reversible reaction takes place,

$$A_1 + A_2 \rightleftharpoons A_3 + A_4, \tag{4}$$
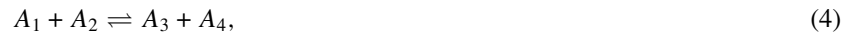
is defined by the one-particle distribution function

$$f_i = f_i(t, \boldsymbol{x}, \boldsymbol{v}), \qquad t \in \mathbb{R}_+, \quad \boldsymbol{x} \in \mathbb{R}^3, \quad \boldsymbol{v} = \{v_x, v_y, v_z\} \in \mathbb{R}^3,$$

for each species A_i, $i = 1, \ldots, 4$, with molecular mass m_i and heat of formation E_i. Masses and heats of formation are arranged so that $m_1 + m_2 = m_3 + m_4$ and $\Delta E = E_3 + E_4 - E_1 - E_2 > 0$, so that the forward reaction is settled as the endothermic one. The time and space dependence will be omitted in the following.

2.1. Kinetic equations

The exact kinetic equations for the reactive gas mixture, derived in paper [14], are given by

$$\frac{\partial f_i}{\partial t} + \boldsymbol{v} \cdot \nabla f_i = J_i[\underline{f}](\boldsymbol{v}) + \mathcal{R}_i[\underline{f}](\boldsymbol{v}), \qquad i = 1, \ldots, 4, \tag{5}$$

where

$$J_i[\underline{f}](\boldsymbol{v}) = G_i[\underline{f}](\boldsymbol{v}) - L_i[\underline{f}](\boldsymbol{v}), \qquad \mathcal{R}_i[\underline{f}](\boldsymbol{v}) = \mathcal{G}_i[\underline{f}](\boldsymbol{v}) - \mathcal{L}_i[\underline{f}](\boldsymbol{v}). \tag{6}$$

The gain and loss terms G_i, L_i due to elastic collisions have the form

$$G_i[\underline{f}](\boldsymbol{v}) = \sum_{j=1}^{4} \int_{\mathbb{R}^3} \mathrm{d}\boldsymbol{w} \int_{\mathcal{S}} B_{ij}^{ij}(g, \mu) f_i(\boldsymbol{v}_{ij}) f_j(\boldsymbol{w}_{ij}) \, \mathrm{d}\Omega' \tag{7}$$

$$L_i[\underline{f}](\boldsymbol{v}) = \nu_i(\boldsymbol{v}) f_i(\boldsymbol{v}), \tag{8}$$

where

$$\nu_i(\boldsymbol{v}) = \sum_{j=1}^{4} \int_{\mathbb{R}^3} \mathrm{d}\boldsymbol{w} \int_{\mathcal{S}} B_{ij}^{ij}(g, \mu) f_j(\boldsymbol{w}) \, \mathrm{d}\Omega', \tag{9}$$

$g = |\boldsymbol{w} - \boldsymbol{v}|$ being the relative pre-collision speed, $\mu = \Omega \cdot \Omega'$, Ω and Ω' denoting the unit vectors of the relative pre-collision and post-collision velocities, respectively. Moreover, $B_{ij}^{ij}(g, \mu)$ are the scattering cross sections and $\nu_i(\boldsymbol{v})$ are the elastic collision frequencies. Finally, the post-collision velocities preserving mass, momentum and kinetic energy are given by

$$\boldsymbol{v}_{ij} = \frac{m_i \boldsymbol{v} + m_j \boldsymbol{w} - m_j g \Omega'}{m_i + m_j}, \qquad \boldsymbol{w}_{ij} = \frac{m_i \boldsymbol{v} + m_j \boldsymbol{w} + m_i g \Omega'}{m_i + m_j}. \tag{10}$$

The source terms $\mathcal{G}_i$ due to chemical reactions are explicitly reported here in the form

$$\begin{aligned}
\mathcal{G}_1[\underline{f}](\boldsymbol{v}) &= M^3 \int_{\mathbb{R}^3} \mathrm{d}\boldsymbol{w} \int_{\mathcal{S}} C_{12}^{34}(g, \mu) f_3(\boldsymbol{v}_1) f_4(\boldsymbol{w}_1) \, \mathrm{d}\Omega' \\
\mathcal{G}_2[\underline{f}](\boldsymbol{v}) &= M^3 \int_{\mathbb{R}^3} \mathrm{d}\boldsymbol{w} \int_{\mathcal{S}} C_{12}^{34}(g, \mu) f_4(\boldsymbol{v}_2) f_3(\boldsymbol{w}_2) \, \mathrm{d}\Omega' \\
\mathcal{G}_3[\underline{f}](\boldsymbol{v}) &= \frac{1}{M^3} \int_{\mathbb{R}^3} \mathrm{d}\boldsymbol{w} \int_{\mathcal{S}} C_{34}^{12}(g, \mu) f_1(\boldsymbol{v}_3) f_2(\boldsymbol{w}_3) \, \mathrm{d}\Omega' \\
\mathcal{G}_4[\underline{f}](\boldsymbol{v}) &= \frac{1}{M^3} \int_{\mathbb{R}^3} \mathrm{d}\boldsymbol{w} \int_{\mathcal{S}} C_{34}^{12}(g, \mu) f_2(\boldsymbol{v}_4) f_1(\boldsymbol{w}_4) \, \mathrm{d}\Omega',
\end{aligned} \tag{11}$$

whereas the sink terms $\mathcal{L}_i$ are given by

$$\mathcal{L}_i[\underline{f}](\boldsymbol{v}) = \sigma_i(\boldsymbol{v}) f_i(\boldsymbol{v}), \qquad i = 1, \ldots, 4, \tag{12}$$

where

$$\begin{aligned}
\sigma_{1(2)}(\boldsymbol{v}) &= \int_{\mathbb{R}^3} \mathrm{d}\boldsymbol{w} \int_{\mathcal{S}} C_{12}^{34}(g, \mu) f_{2(1)}(\boldsymbol{w}) \, \mathrm{d}\Omega' \\
\sigma_{3(4)}(\boldsymbol{v}) &= \int_{\mathbb{R}^3} \mathrm{d}\boldsymbol{w} \int_{\mathcal{S}} C_{34}^{12}(g, \mu) f_{4(3)}(\boldsymbol{w}) \, \mathrm{d}\Omega',
\end{aligned} \tag{13}$$

$M = (m_1 m_2)/(m_3 m_4)$, $\boldsymbol{v}, \boldsymbol{w}$ are the pre-collision velocities, $\boldsymbol{v}_i, \boldsymbol{w}_i$ are the post-collision velocities defined by

$$\begin{aligned}
\boldsymbol{v}_1 &= r_1 \boldsymbol{v} + r_2 \boldsymbol{w} - r_4 V \Omega', & \boldsymbol{w}_1 &= r_1 \boldsymbol{v} + r_2 \boldsymbol{w} + r_3 V \Omega' \\
\boldsymbol{v}_2 &= r_2 \boldsymbol{v} + r_1 \boldsymbol{w} - r_3 V \Omega', & \boldsymbol{w}_2 &= r_2 \boldsymbol{v} + r_1 \boldsymbol{w} + r_4 V \Omega' \\
\boldsymbol{v}_3 &= r_3 \boldsymbol{v} + r_4 \boldsymbol{w} - r_2 \overline{V} \Omega', & \boldsymbol{w}_3 &= r_3 \boldsymbol{v} + r_4 \boldsymbol{w} + r_1 \overline{V} \Omega' \\
\boldsymbol{v}_4 &= r_4 \boldsymbol{v} + r_3 \boldsymbol{w} - r_1 \overline{V} \Omega', & \boldsymbol{w}_4 &= r_4 \boldsymbol{v} + r_3 \boldsymbol{w} + r_2 \overline{V} \Omega',
\end{aligned} \tag{14}$$

with

$$r_i = \frac{m_i}{m_1 + m_2}, \qquad V = \left[M(g^2 - g_s^2)\right]^{1/2}, \qquad \overline{V} = \left[M(g^2 + \overline{g}_s^2)\right]^{-1/2}$$

$$g_s = \left[\frac{2\Delta E(m_1 + m_2)}{m_1 m_2}\right]^{1/2}, \qquad \overline{g}_s = \left[\frac{2\Delta E(m_1 + m_2)}{m_3 m_4}\right]^{1/2}, \qquad \mathbf{\Omega}' = \frac{\boldsymbol{w}_1 - \boldsymbol{w}_2}{|\boldsymbol{w}_1 - \boldsymbol{w}_2|};$$

(15)

C_{34}^{12}, C_{12}^{34} are the cross sections related to the exothermic and endothermic reactions, respectively, obeying the micro-reversibility principle [3] and $\sigma_i(v)$ are the correspondent reactive collision frequencies.

2.2. Properties of the collision terms

As shown in [14], elastic and reactive terms satisfy the following properties:

$$\int_{\mathbb{R}^3} J_i[\underline{f}](\boldsymbol{v}) \, \mathrm{d}\boldsymbol{v} = 0, \qquad i = 1, \dots, 4,$$

(16)

$$\int_{\mathbb{R}^3} \mathcal{R}_1[\underline{f}](\boldsymbol{v}) \, \mathrm{d}\boldsymbol{v} = \int_{\mathbb{R}^3} \mathcal{R}_2[\underline{f}](\boldsymbol{v}) \, \mathrm{d}\boldsymbol{v} = -\int_{\mathbb{R}^3} \mathcal{R}_3[\underline{f}](\boldsymbol{v}) \, \mathrm{d}\boldsymbol{v} = -\int_{\mathbb{R}^3} \mathcal{R}_4[\underline{f}](\boldsymbol{v}) \, \mathrm{d}\boldsymbol{v}.$$

(17)

Property (16) corresponds to the conservation of number of particles of each gas species during elastic interactions only. Equalities (17) are due to the fact that the evolution of the number density of each species is predicted by chemical exchanges according to the bimolecular reaction (4).

Moreover, the vanishing of any integral $\int_{\mathbb{R}^3} \mathcal{R}_i[\underline{f}](\boldsymbol{v}) \, \mathrm{d}\boldsymbol{v}$ traduces the chemical equilibrium condition of the model.

It can be easily shown that if the distribution functions are Maxwellians given by (3), the chemical equilibrium is assured if one of the following equivalent conditions holds true:

$$\begin{aligned}
(m_3 m_4)^3 \, \widetilde{f}_1(\boldsymbol{v}) \widetilde{f}_2(\boldsymbol{w}) &= (m_1 m_2)^3 \, \widetilde{f}_3(\boldsymbol{v}_1) \widetilde{f}_4(\boldsymbol{w}_1) \\
(m_3 m_4)^3 \, \widetilde{f}_1(\boldsymbol{w}) \widetilde{f}_2(\boldsymbol{v}) &= (m_1 m_2)^3 \, \widetilde{f}_3(\boldsymbol{w}_2) \widetilde{f}_4(\boldsymbol{v}_2) \\
(m_1 m_2)^3 \, \widetilde{f}_3(\boldsymbol{v}) \widetilde{f}_4(\boldsymbol{w}) &= (m_3 m_4)^3 \, \widetilde{f}_1(\boldsymbol{v}_3) \widetilde{f}_2(\boldsymbol{w}_3) \\
(m_1 m_2)^3 \, \widetilde{f}_3(\boldsymbol{w}) \widetilde{f}_4(\boldsymbol{v}) &= (m_3 m_4)^3 \, \widetilde{f}_1(\boldsymbol{w}_4) \widetilde{f}_2(\boldsymbol{v}_4).
\end{aligned}$$

(18)

In paper [14] it has been proven that conditions (18) imply the equality

$$\frac{n_1 n_2}{n_3 n_4} = M^{\frac{3}{2}} \exp\left(\frac{\Delta E}{k_B T}\right),$$

(19)

which expresses the mass-action-law of chemical equilibrium. When the number densities n_i do not fulfil the mass-action-law (19), the Maxwellian distributions will be indicated by $f_i^{(1)}$. In contrast, when condition (19) is satisfied, the Maxwellians will be denoted by $f_i^{(2)}$. In conclusion, the distributions $f_i^{(1)}$, relevant for mechanical equilibrium only, assure the vanishing of the elastic terms, whereas the distributions $f_i^{(2)}$, relevant to mechanical and chemical equilibrium, imply the vanishing of the whole collision integral in equation (5).

2.3. Collision invariants

The family of Maxwellians $f_i^{(1)}$ depends on eight parameters $\boldsymbol{u}, T, n_i, i = 1, \dots, 4$, fixed by the eight independent *mechanical collision invariants*:

$$\psi^{(1)} = v_x\{m_1, m_2, m_3, m_4\}, \qquad \psi^{(2)} = v_y\{m_1, m_2, m_3, m_4\}, \qquad \psi^{(3)} = v_z\{m_1, m_2, m_3, m_4\}$$

(20a)

$$\psi^{(4)} = \left\{ \tfrac{1}{2}m_1 v^2 + E_1, \tfrac{1}{2}m_2 v^2 + E_2, \tfrac{1}{2}m_3 v^2 + E_3, \tfrac{1}{2}m_4 v^2 + E_4 \right\} \tag{20b}$$

$$\theta^{(1)} = \{1, 0, 0, 0\}, \qquad \theta^{(2)} = \{0, 1, 0, 0\}, \qquad \theta^{(3)} = \{0, 0, 1, 0\}, \qquad \theta^{(4)} = \{0, 0, 0, 1\}. \tag{20c}$$

The invariants $\theta^{(k)}$, $k = 1, \ldots, 4$, are related to the conservation of individual number densities n_k during elastic collisions only.

Conversely, the family of Maxwellians $f_i^{(2)}$ depends on seven independent parameters, i.e. $\boldsymbol{u}, T$ and number densities correlated by the mass-action-law (19). Introduce then the invariants

$$\psi^{(5)} = \theta^{(1)} + \theta^{(3)}, \qquad \psi^{(6)} = \theta^{(1)} + \theta^{(4)}, \qquad \psi^{(7)} = \theta^{(2)} + \theta^{(4)}, \tag{21}$$

which are joined to the conservation of partial number densities $n_1 + n_3, n_1 + n_4, n_2 + n_4$.

Therefore, the seven independent parameters are fixed by the *model collision invariants*

$$\psi^{(1)}, \ldots, \psi^{(4)}, \qquad \psi^{(5)} = \{1, 0, 1, 0\}, \quad \psi^{(6)} = \{1, 0, 0, 1\}, \quad \psi^{(7)} = \{0, 1, 0, 1\}, \tag{22}$$

where $\psi^{(1)}, \ldots, \psi^{(4)}$ are given in equations (20*a*) and (20*b*).

Remark 1. It should be noted that the choice of the collision invariants (21) associated with partial number densities is pertinent when the constituents of the mixture undergo one chemical reaction only. Conversely, when the chemical mechanism shows an arbitrary complexity, one has to introduce collision invariants associated with the atomic number densities rather than partial number densities, as discussed in [5].

3. BGK-type model in the strong reaction regime (model 1)

As anticipated in the introduction, the strong reaction regime is proper for a mixture in which the dominant effect is the one of elastic collisions driving the gas towards Maxwellian equilibrium. Therefore, in this regime, the approximate elastic and reactive contributions $\widetilde{J}_i$, $\widetilde{\mathcal{R}}_i$ in equation (2) will be derived in terms of the Maxwellians $f_i^{(1)}$ and will be indicated by $J_i^{(1)}$ and $\mathcal{R}_i^{(1)}$, respectively. After some preliminaries, where the fundamental assumptions are stated, the model equations are deduced and the main properties of the approximate collision terms are proven.

3.1. Preliminaries

First of all, let $\nu_i^{(1)}$ and $\sigma_i^{(1)}$ denote the elastic and reactive frequencies obtained from expressions (9) and (13), when the distributions $f_j(\boldsymbol{w})$ are substituted by the Maxwellians $f_j^{(1)}(\boldsymbol{w})$.

The model proposed in this section is based on some pertinent assumptions concerning both elastic mechanism and chemical interaction.

(i) The gas evolves sufficiently near equilibrium conditions, so that after at least one collision particles may reach a local mechanical equilibrium. Thus, in the gain contributions G_i and $\mathcal{G}_i$, defined by equations (7) and (11), the distribution functions f_i are substituted by the Maxwellians $f_i^{(1)}$.

(ii) The scattering cross sections B_{ij}^{ij} are assumed to be of Maxwellian molecules type [16]. The reactive ones C_{12}^{34} and C_{34}^{12} are chosen as those proper for a generalized Maxwellian molecules form, so that all the collision frequencies will be $\boldsymbol{v}$-independent.

(iii) The differences between the integrals defining ν_i and $\nu_i^{(1)}$, and σ_i and $\sigma_i^{(1)}$, are neglected, so that

$$\nu_i^{(1)} = \nu_i, \qquad \sigma_i^{(1)} = \sigma_i, \qquad i = 1, \ldots, 4. \tag{23}$$

(iv) The parameters $\boldsymbol{u}$, T and n_i for the Maxwellians $f_i^{(1)}$ are fixed in terms of the mechanical invariants (20a)–(20c) through the conditions

$$\sum_{i=1}^{4} \int_{\mathbb{R}^3} \psi_i^{(k)}(\boldsymbol{v}) f_i(\boldsymbol{v}) \, \mathrm{d}\boldsymbol{v} = \sum_{i=1}^{4} \int_{\mathbb{R}^3} \psi_i^{(k)}(\boldsymbol{v}) f_i^{(1)}(\boldsymbol{v}) \, \mathrm{d}\boldsymbol{v}, \qquad k = 1, \ldots, 4, \tag{24a}$$

$$\int_{\mathbb{R}^3} \theta_i^{(\ell)} f_i(\boldsymbol{v}) \, \mathrm{d}\boldsymbol{v} = \int_{\mathbb{R}^3} \theta_i^{(\ell)} f_i^{(1)}(\boldsymbol{v}) \, \mathrm{d}\boldsymbol{v}, \qquad \ell = 1, \ldots, 4. \tag{24b}$$

Remark 2. Assumptions (i), (ii) and (iii) extend the classical requirements of the BGK approximation to the present case of a reactive mixture. Moreover, the assumption that the reactive cross sections are of generalized Maxwellian molecules type means that they are isotropic functions of g in such a way that the corresponding frequencies σ_i will be $\boldsymbol{v}$-independent (see section 5).

Remark 3. Assumption (iv) is related to conservation laws of total momentum, energy and individual number densities, for what deals with the elastic terms $J_i^{(1)}$.

3.2. Derivation of the elastic terms $J_i^{(1)}$

The BGK approximation of the elastic collision terms, thanks to assumption (i), leads to

$$J_i^{(1)}[\underline{f}, \underline{f}^{(1)}](\boldsymbol{v}) = \sum_{j=1}^{4} B_{ij}^{ij} \int_{\mathbb{R}^3} \mathrm{d}\boldsymbol{w} \int_{\mathcal{S}} \left[f_i^{(1)}(\boldsymbol{v}_{ij}) f_j^{(1)}(\boldsymbol{w}_{ij}) - f_i(\boldsymbol{v}) f_j(\boldsymbol{w}) \right] \mathrm{d}\Omega'. \tag{25}$$

Recalling that the Maxwellians satisfy the equality $f_i^{(1)}(\boldsymbol{v}_{ij}) f_j^{(1)}(\boldsymbol{w}_{ij}) = f_i^{(1)}(\boldsymbol{v}) f_j^{(1)}(\boldsymbol{w})$, the last equation can be written as

$$J_i^{(1)}[\underline{f}, \underline{f}^{(1)}](\boldsymbol{v}) = \sum_{j=1}^{4} B_{ij}^{ij} \left[f_i^{(1)}(\boldsymbol{v}) \int_{\mathbb{R}^3} \mathrm{d}\boldsymbol{w} \int_{\mathcal{S}} f_j^{(1)}(\boldsymbol{w}) \, \mathrm{d}\Omega' - f_i(\boldsymbol{v}) \int_{\mathbb{R}^3} \mathrm{d}\boldsymbol{w} \int_{\mathcal{S}} f_j(\boldsymbol{w}) \mathrm{d}\Omega' \right] \tag{26}$$

and according to assumption (iii), the final form of $J_i^{(1)}$ is

$$J_i^{(1)}[\underline{f}, \underline{f}^{(1)}](\boldsymbol{v}) = \nu_i [f_i^{(1)}(\boldsymbol{v}) - f_i(\boldsymbol{v})], \qquad i = 1, \ldots, 4. \tag{27}$$

3.3. Derivation of the reactive terms $\mathcal{R}_i^{(1)}$

Consider the definition of $\mathcal{R}_i$ given in equation (6). The approximation of the chemical gain $\mathcal{G}_i$ and loss $\mathcal{L}_i$, say $\mathcal{G}_i^{(1)}$ and $\mathcal{L}_i^{(1)}$ respectively, proceeds as follows.

For what concerns the approximation of $\mathcal{G}_i$, it is enough to substitute in each expression (11) the distributions f_i by the corresponding Maxwellians $f_i^{(1)}$, since $\mathcal{G}_i^{(1)}$ represents relaxation of the chemistry source terms towards mechanical equilibrium only.

Therefore

$$
\mathcal{G}_1^{(1)}[\underline{f}^{(1)}](\boldsymbol{v}) = \int_{\mathbb{R}^3} \mathrm{d}\boldsymbol{w} \int_S M^3 C_{12}^{34}(g) f_3^{(1)}(\boldsymbol{v}_1) f_4^{(1)}(\boldsymbol{w}_1) \, \mathrm{d}\Omega'
$$

$$
\mathcal{G}_2^{(1)}[\underline{f}^{(1)}](\boldsymbol{v}) = \int_{\mathbb{R}^3} \mathrm{d}\boldsymbol{w} \int_S M^3 C_{12}^{34}(g) f_3^{(1)}(\boldsymbol{w}_2) f_4^{(1)}(\boldsymbol{v}_2) \, \mathrm{d}\Omega'
$$

$$
\mathcal{G}_3^{(1)}[\underline{f}^{(1)}](\boldsymbol{v}) = \int_{\mathbb{R}^3} \mathrm{d}\boldsymbol{w} \int_S \frac{1}{M^3} C_{34}^{12}(g) f_1^{(1)}(\boldsymbol{v}_3) f_2^{(1)}(\boldsymbol{w}_3) \, \mathrm{d}\Omega' \tag{28}
$$

$$
\mathcal{G}_4^{(1)}[\underline{f}^{(1)}](\boldsymbol{v}) = \int_{\mathbb{R}^3} \mathrm{d}\boldsymbol{w} \int_S \frac{1}{M^3} C_{34}^{12}(g) f_1^{(1)}(\boldsymbol{w}_4) f_2^{(1)}(\boldsymbol{v}_4) \mathrm{d}\Omega'.
$$

The approximation of the loss terms $\mathcal{L}_i$ is performed adopting a procedure analogous to the one used for the elastic losses. Resorting to equalities (23) one has

$$
\mathcal{L}_i^{(1)}[\underline{f}, \underline{f}^{(1)}](\boldsymbol{v}) = \sigma_i f_i(\boldsymbol{v}). \tag{29}
$$

Therefore, the approximation of $\mathcal{R}_i$ reads

$$
\mathcal{R}_i^{(1)}[\underline{f}, \underline{f}^{(1)}](\boldsymbol{v}) = \mathcal{G}_i^{(1)}[\underline{f}^{(1)}](\boldsymbol{v}) - \sigma_i f_i(\boldsymbol{v}). \tag{30}
$$

In conclusion the BGK-type model in the strong reaction regime is given by

$$
\frac{\partial f_i}{\partial t} + \boldsymbol{v} \cdot \nabla f_i = \nu_i \big[f_i^{(1)}(\boldsymbol{v}) - f_i(\boldsymbol{v}) \big] + \mathcal{G}_i^{(1)}[\underline{f}^{(1)}](\boldsymbol{v}) - \sigma_i f_i(\boldsymbol{v}), \qquad i = 1, \ldots, 4. \tag{31}
$$

Remark 4. In thermodynamical equilibrium the distributions $f_i^{(1)}$, thanks to relations (18), coincide with the distributions $f_i^{(2)}$. Thus, the vanishing of both elastic and reactive contributions on the rhs of equation (31) is assured. In the particular case of absolute equilibrium, the distributions no longer depend on $(t, \boldsymbol{x})$ and therefore the Maxwellian $f_i^{(2)}(\boldsymbol{v})$ is a solution to the model equation (31).

3.4. Consistency of the model

The conservation equations and entropy inequality for model 1 can be stated after some preliminary lemmas presented in the next subsection.

3.4.1. Properties of the collision operators $J_i^{(1)}, \mathcal{R}_i^{(1)}$. The properties of $J_i^{(1)}$ are described by properties 1, 2 whereas those of $\mathcal{R}_i^{(1)}$ are presented in lemmas 1, 2.

Property 1. *The approximate elastic collision term $J_i^{(1)}$ is such that*

$$
\sum_{i=1}^4 \int_{\mathbb{R}^3} \psi_i^{(k)}(\boldsymbol{v}) J_i^{(1)}[\underline{f}, \underline{f}^{(1)}](\boldsymbol{v}) \, \mathrm{d}\boldsymbol{v} = 0, \qquad k = 1, \ldots, 7, \tag{32}
$$

for the collision invariants $\psi^{(k)}(\boldsymbol{v}) = \big\{ \psi_1^{(k)}(\boldsymbol{v}), \ldots, \psi_4^{(k)}(\boldsymbol{v}) \big\}$.

Proof. From (27), it results for $k = 1, \ldots, 7$,

$$
\sum_{i=1}^4 \int_{\mathbb{R}^3} \psi_i^{(k)} J_i^{(1)}[\underline{f}, \underline{f}^{(1)}](\boldsymbol{v}) \, \mathrm{d}\boldsymbol{v} = \sum_{i=1}^4 \nu_i \int_{\mathbb{R}^3} \psi_i^{(k)} \big[f_i^{(1)}(\boldsymbol{v}) - f_i(\boldsymbol{v}) \big] \mathrm{d}\boldsymbol{v}. \tag{33}
$$

In fact, by using conditions (24*a*), it turns out that equalities (32) are satisfied for $k = 1, \ldots, 4$. The further equalities for $k = 5, 6, 7$ hold as well, inserting definitions (21) into equations (33) and taking into account the ansatz (24*b*). $\qquad\square$

Property 2. *The term $J_i^{(1)}$ verifies the equalities*

$$\int_{\mathbb{R}^3} J_i^{(1)}[\underline{f}, \underline{f}^{(1)}](v)\, dv = 0, \qquad i = 1, \ldots, 4. \tag{34}$$

Proof. Again from definition (27), one has

$$\int_{\mathbb{R}^3} J_i^{(1)}[\underline{f}, \underline{f}^{(1)}](v)\, dv = \nu_i \int_{\mathbb{R}^3} \left[f_i^{(1)}(v) - f_i(v) \right] dv, \tag{35}$$

and equalities (34) immediately follow from the BGK ansatz (24*b*). $\square$

Remark 5. The result of property 2 reproduces the analogous property (16) of the exact operator J_i. In other words, property 2 means that the elastic collisions do not modify the number of particles of each species, so that the rate of change of n_i is not affected by elastic collisions.

Lemma 1. *The reactive terms $\mathcal{R}_i^{(1)}$, $i = 1, \ldots, 4$, verify the condition*

$$\sum_{i=1}^{4} \int_{\mathbb{R}^3} \psi_i^{(k)}(v) \mathcal{R}_i^{(1)}[\underline{f}, \underline{f}^{(1)}](v)\, dv = 0, \qquad k = 1, \ldots, 7, \tag{36}$$

for the collision invariants $\psi^{(k)}(v) = \left\{ \psi_1^{(k)}(v), \ldots, \psi_4^{(k)}(v) \right\}$.

Proof. Write each term of the sum on the lhs of equation (36) in explicit form by means of equations (30). Rearrangement of the involved integrals, employment of ansatz (23) and suitable changes of variables according to relations (14) among pre- and post-collision velocities, allow us to derive the equalities valid for $k = 1, \ldots, 7$,

$$\begin{aligned}
\int_{\mathbb{R}^3} \psi_1^{(k)}(v) \mathcal{R}_1^{(1)}[\underline{f}, \underline{f}^{(1)}](v)\, dv &= \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathcal{S}} \psi_1^{(k)}(v) K_1(v, w, \Omega')\, dv\, dw\, d\Omega' \\
\int_{\mathbb{R}^3} \psi_2^{(k)}(v) \mathcal{R}_2^{(1)}[\underline{f}, \underline{f}^{(1)}](v)\, dv &= \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathcal{S}} \psi_2^{(k)}(w) K_1(v, w, \Omega')\, dv\, dw\, d\Omega' \\
\int_{\mathbb{R}^3} \psi_3^{(k)}(v) \mathcal{R}_3^{(1)}[\underline{f}, \underline{f}^{(1)}](v)\, dv &= -\int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathcal{S}} \psi_3^{(k)}(v_1) K_1(v, w, \Omega')\, dv\, dw\, d\Omega' \\
\int_{\mathbb{R}^3} \psi_4^{(k)}(v) \mathcal{R}_4^{(1)}[\underline{f}, \underline{f}^{(1)}](v)\, dv &= -\int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathcal{S}} \psi_4^{(k)}(w_1) K_1(v, w, \Omega')\, dv\, dw\, d\Omega',
\end{aligned} \tag{37}$$

where

$$K_1(v, w, \Omega') = C_{12}^{34}(g) \left[M^3 f_3^{(1)}(v_1) f_4^{(1)}(w_1) - f_2(w) f_1(v) \right]. \tag{38}$$

The sum of equations (37) leads to equality

$$\begin{aligned}
\sum_{i=1}^{4} \int_{\mathbb{R}^3} \psi_i^{(k)}(v) \mathcal{R}_i^{(1)}[\underline{f}, \underline{f}^{(1)}](v)\, dv = \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{S} \big[\psi_1^{(k)}(v) + \psi_2^{(k)}(w) - \psi_3^{(k)}(v_1) \\
- \psi_4^{(k)}(w_1) \big] K_1(v, w, \Omega')\, dv\, dw\, d\Omega',
\end{aligned} \tag{39}$$

which immediately is reduced to condition (36), since each $\psi^{(k)}$ is a model collision invariant.
$\square$

Lemma 2. *The terms $\mathcal{R}_i^{(1)}$, $i = 1, \ldots, 4$, are such that*

$$\begin{aligned}
\int_{\mathbb{R}^3} \mathcal{R}_1^{(1)}[\underline{f}, \underline{f}^{(1)}](v)\, dv &= \int_{\mathbb{R}^3} \mathcal{R}_2^{(1)}[\underline{f}, \underline{f}^{(1)}](v)\, dv \\
&= -\int_{\mathbb{R}^3} \mathcal{R}_3^{(1)}[\underline{f}, \underline{f}^{(1)}](v)\, dv = -\int_{\mathbb{R}^3} \mathcal{R}_4^{(1)}[\underline{f}, \underline{f}^{(1)}](v)\, dv.
\end{aligned} \tag{40}$$

Proof. It is enough to write equation (36) of lemma 1 in explicit form for $k = 5, 6, 7$. □

Remark 6. The property for $\mathcal{R}_i^{(1)}$ stated in lemma 2 results indeed to be analogous to property (17) for the exact reactive operator. In other words, the common rate of change of the reactants due to chemical reaction is opposite to the common rate of change of the products. The chemical mechanism of bimolecular reactions (4) results then to be correctly reproduced.

3.4.2. Physical laws. The BGK collision operator verifies the properties of the true Boltzmann operator consistent with the physical laws.

- *Conservation laws.* Conservation of mass, momentum and total energy can be deduced through the following proposition.

Proposition 1. *For the model collision invariants $\psi^{(k)}, k = 1, \ldots, 7$, the BGK collision operator verifies the equalities*

$$\sum_{i=1}^4 \int_{\mathbb{R}^3} \psi_i^{(k)}(\boldsymbol{v}) \left(J_i^{(1)}[\underline{f}, \underline{f}^{(1)}](\boldsymbol{v}) + \mathcal{R}_i^{(1)}[\underline{f}, \underline{f}^{(1)}](\boldsymbol{v}) \right) \mathrm{d}\boldsymbol{v} = 0, \qquad k = 1, \ldots, 7. \tag{41}$$

Proof. Equation (41) follows directly from conditions (32) of property 1 and (36) of lemma 1; the conservation laws result to be verified recalling the definition (22) of the collision invariants. □

- *Entropy inequality.* Elastic collisions and chemical reactions contribute to increase the entropy of the system, according to the next proposition.

Proposition 2. *Let $\mathcal{H}$ be proportional to the kinetic entropy of the system and $\phi_{\mathcal{H}}$ its diffusive flux defined by*

$$\mathcal{H}(x, t) = \sum_{i=1}^4 \int_{\mathbb{R}^3} f_i \log \left(\frac{f_i}{m_i^3} \right) \mathrm{d}\boldsymbol{v}, \qquad \phi_{\mathcal{H}}(x, t) = \sum_{i=1}^4 \int_{\mathbb{R}^3} f_i \log \left(\frac{f_i}{m_i^3} \right) \boldsymbol{v} \, \mathrm{d}\boldsymbol{v}. \tag{42}$$

Then

$$\frac{\partial \mathcal{H}}{\partial t}(x, t) + \operatorname{div} \phi_{\mathcal{H}}(x, t) \leqslant 0, \tag{43}$$

provided that the distributions of products of the forward reaction satisfy the inequality

$$\sum_{i=3}^4 \int_{\mathbb{R}^3} \log \left(\frac{f_i}{f_i^{(1)}} \right) \mathcal{R}_i^{(1)}[\underline{f}, \underline{f}^{(1)}](\boldsymbol{v}) \, \mathrm{d}\boldsymbol{v} \leqslant 0. \tag{44}$$

Moreover, $\dfrac{\partial \mathcal{H}}{\partial t}(x, t) + \operatorname{div} \phi_{\mathcal{H}}(x, t) = 0$ if and only if

$$f_i = f_i^{(1)} \qquad and \qquad f_1^{(1)}(\boldsymbol{v}) f_2^{(1)}(\boldsymbol{w}) = M^3 f_3^{(1)}(\boldsymbol{v}_1) f_4^{(1)}(\boldsymbol{w}_1). \tag{45}$$

Proof. Recalling the model equations (31), property 2 and lemma 2, one obtains

$$\frac{\partial \mathcal{H}}{\partial t}(x, t) + \operatorname{div} \phi_{\mathcal{H}}(x, t) = \sum_{i=1}^4 \int_{\mathbb{R}^3} \log \left(\frac{f_i}{m_i^3} \right) \left[J_i^{(1)}[\underline{f}, \underline{f}^{(1)}](\boldsymbol{v}) + \mathcal{R}_i^{(1)}[\underline{f}, \underline{f}^{(1)}](\boldsymbol{v}) \right] \mathrm{d}\boldsymbol{v}, \tag{46}$$

where the rhs splits into the sum of the non-reactive and reactive contributions that will be discussed separately in items (a) and (b), respectively.

(a) Recalling property 1, the elastic contribution becomes

$$\sum_{i=1}^{4} \int_{\mathbb{R}^3} \log\left(\frac{f_i}{m_i^3}\right) J_i^{(1)}[\underline{f}, \underline{f}^{(1)}](\boldsymbol{v})\, \mathrm{d}\boldsymbol{v} = \sum_{i=1}^{4} \int_{\mathbb{R}^3} \log\left(\frac{f_i}{f_i^{(1)}}\right) J_i^{(1)}[\underline{f}, \underline{f}^{(1)}](\boldsymbol{v})\, \mathrm{d}\boldsymbol{v}$$

$$= \sum_{i=1}^{4} \nu_i \int_{\mathbb{R}^3} f_i^{(1)} \log\left(\frac{f_i}{f_i^{(1)}}\right)\left(1 - \frac{f_i}{f_i^{(1)}}\right)\, \mathrm{d}\boldsymbol{v}, \tag{47}$$

which is non-positive term by term, and is equal to zero if and only if $f_i = f_i^{(1)}$.

(b) Thanks to definition (38) and constraint (44), the reactive contribution on the rhs of equation (46) assumes the form

$$\sum_{i=1}^{4} \int_{\mathbb{R}^3} \log\left(\frac{f_i}{m_i^3}\right) \mathcal{R}_i^{(1)}[\underline{f}, \underline{f}^{(1)}](\boldsymbol{v})\, \mathrm{d}\boldsymbol{v} \leqslant \sum_{j=3}^{4} \int_{\mathbb{R}^3} \log\left(\frac{f_j^{(1)}}{m_j^3}\right) \mathcal{R}_j^{(1)}[\underline{f}, \underline{f}^{(1)}](\boldsymbol{v})\, \mathrm{d}\boldsymbol{v}$$

$$+ \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathcal{S}} \log\left(\frac{f_1}{m_1^3}\right) K_1(\boldsymbol{v}, \boldsymbol{w}, \boldsymbol{\Omega}')\, \mathrm{d}\boldsymbol{v}\, \mathrm{d}\boldsymbol{w}\, \mathrm{d}\boldsymbol{\Omega}'$$

$$+ \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathcal{S}} \log\left(\frac{f_2}{m_2^3}\right) K_1(\boldsymbol{v}, \boldsymbol{w}, \boldsymbol{\Omega}')\, \mathrm{d}\boldsymbol{v}\, \mathrm{d}\boldsymbol{w}\, \mathrm{d}\boldsymbol{\Omega}'. \tag{48}$$

Adopting a procedure quite similar to the one used to prove lemma 1, equation (48) becomes

$$\sum_{i=1}^{4} \int_{\mathbb{R}^3} \log\left(\frac{f_i}{m_i^3}\right) \mathcal{R}_i^{(1)}[\underline{f}, \underline{f}^{(1)}](\boldsymbol{v})\, \mathrm{d}\boldsymbol{v} \leqslant \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathcal{S}} \left[\log\left(\frac{f_1(\boldsymbol{v})}{m_1^3}\right) + \log\left(\frac{f_2(\boldsymbol{w})}{m_2^3}\right) \right.$$

$$\left. - \log\left(\frac{f_3^{(1)}(\boldsymbol{v}_1)}{m_3^3}\right) - \log\left(\frac{f_4^{(1)}(\boldsymbol{w}_1)}{m_4^3}\right) \right] K_1(\boldsymbol{v}, \boldsymbol{w}, \boldsymbol{\Omega}')\, \mathrm{d}\boldsymbol{v}\, \mathrm{d}\boldsymbol{w}\, \mathrm{d}\boldsymbol{\Omega}', \tag{49}$$

which easily results in the form

$$\sum_{i=1}^{4} \int_{\mathbb{R}^3} \log\left(\frac{f_i}{m_i^3}\right) \mathcal{R}_i^{(1)}[\underline{f}, \underline{f}^{(1)}](\boldsymbol{v})\, \mathrm{d}\boldsymbol{v} \leqslant \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{\mathcal{S}} C_{12}^{34}(g) M^3 f_3^{(1)}(\boldsymbol{v}_1) f_4^{(1)}(\boldsymbol{w}_1)$$

$$\times \log\left(\frac{f_1(\boldsymbol{v}) f_2(\boldsymbol{w})}{M^3 f_3^{(1)}(\boldsymbol{v}_1) f_4^{(1)}(\boldsymbol{w}_1)}\right) \left[1 - \frac{f_1(\boldsymbol{v}) f_2(\boldsymbol{w})}{M^3 f_3^{(1)}(\boldsymbol{v}_1) f_4^{(1)}(\boldsymbol{w}_1)} \right] \mathrm{d}\boldsymbol{v}\, \mathrm{d}\boldsymbol{w}\, \mathrm{d}\boldsymbol{\Omega}'. \tag{50}$$

Thus, also such contribution is non-positive, being, in particular, equal to zero if and only if the equalities in (45) hold. $\square$

Observe that constraint (44) is a mathematical requirement necessary to prove proposition 2 rigorously. In fact, numerical experiments carried out in section 5 confirm that the kinetic entropy production is positive and does not depend on such constraint.

- *Indifferentiability principle.* The BGK-type collision operator satisfies indifferentiability principle as the true Boltzmann operator [11].

Consider the special case in which all gas species of the mixture have equal mass m, equal internal energy E and elastic collision frequencies ν. In this case, the chemical process is absent and the total distribution $f = \sum_i f_i$ satisfies a single species BGK equation. In fact, the sum of equations (31), with elastic contributions only, yields

$$\frac{\partial f}{\partial t} + \boldsymbol{v} \cdot \nabla f = \nu \left[\sum_{i=1}^{4} f_i^{(1)}(\boldsymbol{v}) - f(\boldsymbol{v}) \right], \tag{51}$$

where

$$\sum_{i=1}^{4} f_i^{(1)}(\boldsymbol{v}) = n \left(\frac{m}{2\pi k_{\mathrm{B}} T} \right)^{\frac{3}{2}} \exp \left(-\frac{m(\boldsymbol{v} - \boldsymbol{u})^2}{2 k_{\mathrm{B}} T} \right), \quad \text{with} \quad n = \sum_{i=1}^{4} n_i. \tag{52}$$

Setting $\sum_i f_i^{(1)} = f^{(1)}$, equation (51) becomes the BGK equation for a single gas species, which means that indifferentiability is fulfilled.

4. BGK-type model in the kinetic chemical equilibrium regime (model 2)

The kinetic chemical equilibrium regime, first formally introduced in [17] and further investigated also in [5], is consistent with fluid dynamical processes involving fast chemical reactions, in which, as already said, mechanical and chemical equilibrium have comparable relaxation times. The equations governing such a regime are derived taking into account chemical equilibrium directly at the molecular level. Therefore, as mentioned in the introduction, the collision operators will be indicated with $J_i^{(2)}$ for the elastic contribution and with $\mathcal{R}_i^{(2)}$ for the reactive term, since they depend upon the Maxwellian distributions $f_i^{(2)}$.

4.1. Preliminaries

The model proposed in the considered regime is based on the following assumptions, which slightly modify those of section 3, provided that the $\boldsymbol{v}$-independent collision frequencies $\nu_i^{(2)}, \sigma_i^{(2)}$ are obtained from equations (9), (13) when $f_j(\boldsymbol{w})$ is substituted by the Maxwellians $f_j^{(2)}(\boldsymbol{w})$, and that the independent collision invariants of the model are those specified in equation (22).

(i′) Particles reach a local thermodynamical equilibrium after at least one collision. Thus, gain contributions G_i and $\mathcal{G}_i$ defined in equations (7), (11) are rewritten in terms of the Maxwellians $f_i^{(2)}$.

(ii′) The differences between the integrals defining ν_i and $\nu_i^{(2)}$, and σ_i and $\sigma_i^{(2)}$, are neglected, so that

$$\nu_i^{(2)} = \nu_i, \qquad \sigma_i^{(2)} = \sigma_i, \qquad i = 1, \dots, 4. \tag{53}$$

(iii′) The seven independent parameters for the Maxwellians $f_i^{(2)}$ are fixed in terms of the model invariants (22) through the conditions

$$\sum_{i=1}^{4} \int_{\mathbb{R}^3} \psi_i^{(k)}(\boldsymbol{v}) f_i(\boldsymbol{v}) \, \mathrm{d}\boldsymbol{v} = \sum_{i=1}^{4} \int_{\mathbb{R}^3} \psi_i^{(k)}(\boldsymbol{v}) f_i^{(2)}(\boldsymbol{v}) \, \mathrm{d}\boldsymbol{v}, \quad k = 1, \dots, 7. \tag{54}$$

Remark 7. Assumption (54) refers to conservation laws of total momentum, energy and partial number densities of type $n_1 + n_3, n_1 + n_4, n_2 + n_4$.

4.2. Derivation of terms $J_i^{(2)}, \mathcal{R}_i^{(2)}$

Elastic terms $J_i^{(2)}$ are obtained according to the assumptions (i′), (ii′) by applying the procedure of subsection 3.2, i.e.

$$J_i^{(2)}[\underline{f}, \underline{f}^{(2)}](\boldsymbol{v}) = \nu_i [f_i^{(2)}(\boldsymbol{v}) - f_i(\boldsymbol{v})]. \tag{55}$$

The approximate reactive terms can be deduced in quite a similar way giving, with obvious meaning of symbols,

$$\mathcal{R}_i^{(2)}[\underline{f}, \underline{f}^{(2)}](\boldsymbol{v}) = \mathcal{G}_i^{(2)}[\underline{f}^{(2)}](\boldsymbol{v}) - \sigma_i f_i(\boldsymbol{v}). \tag{56}$$

The explicit form of the terms in the last equation is that of equations (13) and (28), provided that the distributions are substituted by $f_i^{(2)}$. On the other hand, by taking into account chemical equilibrium conditions (18), equation (56) can be rewritten in the simpler form

$$\mathcal{R}_i^{(2)}[\underline{f}, \underline{f}^{(2)}](\boldsymbol{v}) = \sigma_i\big[f_i^{(2)}(\boldsymbol{v}) - f_i(\boldsymbol{v})\big]. \tag{57}$$

In conclusion, gathering expressions (55), (57) of terms $J_i^{(2)}, \mathcal{R}_i^{(2)}$, the model equations in the kinetic chemical equilibrium regime read

$$\frac{\partial f_i}{\partial t} + \boldsymbol{v} \cdot \nabla f_i = (\nu_i + \sigma_i)\big[f_i^{(2)}(\boldsymbol{v}) - f_i(\boldsymbol{v})\big], \quad i = 1, \dots, 4. \tag{58}$$

4.3. Consistency of the model

The approximate collision operator assumes now a unified form through the collision frequencies, coherently with the fact that, in the kinetic chemical equilibrium regime, the characteristic times of elastic collisions and chemical reaction are comparable.

It is straightforward to state the conservation laws directly from assumption (iii′), the indifferentiability principle and the entropy inequality without any constraint, as shown in the next proposition.

Proposition 3. *Let $\mathcal{H}$ and $\phi_{\mathcal{H}}$ be defined by*

$$\mathcal{H}(x, t) = \sum_{i=1}^{4} \int_{\mathbb{R}^3} f_i \log\left(\frac{f_i}{m_i^3}\right) d\boldsymbol{v}, \qquad \phi_{\mathcal{H}}(x, t) = \sum_{i=1}^{4} \int_{\mathbb{R}^3} f_i \log\left(\frac{f_i}{m_i^3}\right) \boldsymbol{v} \, d\boldsymbol{v}. \tag{59}$$

Then

$$\frac{\partial \mathcal{H}}{\partial t}(x, t) + \operatorname{div}\phi_{\mathcal{H}}(x, t) \leqslant 0. \tag{60}$$

Moreover one has $\dfrac{\partial \mathcal{H}}{\partial t}(x, t) + \operatorname{div}\phi_{\mathcal{H}}(x, t) = 0$ if and only if $f_i = f_i^{(2)}$.

Proof. The proof is immediate, since now the reactive terms $\mathcal{R}_i^{(2)}$ have the same functional form as the elastic terms (55). Thus it is enough to apply the procedure carried on in part (a) of the proof of proposition 2. □

5. Applications

In view of applications, explicit expressions for the model equations (31) and (58) will be derived in the next subsection, whereas some numerical experiments related to different reaction mechanisms will be performed in the last subsection.

5.1. Explicit forms of models 1 and 2

With reference to the strong reaction regime, the collision frequencies ν_i, σ_i and gains $\mathcal{G}_i^{(1)}$ must be computed in terms of the elastic B_{ij}^{ij} and reactive C_{12}^{34}, C_{34}^{12} cross sections. As already specified in sections 3 and 4, for elastic interactions, cross sections of Maxwellian molecules have been assumed, that is $B_{ij}^{ij} = \alpha_{ij}$, so that the elastic collision frequencies have the form

$$\nu_i = 4\pi \sum_{j=1}^{4} \alpha_{ij} n_j, \qquad i = 1, \dots, 4. \tag{61}$$

Moreover for the cross section C_{34}^{12}, related to the exothermic reaction, the generalized isotropic Maxwellian molecules form proposed in [18] will be adopted, that is

$$C_{34}^{12}(g) = \beta \left(1 - \frac{\xi^2}{g^2}\right) H(g - \xi), \qquad (62)$$

β being a scalar factor, ξ the threshold velocity of the exothermic reaction and H the Heaviside function. In particular it results

$$\xi = \left(\frac{2E_a}{\Theta}\right)^{1/2}, \qquad \Theta = \frac{m_3 m_4}{m_1 + m_2},$$

E_a being the activation energy of the exothermic reaction. According to the micro-reversibility condition, it turns out that the cross section C_{12}^{34} of the endothermic reaction is expressed by

$$C_{12}^{34}(g) = \beta \left(\frac{1}{M}\right)^{\frac{3}{2}} \left(1 - \frac{g_s^2}{g^2}\right)^{1/2} \left(1 - \frac{\xi^2}{M(g^2 - g_s^2)}\right) H\left(g - \left(\frac{\xi^2}{M} + g_s^2\right)^{1/2}\right). \qquad (63)$$

By inserting expressions (62), (63) on the rhs of equation (31), after some rather cumbersome integrations, the reactive terms of the model can be written as

$$\mathcal{R}_i^{(1)}[\underline{f}, \underline{f}^{(1)}](\boldsymbol{v}) = \gamma_i f_i^{(1)}(\boldsymbol{v}) - \sigma_i f_i(\boldsymbol{v}), \qquad i = 1, \dots, 4, \qquad (64)$$

where γ_i and σ_i are functions of $(t, \boldsymbol{x})$ through temperature and number densities; in fact they are given by

$$
\begin{array}{llll}
\gamma_1 = An_3 n_4 / n_1, & \gamma_2 = An_3 n_4 / n_2, & \gamma_3 = Bn_1 n_2 / n_3, & \gamma_4 = Bn_1 n_2 / n_4 \\
\sigma_1 = Bn_2, & \sigma_2 = Bn_1, & \sigma_3 = An_4, & \sigma_4 = An_3
\end{array}
\qquad (65)
$$

where

$$A(T) = \frac{4\pi\beta\Theta S}{k_B T}, \quad B(T) = A(T) \left(\frac{1}{M}\right)^{\frac{3}{2}} \exp\left(-\frac{\Delta E}{k_B T}\right),$$

$$S(T) = \frac{\xi}{\pi} \left(\frac{2\pi k_B T}{\Theta}\right)^{\frac{1}{2}} \exp\left(-\frac{\Theta \xi^2}{2k_B T}\right) + \left(\frac{k_B T}{\Theta} - \xi^2\right) \left[1 - \text{erf}\left\{\left(\frac{\Theta \xi^2}{2k_B T}\right)^{\frac{1}{2}}\right\}\right]. \qquad (66)$$

The explicit form of model 1 is finally given by

$$\frac{\partial f_i}{\partial t} + \boldsymbol{v} \cdot \nabla f_i = 4\pi \sum_{i=1}^4 \alpha_{ij} n_j \left[f_i^{(1)}(\boldsymbol{v}) - f_i(\boldsymbol{v})\right] + \gamma_i f_i^{(1)}(\boldsymbol{v}) - \sigma_i f_i(\boldsymbol{v}), \quad i = 1, \dots, 4. \quad (67)$$

For what concerns model 2 it is enough to rewrite equations (58) in the form

$$\frac{\partial f_i}{\partial t} + \boldsymbol{v} \cdot \nabla f_i = \left(4\pi \sum_{i=1}^4 \alpha_{ij} n_j + \sigma_i\right) \left[f_i^{(2)}(\boldsymbol{v}) - f_i(\boldsymbol{v})\right], \qquad i = 1, \dots, 4, \qquad (68)$$

where the reactive frequencies σ_i are provided by equations (65). The last equations (68) depend on the distributions $f_i^{(2)}$ which are Maxwellians providing local mechanical and chemical equilibrium. In order to assure that the distributions $f_i^{(2)}$ satisfy chemical equilibrium, they will be constrained to depend on a 'fictitious' temperature $\widehat{T}$ recovered by the mass-action-law (19), namely,

$$\widehat{T} = \frac{\Delta E}{k_B} \left\{\log\left[\frac{n_1 n_2}{n_3 n_4} \left(\frac{1}{M}\right)^{3/2}\right]\right\}^{-1}. \qquad (69)$$
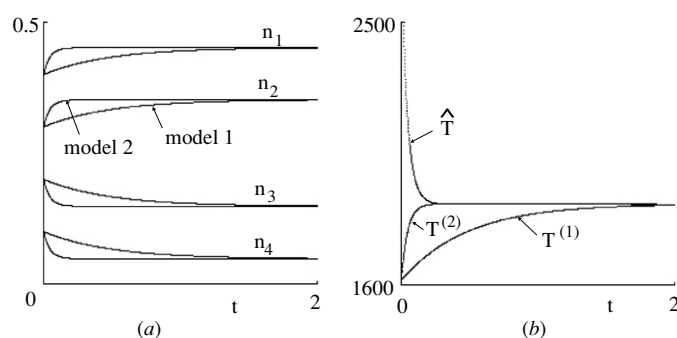
Figure 1. Reaction $H_2O + H \rightleftharpoons OH + H_2$: (*a*) number densities n_i by models 1 and 2 versus time and (*b*) temperatures T and fictitious $\widehat{T}$ versus time.

5.2. Numerical experiments

Numerical experiments for the proposed model equations (67), (68) are performed in the spatial homogeneous case with the aim of showing the behaviour of the reactive mixture in models 1 and 2.

In all the experiments shown below non-symmetric bimodal distribution functions are assumed as initial data for $f_1, \ldots, f_4$.

The constants α_{ij} and β appearing in (61) and (62) are chosen in such a way that, when slow reactions are considered, reactive collision frequencies are at most $1/10$ of the elastic ones. Conversely, in the case of fast reactions, elastic and reactive collision frequencies are assumed to be of the same order of magnitude. The values of β, which is only a scale factor in the modelling of the reactive cross sections, correspond to the correct ratio [19] between reactive and elastic collision frequencies according to the considered reactive flow regime. In all the experiments shown below, the elastic collision constant α_{ij} has been assumed of the order of unit. Moreover, the appropriate values of the activation energy E_a and heats of formation E_i of the reactions considered below can be taken in the books [15, 20].

As a first experiment, the hydrogen–oxygen reaction ($\Delta E = 63\,311$, $E_a = 15\,160$)

$$H_2O + H \rightleftharpoons OH + H_2 \tag{70}$$

is treated by means of models 1 and 2 in order to underline the different transient behaviour of densities and temperature, when the reaction proceeds as either a slow or a fast one ($\beta = 0.96$ and $\beta = 10$, respectively).

In this case, the initial distribution functions provide, through the computation of the corresponding moments, the following initial values:

$$n_{10} = 0.4, \qquad n_{20} = 0.3, \qquad n_{30} = 0.2, \qquad n_{40} = 0.1, \qquad T_0 = 1615,$$

expressed in mole l^{-1} for number densities and kelvin for temperature. This choice, as the one of the next experiment, is justified by the requirement of testing the models starting from initial data far enough from chemical equilibrium.

The results are reported versus time in figure 1(*a*) for the densities and in figure 1(*b*) for temperatures. In particular, figure 1(*a*) shows that both models converge, according to an exothermic process, towards the same equilibrium values but the transient behaviour is quite shorter in the kinetic chemical equilibrium regime (model 2), as expected.

In figure 1(*b*), besides the temperature profiles prescribed by models 1 and 2, denoted there by $T^{(1)}$ and $T^{(2)}$ respectively, the 'fictitious' temperature $\widehat{T}$, defined by (69), is plotted
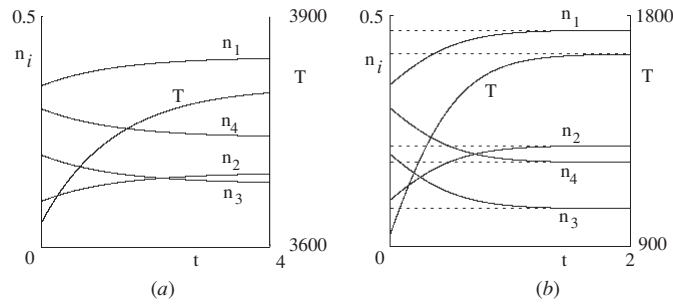
Figure 2. Number densities n_i and temperature T versus time (*a*) for the slow reaction $CO_2 + O \rightleftharpoons O_2 + CO$, and (*b*) for the fast reaction $O_2 + H \rightleftharpoons OH + O$, together with the Euler constant solutions (dashed lines).

as well. The picture shows that such a temperature converges very rapidly to the 'true' temperature $T^{(2)}$. Again the temperatures prescribed by the two models converge then to the same asymptotic value.

As a second experiment, the slow reaction ($\beta = 0.128$) of carbon–oxygen chain ($\Delta E = 33\,820$, $E_a = 171\,380$)

$$CO_2 + O \rightleftharpoons O_2 + CO \tag{71}$$

and a further fast reaction ($\beta = 0.857$) of hydrogen–air mechanism ($\Delta E = 70\,551$, $E_a = 70\,230$)

$$O_2 + H \rightleftharpoons OH + O \tag{72}$$

are tested in terms of their appropriate models (figures 2(*a*) and (*b*), respectively).

The initial distribution functions provide the following initial values for reaction (71):

$$n_{10} = 0.35, \qquad n_{20} = 0.1, \qquad n_{30} = 0.2, \qquad n_{40} = 0.3, \qquad T_0 = 3632,$$

and for reaction (72) the data

$$n_{10} = 0.35, \qquad n_{20} = 0.1, \qquad n_{30} = 0.2, \qquad n_{40} = 0.3, \qquad T_0 = 945.$$

Observe that, as expected, in figure 2(*a*) the slow reaction equilibrium values are reached after a greater time ($t = 4$) than in figure 2(*b*) ($t = 2$).

In order to test the reliability of the two models, as a last experiment, equilibrium number densities and temperatures computed by the proposed models 1 and 2 are compared to those that can be obtained by the reactive Euler equations in the spatial homogeneous case. Such comparisons are reasonable only for asymptotic equilibrium quantities, since during the transient time the results of models 1 and 2 are strongly affected by the initial distributions chosen for the experiment. In fact, the initial conditions for the BGK-type equations correspond to a mesoscopic physical state of the mixture characterized by mechanical and chemical non-equilibrium at the same time, whereas the reactive Euler equations describe the evolution starting from chemical non-equilibrium only. In particular, the initial data of densities and temperature for the Euler equations are those provided by the corresponding moments of the chosen initial distributions.

Table 1. BGK and Euler equilibrium asymptotic values.

		n_1	n_2	n_3	n_4	T
(a)						
$H_2O + H \rightleftharpoons OH + H_2$	BGK	0.4790	0.2342	0.0710	0.1658	2372.07
slow reaction	EUL	0.4792	0.2292	0.0708	0.1708	2373.09
(b)						
$H_2O + H \rightleftharpoons OH + H_2$	BGK	0.4763	0.2407	0.0737	0.1593	2357.16
fast reaction	EUL	0.4806	0.2306	0.0694	0.1694	2380.59
(c)						
$CO_2 + O \rightleftharpoons O_2 + CO$	BGK	0.4095	0.1595	0.1405	0.2405	3802.12
slow reaction	EUL	0.4096	0.1596	0.1404	0.2404	3802.19

For slow reactions, the comparison with the results of model 1 is performed using the spatial homogeneous reactive Euler equations derived in paper [19], i.e.

$$\frac{dn_i}{dt} = \lambda_i[An_3n_4 - Bn_1n_2], \qquad i = 1, \dots, 4, \qquad \lambda_1 = \lambda_2 = 1, \qquad \lambda_3 = \lambda_4 = -1$$
$$\frac{dT}{dt} = \frac{2}{3}\frac{\Delta E}{k_Bn}[An_3n_4 - Bn_1n_2], \qquad n = \sum_{i=1}^{4} n_i, \tag{73}$$

which have been obtained from the true nonlinear Boltzmann equation, assuming the same reactive cross sections modelled by (62) and (63).

Such a comparison is reported in table 1 (frames (a) and (c)) for number densities and temperature. As it can be noticed, the agreement is almost exact for the reaction $CO_2 + O \rightleftharpoons O_2 + CO$, and satisfactory for the other reaction $H_2O + H \rightleftharpoons OH + H_2$: the discrepancies are due to model inaccuracies and, in the worse case, the error is less than 3%.

For fast reactions described by model 2, the same kind of comparison is possible using the fast reactive Euler equations deduced in [21]. From such equations it is rather straightforward to compute explicitly the asymptotic values of number densities and temperature. The computation consists in finding first the asymptotic value of n_1 from the unique zero of the function

$$\mathcal{F}(n_1) = \frac{3(y_2 + y_3 - y_1)\Delta E}{2\log\left[\left(\frac{1}{M}\right)^{3/2}\frac{n_1(n_1-y_1)}{(y_2-n_1)(y_3-n_1)}\right]} - n_1\Delta E - \mathcal{U}, \tag{74}$$

where

$$y_1 = n_{10} - n_{20}, \qquad y_2 = n_{10} + n_{30}, \qquad y_3 = n_{10} + n_{40},$$
$$\mathcal{U} = \frac{3}{2}n_0 k_B T_0 - n_{10}\Delta E, \qquad n_0 = y_2 + y_3 - y_1. \tag{75}$$

The asymptotic values of the other macroscopic quantities are then obtained by

$$n_2 = n_1 - y_1, \qquad n_3 = y_2 - n_1, \qquad n_4 = y_3 - n_1, \qquad T = \frac{2(\mathcal{U} + n_1\Delta E)}{3n_0 k_B} \tag{76}$$

and the results are plotted (dashed lines) in figure 2(b).

This last comparison is not very satisfactory since this time, as can be seen in table 1 (frame (b)), the discrepancy in the worse case is of the order of 6%. However, this result is not completely surprising since model 2 has been derived under stronger assumptions (see item (i')) which are valid for a system closer to equilibrium. It should be observed once more that the numerical experiments of this section, conversely, assume initial conditions rather far from equilibrium.

6. Conclusions

In this work two BGK-type models, describing at the kinetic level the time-space evolution of a mixture of four gases undergoing slow and fast chemical reactions, have been derived. The model equations include reference functions (Maxwellian distributions) dependent on the number densities of each species and on the mean velocity and temperature of the overall mixture. In an absolute thermodynamical equilibrium state, the Maxwellian distributions are also solution to the model equations. Moreover, the BGK collision operator verifies the properties of the true Boltzmann operator [14] consistent with the physical laws of the system. The numerical experiments, proposed at the end of the paper in the spatial homogeneous case, have shown a good qualitative behaviour with respect to the trend to thermodynamical equilibrium.

It may be noted that such results must be interpreted within the limit of validity of the models. In fact a perturbation of velocity distribution, induced by the chemical reactions, was already identified in [1] and, afterwards, in [2] by direct simulations of the Boltzmann equation. In particular, the deviations from the Gaussian character of the velocity distribution, which implies non-vanishing values of the kurtosis, have been observed for both fast and slow reactions, respectively, in papers [22, 23], through Chapman–Enskog expansion of the Boltzmann equation. This discrepancy is essentially due to the BGK framework in which the models have been derived. Therefore, in authors' opinion, a correction should be brought to such a derivation in order to take into account the above-said deviations. This point can be viewed as an open problem to deal with.

Moreover, the relevance of the BGK-type models also far from equilibrium has been discussed for inert flows in [7, 24]. The feasibility of reactive BGK-type models for the computation of transport properties and for more general situations than the one faced in the present paper is the main objective of a work in progress.

In conclusion, the procedure proposed here can be extended, in a rather straightforward way, to systems of reactive chains with several slow and/or fast reactions and a large number of chemical compounds in order to deduce their time-space evolution equations. In authors' opinion, derivation of 'simple' kinetic models, which take into account non-equilibrium chemical processes dependent on their localization in space, may be interesting also in simulations useful for the assessment of industrial plants safety [25].

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