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A BGK relaxation model for polyatomic gas mixtures

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Abstract

We present a BGK approximation of a kinetic Boltzmann model for a mixture of polyatomic gases, in which non-translational degrees of freedom of each gas are represented by means of a set of discrete internal energy levels. We deal also with situations in which even chemical reactions implying transfer of mass may occur. The consistency of the proposed BGK model is proved in both inert and reactive frames, and numerical simulations in space homogeneous settings are presented.

Keywords: Polyatomic gas mixtures, Boltzmann equations, BGK relaxation models.

2010 Mathematics Subject Classification: 82C40, 76P05, 80A30

1 Introduction

A kinetic description of rarefied gas mixtures has been proposed in scientific literature several years ago [11, 10], and suitable generalizations to physical situations with non-conservative collisions, implying transfer of energy and of mass, have been also widely investigated both from the analytical and the numerical point of view (see for instance [23, 13, 4, 18] and the references therein). These kinetic models usually describe the evolution of the distribution functions f^i of single gases by means of suitable integro-differential equations of Boltzmann type. However, such equations are quite awkward to deal with, especially because of energy thresholds appearing in the collision operators relevant to endothermic interactions, that may occur only if the impinging kinetic energy overcomes a suitable potential barrier [22]. For this reason, in recent years interest has been gained by proper extensions to gas mixtures of the relaxation model proposed for a single gas by Bhatnagar, Gross and Krook in [2], in which Boltzmann collision operator is replaced by $\nu(\mathcal{M} - f)$ where ν stands for a collision frequency and \mathcal{M} is a suitable local Maxwellian attractor. Besides BGK-type descriptions for inert mixtures, considered for instance in [19, 1, 7], relaxation models taking into account also simple chemical reactions have been deeply investigated [17, 20, 5, 9]. Such models are able to reproduce the main

features of the kinetic Boltzmann equations they want to approximate, as Maxwellian collision equilibria, the correct collision invariants, classical H -theorem. In reactive frames, the proof of the consistency of a BGK approximation is much more involved than in inert situations, since a transcendental relation between single number densities and global temperature (the mass action law of chemistry [4]) has to be fulfilled by the equilibrium states, and consequently it deeply affects the relations between the fictitious parameters of the Maxwellian attractors and the actual macroscopic fields. Because of these difficulties, to our knowledge all non-conservative BGK models for mixtures deal only with monoatomic gases, even if it is well known that physically meaningful chemical processes usually involve also polyatomic gases.

Kinetic Boltzmann descriptions for polyatomic gases have been proposed in [21, 16, 12], in which single gases are endowed also with a (discrete or continuous) energy variable, to mimic non-translational degrees of freedom. The main aim of this paper is to build up a consistent BGK approximation of the Boltzmann model presented in [16], considering a mixture of Q polyatomic gases G^s , $s = 1, \dots, Q$, each one with a structure of $N > 1$ discrete energy levels. At first we will assume that particles may interact only through binary elastic or inelastic collisions, the latter ones implying changes of the energy levels of the colliding pair; then, we will take into account more complicated situations allowing also chemical reactions with transfer of mass. The BGK models we are proposing follow the same lines as [5, 6], and they will be validated by both analytical proofs and numerical simulations in space homogeneous frames. We know that a drawback of such kind of BGK approach is that the corresponding hydrodynamic equations do not reproduce the correct Prandtl number; to this aim, quite complicated BGK models of ellipsoidal type have been proposed in the literature even for an elastically scattering mixture [14] or for a single polyatomic gas [8], but their extension to polyatomic and reacting gas mixtures is left to a future work.

More precisely, the article is organized as follows. In Section 2, the main features of the kinetic Boltzmann model for polyatomic gases proposed in [16] are summarized, forgetting for now chemical reactions. Then, in Section 3 a BGK relaxation model for (inert) polyatomic gas mixtures is built up in the spirit of [5], determining in a unique way parameters of the Maxwellian attractors in terms of species number densities, mass velocities and temperatures; moreover, fulfillment of correct H -theorem is analytically proved. Section 4 deals with possible generalizations of such BGK model to reactive frames, in which a suitable mass action law affects collision equilibria and, consequently, attractor parameters; at first we deal with a binary reacting mixture, for which mass action law is an explicit relation between number densities of the two gases, and then we consider the case of four reacting species, for which the analytical proof of consistency of the BGK model turns out to be much more complicated. Finally, Section 5 is devoted to the presentation of some numerical results in space homogeneous conditions (both for inert and reacting polyatomic mixtures); time evolution of distribution functions and of macroscopic fields is shown to illustrate the adherence of the BGK model to physical expectations, and to test its response to variation of initial data and of internal energies.

2 Kinetic Boltzmann model for polyatomic gases

We shall start from the kinetic model for internal state transitions proposed in [16], in which a mixture of Q gases G^s , $s = 1, \dots, Q$, is considered, each one endowed with a structure of $N > 1$ discrete energy levels, to mimic non-translational degrees of freedom. In other words, each polyatomic gas G^s is represented as a mixture of monoatomic gases, and each particle is characterized by the usual continuous variable representing its center of mass velocity and also by a discrete variable representing its internal state. For a proper mathematical treatment, the QN different components are labeled according to a single index and ordered in such a way that the s -th chemical species may be regarded as the equivalence class of the indices i which are congruent to s modulo Q (we shall write simply $i \equiv s$). Each component A^i , $1 \leq i \leq QN$, is then identified by the energy E^i of its state, while obviously all molecules A^i with $i \equiv s$ share the same mass m^s . Energies $E^i \geq 0$ are assumed monotonically increasing with their index in the frame of each species.

We deal with binary interactions in which a collision between two particles of components i and j yields a pair of molecules of the same gases, but with possibly different energy levels (we neglect for now more complicated chemical reactions implying also transfer of mass, which will be taken into account in Section 4). The general binary interaction may thus be written as

$$A^i + A^j \rightleftharpoons A^h + A^k \quad h \equiv i \quad k \equiv j. \quad (1)$$

We will denote by ΔE_{ij}^{hk} the net increase of internal energy $E^h + E^k - E^i - E^j$, whose gain or loss must be compensated by an opposite variation of the kinetic energies.

The kinetic equations for the evolution of the distribution functions $f^i(\mathbf{x}, \mathbf{v}, t)$ may be cast as [16]

$$\begin{aligned} \frac{\partial f^i}{\partial t} + \mathbf{v} \cdot \nabla_{\mathbf{x}} f^i &= \sum_{(j, h, k) \in D_i} \iint K_i^{ijhk}[\underline{f}](\mathbf{v}, \mathbf{w}, \hat{\mathbf{n}}') d\mathbf{w} d\hat{\mathbf{n}}', \quad 1 \leq i \leq QN \\ K_i^{ijhk}[\underline{f}](\mathbf{v}, \mathbf{w}, \hat{\mathbf{n}}') &= \Theta(g^2 - \delta_{ij}^{hk}) B_{ij}^{hk}(g, \hat{\mathbf{n}} \cdot \hat{\mathbf{n}}') \\ &\times \left[\left(\frac{\mu^{ij}}{\mu^{hk}} \right)^3 f^h(\mathbf{v}_{ij}^{hk}) f^k(\mathbf{w}_{ij}^{hk}) - f^i(\mathbf{v}) f^j(\mathbf{w}) \right]. \end{aligned} \quad (2)$$

Here $\mathbf{g} = \mathbf{v} - \mathbf{w} = g \hat{\mathbf{n}}$, and the post-collision velocities are given by $\mathbf{v}_{ij}^{hk} = \varepsilon^{ij} \mathbf{v} + \varepsilon^{ji} \mathbf{w} + \varepsilon^{kh} g_{ij}^{hk} \hat{\mathbf{n}}'$ and $\mathbf{w}_{ij}^{hk} = \varepsilon^{ij} \mathbf{v} + \varepsilon^{ji} \mathbf{w} - \varepsilon^{hk} g_{ij}^{hk} \hat{\mathbf{n}}'$, with $g_{ij}^{hk} = \left[\frac{\mu^{ij}}{\mu^{hk}} (g^2 - \delta_{ij}^{hk}) \right]^{1/2}$, ε^{ij} standing for the mass ratio $m^i / (m^i + m^j)$ and μ^{ij} for the reduced mass $\varepsilon^{ij} m^j$. For mechanical interactions (1) it obviously holds $\mu^{ij} / \mu^{hk} = 1$, but we prefer to write here the scattering operator in the most general form, able to describe also collisions with mass transfer that will be dealt with in Section 4. Moreover $B_{ij}^{hk} = g \sigma_{ij}^{hk}$ denotes the collision kernel (σ_{ij}^{hk} is the differential cross section of the interaction $A^i + A^j \rightarrow A^h + A^k$), while δ_{ij}^{hk} stands for $2\Delta E_{ij}^{hk} / \mu^{ij}$; when the latter is positive, the unit step function Θ actually introduces a threshold for the collision. Finally, the set D_i includes all possible collisions, namely it is made up by all triplets (j, h, k) with $h \equiv i$ and $k \equiv j$.

Major moments of each component A^i (number density n^i , drift velocity \mathbf{u}^i , kinetic temperature T^i) reconstruct in the usual way [4] the corresponding moments of each gas G^s and of the whole mixture as

$$N^s = \sum_{i \equiv s} n^i, \quad \mathbf{u}^s = \frac{1}{N^s} \sum_{i \equiv s} n^i \mathbf{u}^i, \quad N^s K T^s = \sum_{i \equiv s} n^i K T^i + \frac{1}{3} m^s \sum_{i \equiv s} n^i (|\mathbf{u}^i|^2 - |\mathbf{u}^s|^2), \quad (3)$$

and

$$\begin{aligned} n &= \sum_{s=1}^Q N^s, & \rho &= \sum_{s=1}^Q m^s N^s, \\ \mathbf{u} &= \frac{1}{\rho} \sum_{s=1}^Q m^s N^s \mathbf{u}^s, & n K T &= \sum_{s=1}^Q N^s K T^s + \frac{1}{3} \sum_{s=1}^Q m^s N^s (|\mathbf{u}^s|^2 - |\mathbf{u}|^2) \end{aligned} \quad (4)$$

where K is the Boltzmann constant. Analogous relations hold for the pressure tensor \mathbf{P} and the thermal heat flux \mathbf{q} .

The main properties of the collision operator (collision invariants, equilibria, H -theorem) are a byproduct of the detailed investigation performed in [16]. In our frame there exist $Q + 4$ independent collision invariants for the global collision operator, and they correspond to the preservation of species number densities N^s , of global mass velocity \mathbf{u} , and of total energy, sum of the kinetic contribution and of the internal one. Consequently, $Q + 4$ exact non-closed macroscopic conservation equations hold

$$\begin{aligned} \frac{\partial N^s}{\partial t} + \nabla_{\mathbf{x}} \cdot (N^s \mathbf{u}^s) &= 0, & s &= 1, \dots, Q, \\ \frac{\partial}{\partial t} (\rho \mathbf{u}) + \nabla_{\mathbf{x}} \cdot (\rho \mathbf{u} \otimes \mathbf{u} + \mathbf{P}) &= \mathbf{0}, \\ \frac{\partial}{\partial t} \left(\frac{1}{2} \rho |\mathbf{u}|^2 + \frac{3}{2} n K T + \sum_{i=1}^{QN} E^i n^i \right) + \nabla_{\mathbf{x}} \cdot \left[\left(\frac{1}{2} \rho |\mathbf{u}|^2 + \frac{3}{2} n K T \right) \mathbf{u} \right. \\ &\quad \left. + \mathbf{P} \cdot \mathbf{u} + \mathbf{q} + \sum_{i=1}^{QN} E^i n^i \mathbf{u}^i \right] &= 0. \end{aligned} \quad (5)$$

Collision equilibria are a $(Q + 4)$ -parameter family of Maxwellians with a common drift velocity and temperature

$$f_M^i(\mathbf{v}) = n^i \left(\frac{m^s}{2\pi K T} \right)^{3/2} \exp \left[-\frac{m^s}{2K T} |\mathbf{v} - \mathbf{u}|^2 \right] \quad \forall i \equiv s, \quad \forall s = 1, \dots, Q, \quad (6)$$

with equilibrium number densities related by the constraints

$$n^i = N^s \psi(E^i, T), \quad (7)$$

where

$$\psi(E^i, T) = \frac{\exp \left(-\frac{E^i - E^s}{K T} \right)}{\sum_{i \equiv s} \exp \left(-\frac{E^i - E^s}{K T} \right)} = \frac{\exp \left(-\frac{E^i - E^s}{K T} \right)}{Z^s(T)}. \quad (8)$$

Note that $\psi(E^i, T)$ represents the fraction of particles of species G^s ($s \equiv i$) that belongs to the component A^i in any equilibrium configuration. For any component $i = 1, \dots, QN$ we have $0 \leq \psi(E^i, T) \leq 1$, and for any gas G^s it holds $\sum_{i \equiv s} \psi(E^i, T) = 1$. Moreover, for any i, j with $i \equiv j$ and $i < j$, we have $\psi(E^i, T) > \psi(E^j, T)$, hence in any equilibrium state the highest fraction of particles G^s has the lowest energy level E^s .

In space homogeneous conditions, a strict entropy inequality can also be established in terms of the classical H -functional

$$H = \sum_{s=1}^Q \sum_{i \equiv s} \int f^i \log f^i d\mathbf{v}, \quad (9)$$

quantifying relaxation rate to the unique collision equilibrium corresponding to the initial data.

3 BGK relaxation model for polyatomic gas mixtures

BGK approaches for mixtures proposed in the literature are usually not trivial generalization of the classical BGK model for a single gas, since one must take care of reproducing some further basic principles, as positivity of densities and temperatures of all interacting species, and “indifferentiability”, namely the requirement that when all species are identical one must recover the BGK model for a single gas. These fundamental issues are satisfied by the model proposed in [1] for inert monoatomic gas mixtures and extended in [5, 6] to reactive frames, and for this reason we build up here a BGK model for polyatomic gases following the same lines. The crucial idea of this kind of relaxation models consists in replacing the actual i -th Boltzmann collision operator by a single BGK operator $\nu^i(\mathcal{M}^i - f^i)$, $i = 1, \dots, QN$, where ν^i are suitable \mathbf{v} -independent macroscopic collision frequencies (or inverse relaxation times), and the “attractors” \mathcal{M}^i are fictitious Maxwellians with macroscopic parameters to be properly determined:

$$\frac{\partial f^i}{\partial t} + \mathbf{v} \cdot \nabla_{\mathbf{x}} f^i = \nu^i(\mathcal{M}^i - f^i), \quad i = 1, \dots, QN. \quad (10)$$

Attractors \mathcal{M}^i are assumed accommodated at a common auxiliary velocity $\tilde{\mathbf{u}}$ and temperature \tilde{T}

$$\mathcal{M}^i(\mathbf{v}) = \tilde{n}^i \left(\frac{m^i}{2\pi K \tilde{T}} \right)^{3/2} \exp \left[-\frac{m^i}{2K \tilde{T}} |\mathbf{v} - \tilde{\mathbf{u}}|^2 \right], \quad (11)$$

while fictitious densities \tilde{n}^i are taken bound together as

$$\tilde{n}^i = \tilde{N}^s \psi(E^i, \tilde{T}). \quad (12)$$

Note that the attractors (11)–(12) are chosen in such a way that they fulfill all equilibrium conditions, namely they are Maxwellian distributions with a unique drift velocity and temperature, and with number densities provided by (12), the equilibrium constraint specific of the polyatomic structure of gases. Therefore, this BGK model will describe a general relaxation of all components A^i towards an equilibrium configuration, loosing in some

sense the details of interactions between different species: in the Boltzmann equations (2) there is a collision operator for each admissible interaction $A^i + A^j \rightleftharpoons A^h + A^k$, while in the BGK approximation (10) the effects on velocity \mathbf{u}^i and temperature T^i due to collisions with all possible other components have to be included in the parameters of $\mathcal{M}^i(\tilde{n}^i, \tilde{\mathbf{u}}, \tilde{T})$. Relaxation-type kinetic models with attracting distributions $\tilde{\mathcal{M}}^i(\tilde{n}^i, \tilde{\mathbf{u}}^i, \tilde{T}^i)$ having a different fictitious velocity and temperature for each species have been widely used (for monoatomic mixtures) in a recent past, but the proof of their consistency from the mathematical point of view still has some open problems (for instance, for the model proposed in [17] a rigorous proof of H -theorem is lacking).

Our attractors (11) are then defined in terms of the $QN + 4$ auxiliary variables \tilde{n}^i , $\tilde{\mathbf{u}}$, \tilde{T} , related by the constraints (12), so that only the $Q + 4$ quantities \tilde{N}^s , $\tilde{\mathbf{u}}$, \tilde{T} are actually disposable parameters to be suitably determined to make the BGK approximation consistent.

Following the procedure described in [1, 5, 6], we impose that the BGK model (10) shares the same collision invariants of the original Boltzmann kinetic model (2). This yields the equations

$$\sum_{i \equiv s} \nu^i \int (\mathcal{M}^i - f^i) d\mathbf{v} = 0 \quad s = 1, \dots, Q, \quad (13)$$

$$\sum_{s=1}^Q \sum_{i \equiv s} \nu^i \int m^s \mathbf{v} (\mathcal{M}^i - f^i) d\mathbf{v} = \mathbf{0}, \quad (14)$$

$$\sum_{s=1}^Q \sum_{i \equiv s} \nu^i \int \left(\frac{1}{2} m^s |\mathbf{v}|^2 + E^i \right) (\mathcal{M}^i - f^i) d\mathbf{v} = 0, \quad (15)$$

representing preservation of species number densities, global mass velocity, and total energy, respectively. These are $Q + 4$ equations for the $Q + 4$ unknowns \tilde{N}^s , $\tilde{\mathbf{u}}$, \tilde{T} , and the main part of this section will be devoted to proving that system (13)–(15) has a unique admissible solution for any choice of collision frequencies ν^i , masses m^s and internal energies E^i .

For any $s = 1, \dots, Q$, condition (13) provides

$$\sum_{i \equiv s} \nu^i \tilde{n}^i = \sum_{i \equiv s} \nu^i n^i \quad (16)$$

(relation that will be very useful in the sequel), from which, bearing in mind the constraint (12) for the auxiliary number densities, we get

$$\tilde{N}^s = \left(\sum_{i \equiv s} \nu^i n^i \right) / \left(\sum_{i \equiv s} \nu^i \psi(E^i, \tilde{T}) \right). \quad (17)$$

Thus \tilde{N}^s are positive quantities, uniquely determined in terms of actual number densities n^i and auxiliary temperature \tilde{T} .

Coming to equation (14), it yields

$$\sum_{s=1}^Q m^s \sum_{i \equiv s} \nu^i (\tilde{n}^i \tilde{\mathbf{u}} - n^i \mathbf{u}^i) = \mathbf{0}, \quad (18)$$

that owing to (16) provides

$$\tilde{\mathbf{u}} = \left(\sum_{s=1}^Q m^s \sum_{i \equiv s} \nu^i n^i \mathbf{u}^i \right) / \left(\sum_{s=1}^Q m^s \sum_{i \equiv s} \nu^i n^i \right), \quad (19)$$

hence $\tilde{\mathbf{u}}$ is explicitly given as combination of actual number densities n^i and mass velocities \mathbf{u}^i .

The investigation of constraint (15) turns out to be much more complicated, since it gives the relation

$$\sum_{s=1}^Q \sum_{i \equiv s} \nu^i \left[\frac{1}{2} m^s \tilde{n}^i |\tilde{\mathbf{u}}|^2 + \frac{3}{2} \tilde{n}^i K \tilde{T} + E^i \tilde{n}^i - \frac{1}{2} m^s n^i |\mathbf{u}^i|^2 - \frac{3}{2} n^i K T^i - E^i n^i \right] = 0, \quad (20)$$

that resorting again to (12) and (16) may be cast as

$$\begin{aligned} & \frac{3}{2} \sum_{s=1}^Q \left(\sum_{i \equiv s} \nu^i n^i \right) K \tilde{T} + \sum_{s=1}^Q \tilde{N}^s \sum_{i \equiv s} \nu^i E^i \psi(E^i, \tilde{T}) \\ &= \frac{1}{2} \sum_{s=1}^Q m^s \sum_{i \equiv s} \nu^i n^i (|\mathbf{u}^i|^2 - |\tilde{\mathbf{u}}|^2) + \frac{3}{2} \sum_{s=1}^Q \sum_{i \equiv s} \nu^i n^i K T^i + \sum_{s=1}^Q \sum_{i \equiv s} \nu^i E^i n^i. \end{aligned} \quad (21)$$

This is a transcendental equation for the auxiliary temperature \tilde{T} of the form

$$F(\tilde{T}) = \frac{1}{2} \sum_{s=1}^Q m^s \sum_{i \equiv s} \nu^i n^i (|\mathbf{u}^i|^2 - |\tilde{\mathbf{u}}|^2) + \frac{3}{2} \sum_{s=1}^Q \sum_{i \equiv s} \nu^i n^i K T^i + \sum_{s=1}^Q \sum_{i \equiv s} \nu^i E^i n^i, \quad (22)$$

where

$$F(\tilde{T}) = \sum_{s=1}^Q \left(\sum_{j \equiv s} \nu^j n^j \right) \left[\frac{3}{2} K \tilde{T} + \frac{\sum_{i \equiv s} \nu^i E^i \psi(E^i, \tilde{T})}{\sum_{j \equiv s} \nu^j \psi(E^j, \tilde{T})} \right]. \quad (23)$$

The BGK approximation is consistent if equation (22) has a unique solution, since the auxiliary variable \tilde{N}^s is determined in a unique way in terms of \tilde{T} (see (17)) and $\tilde{\mathbf{u}}$ is explicitly given by the expression (19). Uniqueness of solution to the transcendental equation (22) is a consequence of the two following lemmas:

Lemma 3.1 *For the right hand side of (22) the following lower bound holds:*

$$\frac{1}{2} \sum_{s=1}^Q m^s \sum_{i \equiv s} \nu^i n^i (|\mathbf{u}^i|^2 - |\tilde{\mathbf{u}}|^2) + \frac{3}{2} \sum_{s=1}^Q \sum_{i \equiv s} \nu^i n^i K T^i + \sum_{s=1}^Q \sum_{i \equiv s} \nu^i E^i n^i \geq \sum_{s=1}^Q \left(\sum_{i \equiv s} \nu^i n^i \right) E^s. \quad (24)$$

As a consequence the right hand side of (22) is positive.

Proof.- Since $E^i \geq E^s \forall i \equiv s$, it suffices to prove that

$$\sum_{s=1}^Q m^s \sum_{i \equiv s} \nu^i n^i (|\mathbf{u}^i|^2 - |\tilde{\mathbf{u}}|^2) \geq 0, \quad (25)$$

which, bearing in mind the expression (19) for $\tilde{\mathbf{u}}$, is equivalent to

$$\left(\sum_{s=1}^Q m^s \sum_{j \equiv s} \nu^j n^j \right) \left(\sum_{r=1}^Q m^r \sum_{i \equiv r} \nu^i n^i |\mathbf{u}^i|^2 \right) - \left(\sum_{s=1}^Q m^s \sum_{i \equiv s} \nu^i n^i \mathbf{u}^i \right)^2 \geq 0.$$

The left hand side of this latter formula is nothing but

$$\begin{aligned} & \sum_{s=1}^Q \sum_{j \equiv s} \sum_{r=1}^Q \sum_{i \equiv r} m^s m^r \nu^i \nu^j n^i n^j (|\mathbf{u}^i|^2 - \mathbf{u}^i \cdot \mathbf{u}^j) \\ &= \frac{1}{2} \sum_{s=1}^Q \sum_{j \equiv s} \sum_{r=1}^Q \sum_{i \equiv r} m^s m^r \nu^i \nu^j n^i n^j |\mathbf{u}^i - \mathbf{u}^j|^2 \end{aligned}$$

(last equality has been obtained by exchanging the indices $s \leftrightarrow r$ and $i \leftrightarrow j$), and this concludes the proof. \square

Lemma 3.2 *The function $F(\tilde{T})$ defined in (23) is a monotonically increasing function.*

Proof.- We want to prove that the first derivative $F'(\tilde{T})$ is positive for any admissible values of masses, energies, collision frequencies and number densities.

After some computations we get

$$F'(\tilde{T}) = \sum_{s=1}^Q \left(\sum_{j \equiv s} \nu^j n^j \right) \left\{ \frac{3}{2} K + \frac{1}{K\tilde{T}^2} \left[\sum_{j \equiv s} \nu^j \exp \left(-\frac{E^j - E^s}{K\tilde{T}} \right) \right]^{-2} G(\tilde{T}) \right\}, \quad (26)$$

where

$$G(\tilde{T}) = \sum_{i \equiv s} \sum_{j \equiv s} \nu^i \nu^j \exp \left(-\frac{E^i - E^s}{K\tilde{T}} \right) \exp \left(-\frac{E^j - E^s}{K\tilde{T}} \right) \left[(E^i)^2 - E^i E^j \right].$$

Exchanging the indices $i \leftrightarrow j$ yields

$$G(\tilde{T}) = \frac{1}{2} \sum_{i \equiv s} \sum_{j \equiv s} \nu^i \nu^j \exp \left(-\frac{E^i - E^s}{K\tilde{T}} \right) \exp \left(-\frac{E^j - E^s}{K\tilde{T}} \right) (E^i - E^j)^2 \geq 0,$$

so that $F'(\tilde{T}) > 0$. \square

To conclude the proof of existence and uniqueness of solution to equation (22) we observe that, since energy levels $E^i \geq 0$ relevant to any gas G^s are assumed increasing with their index, we get

$$\frac{\sum_{i \equiv s} \nu^i E^i \psi(E^i, \tilde{T})}{\sum_{j \equiv s} \nu^j \psi(E^j, \tilde{T})} = \frac{\nu^s E^s + \sum_{\substack{i \equiv s \\ i \neq s}} \nu^i E^i \exp\left(-\frac{E^i - E^s}{K\tilde{T}}\right)}{\nu^s + \sum_{\substack{i \equiv s \\ i \neq s}} \nu^i \exp\left(-\frac{E^i - E^s}{K\tilde{T}}\right)} \geq \min_{i \equiv s} E^i = E^s, \quad (27)$$

therefore

$$\lim_{\tilde{T} \rightarrow 0} F(\tilde{T}) = \sum_{s=1}^Q \left(\sum_{i \equiv s} \nu^i n^i \right) E^s, \quad \lim_{\tilde{T} \rightarrow +\infty} F(\tilde{T}) = +\infty.$$

In conclusion, we have proved that $F(\tilde{T})$ is a strictly increasing function that for positive \tilde{T} varies from the minimum admissible value for the right hand side of (22) to $+\infty$, hence existence and uniqueness of solution to equation (22) is guaranteed. The BGK algorithm proposed in this section works then properly, since all auxiliary variables may be determined in a unique way (through relations (17), (19), (22)) in terms of the actual macroscopic fields, without no restriction on the collision model, or on energy level properties.

3.1 Steady states of the BGK model for the homogeneous case

As regards collision equilibria of the relaxation model (10), they are defined by $f^i = \mathcal{M}^i$, $\forall i = 1, \dots, QN$, hence they are Maxwellian distributions sharing a common mass velocity $\mathbf{u} = \tilde{\mathbf{u}}$ and a common temperature $T = \tilde{T}$, and with number densities $n^i = \tilde{n}^i$ satisfying thus the relations (12) (assumed for \tilde{n}^i from the beginning), so that they reproduce the correct $(Q+4)$ -parameter family (6)–(7) of collision equilibria deduced from the original Boltzmann equations.

This BGK model yields immediately by its construction the preservation of the same conservation equations obtained from the Boltzmann model. In particular, in space homogeneous conditions, $Q+4$ conservation laws hold:

$$\begin{aligned} N^s &= \sum_{i \equiv s} n^i = \text{constant}, \quad s = 1, \dots, Q, & \rho \mathbf{u} &= \text{constant}, \\ \frac{1}{2} \rho |\mathbf{u}|^2 + \frac{3}{2} nKT + \sum_{s=1}^Q \sum_{i \equiv s} E^i n^i &= \text{constant}. \end{aligned} \quad (28)$$

Because of these first integrals, once the initial parameters n_0^i , \mathbf{u}_0^i , T_0^i are assigned, the

corresponding equilibrium values n_M^i , \mathbf{u}_M , T_M are related to them by

$$\begin{aligned}
\sum_{i \equiv s} n_M^i &= \sum_{i \equiv s} n_0^i & s = 1, \dots, Q, \\
\sum_{s=1}^Q m^s \sum_{i \equiv s} n_M^i \mathbf{u}_M &= \sum_{s=1}^Q m^s \sum_{i \equiv s} n_0^i \mathbf{u}_0^i, \\
\sum_{s=1}^Q \sum_{i \equiv s} \left[\frac{1}{2} m^s n_M^i |\mathbf{u}_M|^2 + \frac{3}{2} n_M^i K T_M + E^i n_M^i \right] & \\
= \sum_{s=1}^Q \sum_{i \equiv s} \left[\frac{1}{2} m^s n_0^i |\mathbf{u}_0^i|^2 + \frac{3}{2} n_0^i K T_0^i + E^i n_0^i \right], & \tag{29}
\end{aligned}$$

and, in addition, they have to fulfill the equilibrium constraint (7). This system is actually a special case of conditions (16), (18), (20) already investigated above, with $\nu^i = 1$ for each gas component, n_M^i , \mathbf{u}_M , T_M in place of \tilde{n}^i , $\tilde{\mathbf{u}}$, \tilde{T} , and with n_0^i , \mathbf{u}_0^i , T_0^i in place of n^i , \mathbf{u}^i , T^i . Therefore the proof of existence and uniqueness of a solution is the same as above, and guarantees that equilibrium values may be uniquely determined in terms of initial data. In particular, it holds $\mathbf{u}_M = \mathbf{u}_0$, $n_M^i = N_0^s \psi(E^i, T_M)$, and T_M is given by the solution of an equation of the form (21) with $\nu^i = 1$:

$$\begin{aligned}
\frac{3}{2} n_0 K T_M + \sum_{s=1}^Q N_0^s \sum_{i \equiv s} E^i \psi(E^i, T_M) & \\
= \frac{1}{2} \sum_{s=1}^Q m^s \sum_{i \equiv s} n_0^i (|\mathbf{u}_0^i|^2 - |\mathbf{u}_0|^2) + \frac{3}{2} \sum_{s=1}^Q \sum_{i \equiv s} n_0^i K T_0^i + \sum_{s=1}^Q \sum_{i \equiv s} E^i n_0^i. & \tag{30}
\end{aligned}$$

3.2 H -Theorem for the BGK model for the homogeneous case

Another significant result of the present BGK model is that it is possible to prove that, in space homogeneous conditions, the physical entropy (9) holding at Boltzmann level is a suitable Lyapunov functional also for the approximated relaxation model (10). Indeed, it has been already proved [16] that such a functional, in the class of admissible distribution functions $\underline{f} = (f^1, \dots, f^{Q_N})$ for which conservations (28) are in order, attains its minimum exactly at the unique Maxwellian stationary point \underline{f}_M relevant to the conserved quantities: for any \underline{f} in that class, we have $H[\underline{f}] > H[\underline{f}_M]$, $\forall \underline{f} \neq \underline{f}_M$. In order to achieve the H -theorem it suffices then to prove the dissipation property

$$\dot{H}[\underline{f}] = \sum_{s=1}^Q \sum_{i \equiv s} \nu^i \int (\mathcal{M}^i - f^i) \log f^i d\mathbf{v} < 0 \quad \forall \underline{f} \neq \underline{f}_M. \tag{31}$$

We start by proving the following equality:

Lemma 3.3

$$\sum_{s=1}^Q \sum_{i \equiv s} \nu^i \int (\mathcal{M}^i - f^i) \log \mathcal{M}^i d\mathbf{v} = 0 \quad \forall \underline{f}. \tag{32}$$

Proof.- It can be easily checked that

$$\begin{aligned} & \sum_{s=1}^Q \sum_{i \equiv s} \nu^i \int (\mathcal{M}^i - f^i) \log \mathcal{M}^i d\mathbf{v} \\ &= \sum_{s=1}^Q \sum_{i \equiv s} \nu^i \int (\mathcal{M}^i - f^i) \left[\log \tilde{n}^i + \frac{3}{2} \log m^s - \frac{3}{2} \log(2\pi K\tilde{T}) - \frac{m^s}{2K\tilde{T}} (|\mathbf{v}|^2 - 2\tilde{\mathbf{u}} \cdot \mathbf{v} + |\tilde{\mathbf{u}}|^2) \right] d\mathbf{v} \end{aligned}$$

and the right hand side, bearing in mind conservations (13), (14), (15), simplifies to

$$\sum_{s=1}^Q \sum_{i \equiv s} \nu^i (\tilde{n}^i - n^i) \left[\log \tilde{n}^i + \frac{E^i}{K\tilde{T}} \right] = \sum_{s=1}^Q \sum_{i \equiv s} \nu^i (\tilde{n}^i - n^i) \left[\log \tilde{N}^s + \frac{E^s}{K\tilde{T}} - \log \left(Z^s(\tilde{T}) \right) \right] = 0, \quad (33)$$

where in last equality we resorted again to condition (16). \square

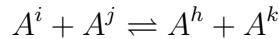
Previous lemma allows to write

$$\dot{H}[\underline{f}] = - \sum_{s=1}^Q \sum_{i \equiv s} \nu^i \int (f^i - \mathcal{M}^i) \log \frac{f^i}{\mathcal{M}^i} d\mathbf{v} \quad (34)$$

and now the usual convexity argument applies for the function $(x-1)\log x$, and we may conclude that $\dot{H}[\underline{f}] \leq 0$, with equal sign if and only if $f^i = \mathcal{M}^i$, $\forall i$, i.e. correspondingly to the unique collision equilibrium \underline{f}_M determined by initial conditions. This completes the proof of (31) and of the H -theorem.

4 Generalization of the BGK approximation to chemically reactive frames

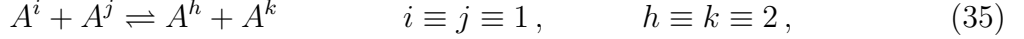
In this section we consider mixtures of polyatomic gases that, besides elastic and inelastic mechanical scattering dealt with in previous sections, may undergo also (bimolecular and reversible) chemical interactions implying also transfer of mass between the colliding particles. More precisely, we will include interactions of the type



with the input particles (A^i, A^j) belonging to gases (G^s, G^r) and the output ones (A^h, A^k) belonging to different species (G^p, G^q) . Without loss of generality we may order species in such a way that $\Delta E_{sr}^{pq} = E^p + E^q - E^s - E^r > 0$; moreover, notice that conservation of total mass in each chemical encounter implies $m^s + m^r = m^p + m^q$. The additional reactive processes entail that collision equilibria of the Boltzmann equations are again Maxwellian distributions (6) with number densities and temperature satisfying conditions (7), but a further constraint appears relating total number densities (N^s, N^r, N^p, N^q) of the gases involved in chemical reactions, that is the mass action law of chemistry [22, 16]. We will emphasize in the sequel how this additional requirement deeply affects the proof of the

consistency of our BGK model. For this reason, we divide this section in two separate parts.

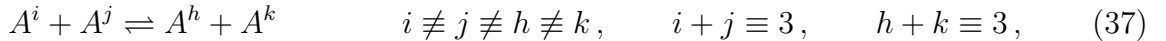
At first, in Subsection 4.1, we consider a binary mixture (of gases G^1 , G^2), whose particles are subject to the reaction



with the assumption $\Delta E_{11}^{22} = 2(E^2 - E^1) > 0$. Conservation of mass simply yields $m^1 = m^2 = m$ therefore in this very simplified case mass transfer disappears; in this sense this may not be considered a real chemical process and G^1 and G^2 should be represented as two different components of the same gas (G^1 in the fundamental state and G^2 in an excited one). However, we believe this case meaningful from the mathematical point of view, to study the effects on the BGK parameters of the simplest mass action law, that is nothing but a linear relation between N^1 and N^2 , with a temperature depending coefficient:

$$N^2 = \frac{Z^2(T)}{Z^1(T)} e^{-\frac{E^2 - E^1}{KT}} N^1. \quad (36)$$

Then, we shall consider a more realistic situation, namely a mixture of four gases G^s , $s = 1, 2, 3, 4$, each one with N different energy levels, subject to a chemical reaction in which a collision between a pair of species G^1 and G^2 may give rise to a pair of particles G^3 and G^4 or vice versa:



with $\Delta E_{12}^{34} = E^3 + E^4 - E^1 - E^2 > 0$. Now conservation of mass yields the relation $m^1 + m^2 = m^3 + m^4$, and mass action law characterizing collision equilibria reads as

$$\frac{N^1 N^2}{N^3 N^4} = \left(\frac{\mu^{12}}{\mu^{34}} \right)^{3/2} \frac{Z^1(T) Z^2(T)}{Z^3(T) Z^4(T)} e^{\frac{\Delta E_{12}^{34}}{KT}}, \quad (38)$$

that is a transcendental equation involving number densities of all interacting gases. The further difficulties in the construction of the BGK model for this reactive frame will be outlined in Subsections 4.2 and 4.3, and also in the relevant numerical simulations presented in Section 5.

4.1 BGK model for a binary mixture

We start considering a mixture of two gases G^1 , G^2 subject to the chemical reaction (35). Collision equilibria of the relevant Boltzmann equations are provided by (6)–(7)–(36), hence they constitute a 5-parameter family. We aim at building up BGK equations like (10)

$$\frac{\partial f^i}{\partial t} + \mathbf{v} \cdot \nabla_{\mathbf{x}} f^i = \nu^i (\mathcal{M}^i - f^i), \quad i = 1, \dots, 2N, \quad (39)$$

where Maxwellian attractor parameters fulfil the constraints

$$\tilde{n}^i = \tilde{N}^s \psi(E^i, \tilde{T}), \quad (40)$$

$$\tilde{N}^2 = \tilde{N}^1 \frac{Z^2(\tilde{T})}{Z^1(\tilde{T})} e^{-\frac{E^2-E^1}{K\tilde{T}}}. \quad (41)$$

We want to obtain the auxiliary parameters in terms of the actual ones by imposing that BGK equations preserve the same collision invariants of the Boltzmann model, that for the present problem read as

$$\sum_{i \equiv 1} \nu^i \int (\mathcal{M}^i - f^i) d\mathbf{v} + \sum_{i \equiv 2} \nu^i \int (\mathcal{M}^i - f^i) d\mathbf{v} = 0, \quad (42)$$

$$m \sum_{s=1}^2 \sum_{i \equiv s} \nu^i \int \mathbf{v} (\mathcal{M}^i - f^i) d\mathbf{v} = \mathbf{0}, \quad (43)$$

$$\sum_{s=1}^2 \sum_{i \equiv s} \nu^i \int \left(\frac{1}{2} m |\mathbf{v}|^2 + E^i \right) (\mathcal{M}^i - f^i) d\mathbf{v} = 0; \quad (44)$$

equations (43), (44) coincide with (14), (15) for a non reactive mixture, corresponding to preservation of global momentum and energy, while the $Q = 2$ equations for single gas densities (13) are here replaced by a unique equation (42) representing conservation of total density only.

Condition (42) provides

$$\sum_{i \equiv 1} \nu^i (\tilde{n}^i - n^i) + \sum_{i \equiv 2} \nu^i (\tilde{n}^i - n^i) = 0, \quad (45)$$

hence

$$\sum_{i=1}^{2N} \nu^i \tilde{n}^i = \sum_{i=1}^{2N} \nu^i n^i. \quad (46)$$

By inserting the expressions (40) into (45) we get

$$\tilde{N}^1 \sum_{i \equiv 1} \nu^i \psi(E^i, \tilde{T}) + \tilde{N}^2 \sum_{i \equiv 2} \nu^i \psi(E^i, \tilde{T}) = \sum_{i=1}^{2N} \nu^i n^i, \quad (47)$$

from which, taking into account (41) and the expression of $\psi(E^i, \tilde{T})$ given in (8), we get

$$\frac{\tilde{N}^1}{Z^1(\tilde{T})} = \left(\sum_{i=1}^{2N} \nu^i n^i \right) / \sum_{i=1}^{2N} \nu^i e^{-\frac{E^i-E^1}{K\tilde{T}}}. \quad (48)$$

Consequently, again from (41),

$$\frac{\tilde{N}^2}{Z^2(\tilde{T})} = \left(\sum_{i=1}^{2N} \nu^i n^i \right) / \sum_{i=1}^{2N} \nu^i e^{-\frac{E^i-E^2}{K\tilde{T}}} \quad (49)$$

hence, in compact form,

$$\frac{\tilde{N}^s}{Z^s(\tilde{T})} = \left(\sum_{i=1}^{2N} \nu^i n^i \right) e^{-\frac{E^s-E^1}{K\tilde{T}}} / \sum_{s=1}^2 \sum_{i \equiv s} \nu^i e^{-\frac{E^i-E^1}{K\tilde{T}}} \quad s = 1, 2. \quad (50)$$

Equations (48), (49) (or, equivalently, (50)) give the auxiliary number densities \tilde{N}^1 , \tilde{N}^2 in terms of the actual densities n^i and the auxiliary temperature \tilde{T} .

Analogously to previous section, equation (43) yields

$$\tilde{\mathbf{u}} = \left(\sum_{i=1}^{2N} \nu^i n^i \mathbf{u}^i \right) / \sum_{i=1}^{2N} \nu^i n^i; \quad (51)$$

finally, skipping intermediate details, constraint (44) provides, analogously to (21),

$$\begin{aligned} & \frac{3}{2} \left(\sum_{i=1}^{2N} \nu^i n^i \right) K\tilde{T} + \sum_{s=1}^2 \frac{\tilde{N}^s}{Z^s(\tilde{T})} \sum_{i \equiv s} \nu^i E^i e^{-\frac{E^i - E^s}{K\tilde{T}}} \\ &= \frac{1}{2} m \sum_{i=1}^{2N} \nu^i n^i (|\mathbf{u}^i|^2 - |\tilde{\mathbf{u}}|^2) + \frac{3}{2} \sum_{i=1}^{2N} \nu^i n^i K T^i + \sum_{i=1}^{2N} \nu^i E^i n^i. \end{aligned} \quad (52)$$

This is a transcendental equation for \tilde{T} that may be cast as

$$\mathcal{H}(\tilde{T}) = \left(\sum_{i=1}^{2N} \nu^i n^i \right)^{-1} \left[\frac{1}{2} m \sum_{i=1}^{2N} \nu^i n^i (|\mathbf{u}^i|^2 - |\tilde{\mathbf{u}}|^2) + \frac{3}{2} \sum_{i=1}^{2N} \nu^i n^i K T^i + \sum_{i=1}^{2N} \nu^i E^i n^i \right], \quad (53)$$

where, taking into account (50) for $\tilde{N}^s/Z^s(\tilde{T})$,

$$\mathcal{H}(\tilde{T}) = \frac{3}{2} K\tilde{T} + \left(\sum_{s=1}^2 \sum_{i \equiv s} \nu^i E^i e^{-\frac{E^i - E^1}{K\tilde{T}}} \right) / \left(\sum_{r=1}^2 \sum_{j \equiv r} \nu^j e^{-\frac{E^j - E^1}{K\tilde{T}}} \right). \quad (54)$$

As already done for a non reactive mixture, we are able to prove that $\mathcal{H}(\tilde{T})$ is an increasing function of its argument. In fact

$$\mathcal{H}'(\tilde{T}) = \frac{3}{2} K + \left(\sum_{r=1}^2 \sum_{j \equiv r} \nu^j e^{-\frac{E^j - E^1}{K\tilde{T}}} \right)^{-2} \frac{1}{K\tilde{T}^2} \mathcal{G}(\tilde{T})$$

where

$$\begin{aligned} \mathcal{G}(\tilde{T}) &= \sum_{s=1}^2 \sum_{r=1}^2 \sum_{i \equiv s} \sum_{j \equiv r} \nu^i \nu^j e^{-\frac{E^i + E^j - 2E^1}{K\tilde{T}}} [(E^i)^2 - E^i E^j] \\ &= \frac{1}{2} \sum_{s=1}^2 \sum_{r=1}^2 \sum_{i \equiv s} \sum_{j \equiv r} \nu^i \nu^j e^{-\frac{E^i + E^j - 2E^1}{K\tilde{T}}} (E^i - E^j)^2 \geq 0. \end{aligned}$$

Moreover, since $E^1 < E^2$ and energy levels of each gas are assumed increasing with their index, we have

$$\lim_{\tilde{T} \rightarrow 0} \mathcal{H}(\tilde{T}) = E^1, \quad \lim_{\tilde{T} \rightarrow +\infty} \mathcal{H}(\tilde{T}) = +\infty,$$

and these are exactly the lower and upper bounds of the right hand side of (53), therefore existence of a unique solution to (53) is guaranteed. In conclusion, following a strategy very similar to the one explained in Section 3 for a non reacting mixture, we have proved that all auxiliary parameters are well defined in terms of the actual ones.

4.2 BGK model for a four–species mixture

The proof of consistency of our BGK model turns out to be much more involved if we consider a mixture of four polyatomic gases G^s , $s = 1, 2, 3, 4$, with chemical reactions (37) in which encounters between particles of species G^1 and G^2 may provide, as output, a pair of gases G^3 and G^4 or vice versa. For this physical situation equilibria are given by distributions (6), with the constraints (7) and (38) for the macroscopic parameters, hence they constitute a 7–parameter family. Consequently, we impose that Maxwellian attractor parameters of our BGK model fulfil the analogous constraints

$$\tilde{n}^i = \tilde{N}^s \psi(E^i, \tilde{T}), \quad (55)$$

$$\frac{\tilde{N}^1 \tilde{N}^2}{\tilde{N}^3 \tilde{N}^4} = \left(\frac{\mu^{12}}{\mu^{34}} \right)^{3/2} \frac{Z^1(\tilde{T}) Z^2(\tilde{T})}{Z^3(\tilde{T}) Z^4(\tilde{T})} e^{\frac{\Delta E_{12}^{34}}{\kappa \tilde{T}}}. \quad (56)$$

Independent collision invariants for the Boltzmann equations correspond to preservation of global momentum and total (kinetic plus internal) energy, and of three suitable combinations of gas densities, for instance $N^1 + N^3$, $N^1 + N^4$, $N^2 + N^4$. Hence, imposing the same also for the BGK model yields

$$\sum_{i \equiv 1} \nu^i \int (\mathcal{M}^i - f^i) d\mathbf{v} + \sum_{i \equiv 3} \nu^i \int (\mathcal{M}^i - f^i) d\mathbf{v} = 0, \quad (57)$$

$$\sum_{i \equiv 1} \nu^i \int (\mathcal{M}^i - f^i) d\mathbf{v} + \sum_{i \equiv 4} \nu^i \int (\mathcal{M}^i - f^i) d\mathbf{v} = 0, \quad (58)$$

$$\sum_{i \equiv 2} \nu^i \int (\mathcal{M}^i - f^i) d\mathbf{v} + \sum_{i \equiv 4} \nu^i \int (\mathcal{M}^i - f^i) d\mathbf{v} = 0, \quad (59)$$

$$\sum_{s=1}^4 \sum_{i \equiv s} \nu^i \int m^s \mathbf{v} (\mathcal{M}^i - f^i) d\mathbf{v} = \mathbf{0}, \quad (60)$$

$$\sum_{s=1}^4 \sum_{i \equiv s} \nu^i \int \left(\frac{1}{2} m^s |\mathbf{v}|^2 + E^i \right) (\mathcal{M}^i - f^i) d\mathbf{v} = 0. \quad (61)$$

Equations (57)–(59) provide

$$\sum_{i \equiv s} \nu^i (\tilde{n}^i - n^i) + \sum_{i \equiv r} \nu^i (\tilde{n}^i - n^i) = 0 \quad (s, r) = (1, 3), (1, 4), (2, 4).$$

Linear combinations of these equalities yield

$$\sum_{i=1}^{4N} \nu^i \tilde{n}^i = \sum_{i=1}^{4N} \nu^i n^i \quad (62)$$

and

$$\sum_{s=1}^4 m^s \sum_{i \equiv s} \nu^i \tilde{n}^i = \sum_{s=1}^4 m^s \sum_{i \equiv s} \nu^i n^i. \quad (63)$$

More precisely, bearing in mind the expression (55), conditions (57)–(59) allow to express three among the auxiliary number densities (i.e. \tilde{N}^2 , \tilde{N}^3 , \tilde{N}^4) in terms of the fourth one (\tilde{N}^1), the auxiliary temperature \tilde{T} and the actual number densities n^i :

$$\begin{aligned}\tilde{N}^2 &= \frac{1}{\sum_{i \equiv 2} \nu^i \psi(E^i, \tilde{T})} \left\{ \sum_{i \equiv 2} \nu^i n^i - \sum_{i \equiv 1} \nu^i n^i + \left(\sum_{i \equiv 1} \nu^i \psi(E^i, \tilde{T}) \right) \tilde{N}^1 \right\}, \\ \tilde{N}^3 &= \frac{1}{\sum_{i \equiv 3} \nu^i \psi(E^i, \tilde{T})} \left\{ \sum_{i \equiv 3} \nu^i n^i + \sum_{i \equiv 1} \nu^i n^i - \left(\sum_{i \equiv 1} \nu^i \psi(E^i, \tilde{T}) \right) \tilde{N}^1 \right\}, \\ \tilde{N}^4 &= \frac{1}{\sum_{i \equiv 4} \nu^i \psi(E^i, \tilde{T})} \left\{ \sum_{i \equiv 4} \nu^i n^i + \sum_{i \equiv 1} \nu^i n^i - \left(\sum_{i \equiv 1} \nu^i \psi(E^i, \tilde{T}) \right) \tilde{N}^1 \right\},\end{aligned}\quad (64)$$

that may be written in compact form as

$$\frac{\tilde{N}^s}{Z^s(\tilde{T})} = \frac{1}{\sum_{i \equiv s} \nu^i e^{-\frac{E^i - E^s}{KT}}} \left\{ \sum_{i \equiv s} \nu^i n^i - \lambda^s \sum_{i \equiv 1} \nu^i n^i + \lambda^s \left(\sum_{i \equiv 1} \nu^i e^{-\frac{E^i - E^1}{KT}} \right) \frac{\tilde{N}^1}{Z^1(\tilde{T})} \right\} \quad (65)$$

where λ^s are the stoichiometric coefficients $\lambda^1 = \lambda^2 = 1$, $\lambda^3 = \lambda^4 = -1$.

Momentum conservation (60), analogously to previous sections and taking into account (63), yields

$$\tilde{\mathbf{u}} = \left(\sum_{s=1}^4 m^s \sum_{i \equiv s} \nu^i n^i \mathbf{u}^i \right) / \left(\sum_{s=1}^4 m^s \sum_{i \equiv s} \nu^i n^i \right), \quad (66)$$

while energy conservation (61) provides an equation very similar to (52)

$$\begin{aligned}\frac{3}{2} \left(\sum_{i=1}^{4N} \nu^i n^i \right) K\tilde{T} + \sum_{s=1}^4 \frac{\tilde{N}^s}{Z^s(\tilde{T})} \sum_{i \equiv s} \nu^i E^i e^{-\frac{E^i - E^s}{KT}} \\ = \frac{1}{2} \sum_{s=1}^4 m^s \sum_{i \equiv s} \nu^i n^i (|\mathbf{u}^i|^2 - |\tilde{\mathbf{u}}|^2) + \frac{3}{2} \sum_{i=1}^{4N} \nu^i n^i K T^i + \sum_{i=1}^{4N} \nu^i E^i n^i.\end{aligned}\quad (67)$$

At this point (and this is the main difference with respect to the inert case and the binary mixture), last equality (67) together with the mass action law (56) are a set of two transcendental equations for the two unknown fields \tilde{N}^1 and \tilde{T} , and the rest of this subsection will be devoted to proving that, for any values of actual parameters and collision frequencies, equations (56)–(67) have a unique admissible solution

$$(\tilde{N}^1, \tilde{T}) \in \left\{ \tilde{N}^1 > 0, \quad \tilde{T} > 0 : \tilde{N}^2 > 0, \quad \tilde{N}^3 > 0, \quad \tilde{N}^4 > 0 \right\},$$

where \tilde{N}^2 , \tilde{N}^3 , \tilde{N}^4 are provided by (64). For future convenience it is better to write the system which is investigated using as unknown variables \tilde{T} and

$$Y^1 = \frac{\tilde{N}^1}{Z^1(\tilde{T})} \sum_{i \equiv 1} \nu^i e^{-\frac{E^i - E^1}{KT}}. \quad (68)$$

With these notations, equations (67) and (56) may be cast as

$$\frac{3}{2} \left(\sum_{i=1}^{4N} \nu^i n^i \right) K\tilde{T} + \sum_{s=1}^4 Y^s \frac{\sum_{i \equiv s} \nu^i E^i e^{-\frac{E^i - E^s}{K\tilde{T}}}}{\sum_{j \equiv s} \nu^j e^{-\frac{E^j - E^s}{K\tilde{T}}}} = \Lambda, \quad (69)$$

$$\frac{Y^1 Y^2}{Y^3 Y^4} = \left(\frac{\mu^{12}}{\mu^{34}} \right)^{3/2} \frac{\sum_{i \equiv 1} \nu^i e^{-E^i/K\tilde{T}} \sum_{j \equiv 2} \nu^j e^{-E^j/K\tilde{T}}}{\sum_{h \equiv 3} \nu^h e^{-E^h/K\tilde{T}} \sum_{k \equiv 4} \nu^k e^{-E^k/K\tilde{T}}} \quad (70)$$

where Λ is simply the right hand side of (67), thus it is a known explicit function of the actual parameters (it is independent from our unknown fields), and

$$Y^s = \frac{\tilde{N}^s}{Z^s(\tilde{T})} \sum_{i \equiv s} \nu^i e^{-\frac{E^i - E^s}{K\tilde{T}}} = \sum_{i \equiv s} \nu^i n^i - \lambda^s \sum_{i \equiv 1} \nu^i n^i + \lambda^s Y^1 \quad s = 2, 3, 4. \quad (71)$$

We note that by inserting expressions (71) into (69), this becomes a linear equation in the unknown Y^1 , so it is possible to obtain a (very complicated, but explicit) expression for Y^1 in terms of \tilde{T} . Skipping calculation details, we get

$$Y^1 = \sum_{i \equiv 1} \nu^i n^i + \mathcal{S}(\tilde{T}) \quad (72)$$

with

$$\mathcal{S}(\tilde{T}) = \frac{\mathcal{N}(\tilde{T})}{\mathcal{D}(\tilde{T})}, \quad (73)$$

where the numerator \mathcal{N} takes the form

$$\mathcal{N}(\tilde{T}) = \Lambda - \frac{3}{2} \sum_{s=1}^4 \left(\sum_{i \equiv s} \nu^i n^i \right) K\tilde{T} - \sum_{s=1}^4 \left(\sum_{i \equiv s} \nu^i n^i \right) \frac{\sum_{i \equiv s} \nu^i E^i e^{-\frac{E^i - E^s}{K\tilde{T}}}}{\sum_{j \equiv s} \nu^j e^{-\frac{E^j - E^s}{K\tilde{T}}}}, \quad (74)$$

and the denominator \mathcal{D} is given by

$$\mathcal{D}(\tilde{T}) = \sum_{s=1}^4 \lambda^s \frac{\sum_{i \equiv s} \nu^i E^i e^{-\frac{E^i - E^s}{K\tilde{T}}}}{\sum_{j \equiv s} \nu^j e^{-\frac{E^j - E^s}{K\tilde{T}}}}. \quad (75)$$

Therefore there remains only one transcendental equation, coming from mass action law (70); using (71) and (72), it may be cast as

$$\mathcal{G}(\tilde{T}) = \left(\frac{\mu^{12}}{\mu^{34}} \right)^{3/2}, \quad (76)$$

where

$$\mathcal{G}(\tilde{T}) = \frac{\left[\sum_{i \equiv 1} \nu^i n^i + \mathcal{S}(\tilde{T}) \right] \left[\sum_{j \equiv 2} \nu^j n^j + \mathcal{S}(\tilde{T}) \right]}{\left[\sum_{h \equiv 3} \nu^h n^h - \mathcal{S}(\tilde{T}) \right] \left[\sum_{k \equiv 4} \nu^k n^k - \mathcal{S}(\tilde{T}) \right]} \frac{\sum_{h \equiv 3} \nu^h e^{-\frac{E^h - E^3}{K\tilde{T}}} \sum_{k \equiv 4} \nu^k e^{-\frac{E^k - E^4}{K\tilde{T}}}}{\sum_{i \equiv 1} \nu^i e^{-\frac{E^i - E^1}{K\tilde{T}}} \sum_{j \equiv 2} \nu^j e^{-\frac{E^j - E^2}{K\tilde{T}}}} e^{-\frac{\Delta E_{12}^{34}}{K\tilde{T}}}. \quad (77)$$

We must prove that equation (76) admits a positive solution in the range for which all densities, hence all Y^s , are positive; this means that we have to prove existence and uniqueness of a solution to (76) in the set

$$A = \left\{ \tilde{T} > 0 : \max \left(-\sum_{i \equiv 1} \nu^i n^i, -\sum_{i \equiv 2} \nu^i n^i \right) < \mathcal{S}(\tilde{T}) < \min \left(\sum_{i \equiv 3} \nu^i n^i, \sum_{i \equiv 4} \nu^i n^i \right) \right\}. \quad (78)$$

The proof will be divided into several steps:

- at first we prove that in any interval $(\tilde{T}_1, \tilde{T}_2) \subseteq A$ in which the sign of the denominator $\mathcal{D}(\tilde{T})$ does not change, the function $\mathcal{S}(\tilde{T})$ is strictly monotone;
- then, we actually notice that A is a connected set of \mathbb{R}^+ and, except for a very particular choice of initial data, the sign of $\mathcal{D}(\tilde{T})$ does not change in A ;
- finally we prove that $\mathcal{G}(\tilde{T})$ is strictly monotone in A and it ranges from 0 to $+\infty$, providing does a unique solution to equation (76).

Let us start by the first point:

Lemma 4.1 *In any interval $(\tilde{T}_1, \tilde{T}_2) \subseteq A$ in which the sign of $\mathcal{D}(\tilde{T})$ (given in (75)) does not change, the function $\mathcal{S}(\tilde{T})$ (given in (73)) is strictly monotone: more precisely, $\mathcal{S}(\tilde{T})$ is increasing if $\mathcal{D}(\tilde{T}) < 0$, and $\mathcal{S}(\tilde{T})$ is decreasing if $\mathcal{D}(\tilde{T}) > 0$.*

Proof.- Since $\mathcal{S}(\tilde{T}) = \mathcal{N}(\tilde{T})/\mathcal{D}(\tilde{T})$ with \mathcal{N} and \mathcal{D} given in (74) and (75), respectively, we have

$$\mathcal{S}'(\tilde{T}) = \frac{1}{\mathcal{D}^2(\tilde{T})} \left(\mathcal{N}'(\tilde{T})\mathcal{D}(\tilde{T}) - \mathcal{N}(\tilde{T})\mathcal{D}'(\tilde{T}) \right) = \frac{\mathcal{N}'(\tilde{T})}{\mathcal{D}(\tilde{T})} - \mathcal{S}(\tilde{T}) \frac{\mathcal{D}'(\tilde{T})}{\mathcal{D}(\tilde{T})}. \quad (79)$$

It can be easily checked that

$$\mathcal{D}'(\tilde{T}) = \sum_{s=1}^4 \lambda^s \frac{1}{\left[\sum_{k \equiv s} \nu^k e^{-\frac{E^k - E^s}{K\tilde{T}}} \right]^2} \frac{1}{K\tilde{T}^2} \sum_{i \equiv s} \sum_{j \equiv s} \nu^i \nu^j \left[(E^i)^2 - E^i E^j \right] e^{-\frac{E^i - E^s}{K\tilde{T}}} e^{-\frac{E^j - E^s}{K\tilde{T}}}$$

hence, by exchanging indices $i \leftrightarrow j$,

$$\mathcal{D}'(\tilde{T}) = \sum_{s=1}^4 \lambda^s F^s(\tilde{T}) \quad (80)$$

where

$$F^s(\tilde{T}) = \frac{1}{2K\tilde{T}^2} \frac{1}{\left[\sum_{k \equiv s} \nu^k e^{-\frac{E^k - E^s}{K\tilde{T}}} \right]^2} \sum_{i \equiv s} \sum_{j \equiv s} \nu^i \nu^j (E^i - E^j)^2 e^{-\frac{E^i - E^s}{K\tilde{T}}} e^{-\frac{E^j - E^s}{K\tilde{T}}} \geq 0. \quad (81)$$

On the other hand, owing to analogous arguments,

$$\mathcal{N}'(\tilde{T}) = -\frac{3}{2} K \sum_{s=1}^4 \left(\sum_{i \equiv s} \nu^i n^i \right) - \sum_{s=1}^4 \left(\sum_{i \equiv s} \nu^i n^i \right) F^s(\tilde{T}) < 0. \quad (82)$$

Coming back to (79) we get

$$\begin{aligned} \mathcal{S}'(\tilde{T}) &= -\frac{1}{\mathcal{D}(\tilde{T})} \left\{ \frac{3}{2} K \sum_{s=1}^4 \left(\sum_{i \equiv s} \nu^i n^i \right) + \sum_{s=1}^4 \left(\sum_{i \equiv s} \nu^i n^i \right) F^s(\tilde{T}) + \mathcal{S}(\tilde{T}) \sum_{s=1}^4 \lambda^s F^s(\tilde{T}) \right\} \\ &= -\frac{1}{\mathcal{D}(\tilde{T})} \left\{ \frac{3}{2} K \sum_{s=1}^4 \left(\sum_{i \equiv s} \nu^i n^i \right) + \sum_{s=1}^4 \left[\sum_{i \equiv s} \nu^i n^i + \lambda^s \mathcal{S}(\tilde{T}) \right] F^s(\tilde{T}) \right\} \end{aligned} \quad (83)$$

where the content of the curly brackets is strictly positive for $\tilde{T} \in A$, hence the sign of $\mathcal{S}'(\tilde{T})$ is opposite to the one of $\mathcal{D}(\tilde{T})$, and this concludes the proof. \square

From the proof of the previous lemma we can note that the numerator \mathcal{N} is a strictly decreasing function (see (82)) ranging from

$$\begin{aligned} \lim_{\tilde{T} \rightarrow 0} \mathcal{N}(\tilde{T}) &= \Lambda - \sum_{s=1}^4 \sum_{i \equiv s} \nu^i n^i E^s \\ &= \frac{1}{2} \sum_{s=1}^4 m^s \sum_{i \equiv s} \nu^i n^i (|\mathbf{u}^i|^2 - |\tilde{\mathbf{u}}|^2) + \frac{3}{2} \sum_{i=1}^{4N} \nu^i n^i K T^i + \sum_{s=1}^4 \sum_{i \equiv s} \nu^i (E^i - E^s) n^i > 0 \end{aligned}$$

(see also Lemma 3.1) to

$$\lim_{\tilde{T} \rightarrow +\infty} \mathcal{N}(\tilde{T}) = -\infty,$$

therefore $\mathcal{S}(\tilde{T})$ admits a unique root $\tilde{T}^* \in A$. In order to avoid special singularities in the definition of $\mathcal{S}(\tilde{T})$ we neglect here the very particular situation in which initial data, internal energies and collision frequencies are chosen in such a way that even $\mathcal{D}(\tilde{T}^*) = 0$: in this case $\tilde{T} = T^*$ would be a trivial solution of (69), and correspondingly equation (70) would become an algebraic second order equation for the unknown Y^1 .

As concerns $\mathcal{D}(\tilde{T})$, using the same technique as in (27) we note that

$$\lim_{\tilde{T} \rightarrow 0} \mathcal{D}(\tilde{T}) = -\Delta E_{12}^{34} < 0, \quad \lim_{\tilde{T} \rightarrow +\infty} \mathcal{D}(\tilde{T}) = \sum_{s=1}^4 \lambda^s \frac{\sum_{i \equiv s} \nu^i E^i}{\sum_{j \equiv s} \nu^j}. \quad (84)$$

The sign of $\lim_{\tilde{T} \rightarrow +\infty} \mathcal{D}(\tilde{T})$ depends on internal energies and collision frequencies; in any case, if there is a change of sign of the function $\mathcal{D}(\tilde{T})$, namely a value $\tilde{T}^\# \neq \tilde{T}^*$ such that $\mathcal{D}(\tilde{T}^\#) = 0$, correspondingly we have $\lim_{\tilde{T} \rightarrow \tilde{T}^\#} \mathcal{S}(\tilde{T}) = \pm\infty$, hence in a suitable neighborhood of $\tilde{T}^\#$ the constraint (78) is certainly not fulfilled, and this zone is thus out of interest for our physical problem. Therefore we may assert that in each interval $(\tilde{T}_1, \tilde{T}_2) \subseteq A$, the sign of $\mathcal{D}(\tilde{T})$ does not change. Consequently, we may prove the following:

Lemma 4.2 *The set A defined in (78) is a connected set of \mathbb{R}^+ ; in other words, if $\tilde{T}_1, \tilde{T}_2 \in A$ (with $\tilde{T}_1 < \tilde{T}_2$), then also each $\tilde{T} \in \mathbb{R}^+$ such that $\tilde{T}_1 < \tilde{T} < \tilde{T}_2$ belongs to the set A .*

Proof.- First of all notice that in each maximal connected subset $(\tilde{T}_a, \tilde{T}_b)$ (i.e. “connected component”) of A the function $\mathcal{S}(\tilde{T}) = \mathcal{N}(\tilde{T})/\mathcal{D}(\tilde{T})$ is a continuous and strictly monotone function ranging from its infimum admissible value, that is $\max(-\sum_{i \equiv 1} \nu^i n^i, -\sum_{i \equiv 2} \nu^i n^i)$ if $\tilde{T}_a \neq 0$ or $\mathcal{S}(0) < 0$ if $\tilde{T}_a = 0$, to its supremum: $\min(\sum_{i \equiv 3} \nu^i n^i, \sum_{i \equiv 4} \nu^i n^i)$. Hence there is a suitable value in $(\tilde{T}_a, \tilde{T}_b)$ making the function \mathcal{S} vanish; this is of course \tilde{T}^* , the unique root of $\mathcal{N}(\tilde{T})$, and this implies that the set A is connected. \square

Finally, we may prove the last step:

Lemma 4.3 *In the set A , the function $\mathcal{G}(\tilde{T})$ ranges from 0 to $+\infty$ in a strictly monotone way: more precisely, $\mathcal{G}(\tilde{T})$ increases if $\mathcal{D}(\tilde{T}) < 0$, and decreases if $\mathcal{D}(\tilde{T}) > 0$.*

Proof.- Skipping details, it can be checked that the derivative of $\mathcal{G}(\tilde{T})$ may be cast as

$$\begin{aligned} \mathcal{G}'(\tilde{T}) &= \\ &= \mathcal{G}(\tilde{T}) \left\{ \mathcal{S}'(\tilde{T}) \sum_{s=1}^4 \frac{1}{\sum_{i \equiv s} \nu^i n^i + \lambda^s \mathcal{S}(\tilde{T})} - \frac{1}{K\tilde{T}^2} \sum_{s=1}^4 \lambda^s \frac{\sum_{i \equiv s} \nu^i (E^i - E^s) e^{-\frac{E^i - E^s}{K\tilde{T}}}}{\sum_{j \equiv s} \nu^j e^{-\frac{E^j - E^s}{K\tilde{T}}}} + \frac{\Delta E_{12}^{34}}{K\tilde{T}^2} \right\} \\ &= \mathcal{G}(\tilde{T}) \left\{ \mathcal{S}'(\tilde{T}) \sum_{s=1}^4 \frac{1}{\sum_{i \equiv s} \nu^i n^i + \lambda^s \mathcal{S}(\tilde{T})} - \frac{1}{K\tilde{T}^2} \mathcal{D}(\tilde{T}) \right\} \end{aligned} \tag{85}$$

and, bearing in mind also Lemma 4.1, the content of the curly brackets has a sign opposite to the one of $\mathcal{D}(\tilde{T})$. Moreover, notice that for \tilde{T} ranging in the interval $A = (\tilde{T}_{\min}, \tilde{T}_{\max})$ defined in (78), the function $\mathcal{G}(\tilde{T})$ varies (in a monotonic way) from 0 to $+\infty$. This is true even if $\tilde{T}_{\min} = 0$ since $\lim_{\tilde{T} \rightarrow 0} \mathcal{G}(\tilde{T}) = 0$. Therefore existence of a unique solution to (76) in the range (78) is guaranteed. \square

4.3 H -Theorem for the homogeneous case

To conclude this section we show that, in space homogeneous conditions, the H -Theorem holds also when chemical reactions are considered. At the Boltzmann level, it has been already proved [16] that the physical entropy (9) attains its minimum exactly at the unique

Maxwellian stationary point \underline{f}_M relevant to the conserved quantities: $H[\underline{f}] > H[\underline{f}_M]$, $\forall \underline{f} \neq \underline{f}_M$. Therefore, H -theorem is proved if the entropy production is negative:

$$\dot{H}[\underline{f}] = \sum_{s=1}^4 \sum_{i \equiv s} \nu^i \int (\mathcal{M}^i - f^i) \log f^i d\mathbf{v} < 0 \quad \forall \underline{f} \neq \underline{f}_M.$$

To obtain the sign of entropy production we follow a well known strategy (as in Subsection 3.2), whose principal ingredient is the following equality (as Lemma 3.3 for the case without chemical reactions):

Lemma 4.4

$$\sum_{s=1}^4 \sum_{i \equiv s} \nu^i \int (\mathcal{M}^i - f^i) \log \mathcal{M}^i d\mathbf{v} = 0 \quad \forall \underline{f}. \quad (86)$$

Proof.- We can generalize the calculations done in [5] to the case of several energy levels. Using the conservation equations (57), (58), (59), (60) and (61) and the fact that equations (57)-(59) can be rewritten as:

$$\sum_{i \equiv s} \nu^i (\tilde{n}^i - n^i) = \lambda^s \sum_{i \equiv 1} \nu^i (\tilde{n}^i - n^i),$$

it can be easily checked that

$$\begin{aligned} & \sum_{s=1}^4 \sum_{i \equiv s} \nu^i \int (\mathcal{M}^i - f^i) \log \mathcal{M}^i d\mathbf{v} \\ &= \sum_{s=1}^4 \sum_{i \equiv s} \nu^i (\tilde{n}^i - n^i) \left[\log \tilde{N}^s + \frac{E^s}{K\tilde{T}} - \log \left(Z^s(\tilde{T}) \right) + \frac{3}{2} \log m^s \right] \\ &= \sum_{i \equiv 1} \nu^i (\tilde{n}^i - n^i) \sum_{s=1}^4 \lambda^s \left[\log \tilde{N}^s + \frac{E^s}{K\tilde{T}} - \log \left(Z^s(\tilde{T}) \right) + \frac{3}{2} \log m^s \right] \\ &= \sum_{i \equiv 1} \nu^i (\tilde{n}^i - n^i) \log \left[\frac{\tilde{N}^1 \tilde{N}^2}{\tilde{N}^3 \tilde{N}^4} \left(\frac{m^3 m^4}{m^1 m^2} \right)^{3/2} \frac{Z^3(\tilde{T}) Z^4(\tilde{T})}{Z^1(\tilde{T}) Z^2(\tilde{T})} e^{-\frac{\Delta E_{12}^{34}}{K\tilde{T}}} \right] = 0, \end{aligned}$$

where last equality holds because of the constraint (56). \square

And again, using this lemma we can write

$$\dot{H}[\underline{f}] = - \sum_{s=1}^4 \sum_{i \equiv s} \nu^i \int (f^i - \mathcal{M}^i) \log \frac{f^i}{\mathcal{M}^i} d\mathbf{v} \quad (87)$$

and the usual convexity argument applies for the function $(x-1) \log x$ giving us $\dot{H}[\underline{f}] \leq 0$, with equal sign if and only if $f^i = \mathcal{M}^i$, $\forall i$, i.e. correspondingly to the unique collision equilibrium \underline{f}_M determined by initial conditions. This completes the proof of the H -theorem.

5 Numerical simulations

In this section we report some calculations in order to check the response of the BGK model proposed in the previous sections both for inert and for reactive situations. Some preliminary test cases will be shown only for illustrative purposes, while the comparison between Boltzmann and BGK descriptions for physically meaningful problems, such as travelling shock waves or Riemann problem, is left as future work.

At first, we specialize our BGK equations to gases drifting only along the axial direction (with respect to $x_1 = x$), but with distribution functions still depending on the three-dimensional velocity vector \mathbf{v} . As pointed out in [3], in this frame it is convenient to introduce the new unknowns

$$\Phi^i = \int_{\mathbb{R}} \int_{\mathbb{R}} f^i dv_2 dv_3, \quad \Psi^i = \int_{\mathbb{R}} \int_{\mathbb{R}} (v_2^2 + v_3^2) f^i dv_2 dv_3, \quad i = 1, \dots, QN, \quad (88)$$

depending only on one space and one velocity variable. With these new unknowns, the fundamental macroscopic fields may be reconstructed as

$$\begin{aligned} n^i &= \int_{\mathbb{R}} \Phi^i dv, & u^i &= \frac{1}{n^i} \int_{\mathbb{R}} v \Phi^i dv, \\ \frac{3KT^i}{m^i} &= \frac{1}{n^i} \left[\int_{\mathbb{R}} (v - u^i)^2 \Phi^i dv + \int_{\mathbb{R}} \Psi^i dv \right], & i &= 1, \dots, QN, \end{aligned} \quad (89)$$

while the BGK equations for Φ^i , Ψ^i , for $i = 1, \dots, QN$, read as

$$\begin{aligned} \frac{\partial \Phi^i}{\partial t} + v \frac{\partial \Phi^i}{\partial x} &= \nu^i (M^i - \Phi^i) \\ \frac{\partial \Psi^i}{\partial t} + v \frac{\partial \Psi^i}{\partial x} &= \nu^i \left(\frac{2K\tilde{T}}{m^i} M^i - \Psi^i \right), \end{aligned} \quad (90)$$

where

$$M^i(v) = \tilde{N}^s \frac{\exp\left(-\frac{E^i - E^s}{K\tilde{T}}\right)}{Z^s(\tilde{T})} \left(\frac{m^i}{2\pi K\tilde{T}}\right)^{1/2} \exp\left[-\frac{m^i}{2K\tilde{T}}(v - \tilde{u})^2\right], \quad (91)$$

and \tilde{N}^s , \tilde{u} and \tilde{T} are the auxiliary parameters of our BGK model.

In this paper we simulate only the space homogeneous version of system (90), using a third order TVD (*Total Variation Diminishing*) Runge-Kutta explicit method which describes its evolution on time. In this way, we can get the distribution functions for every time step and, consequently, all the macroscopic quantities, by simple integrations of the distribution functions. Moreover, the evolution on time of the entropy functional is obtained using the solutions f^i , which are approximated by means of an explicit Runge-Kutta scheme, since the collision operator (namely right hand side of equation (10)) can be approximated through the macroscopic quantities. To define auxiliary macroscopic quantities we follow the described algorithms in Section 3, for the case with only mechanical interaction, and Section 4, where chemical effect is also taken into account. We recall that for inert mixtures expressions of \tilde{N}^s and \tilde{u} are given in (17) and (19), respectively,

while temperature \tilde{T} is provided by the transcendental equation (22); in the case of four reactive gases, \tilde{u} has the same expression (see (66)), number densities are provided by (64) and (72) (with Y^1 defined in (68)), while temperature is defined through the transcendental equation (76). Thus, in both cases we must solve a transcendental equation and we do it numerically using the bisection method. Notice that the numerical scheme to solve the equation (76) has an additional ingredient (not necessary for equation (22)): we need to find the solution of the equation in the range of values of \tilde{T} which are in A (see (78)). This means that, for the bisection method, at every time step the left and the right \tilde{T} values have to be suitably determined in order to restrict our analysis to the admissible set A . To do that, we start with a small value of \tilde{T} which is increasing, with a tiny step, until it satisfies

$$\max \left(-\sum_{i \equiv 1} \nu^i n^i, -\sum_{i \equiv 2} \nu^i n^i \right) < \mathcal{S}(\tilde{T}).$$

This value is fixed as left value, a , for the bisection method. To obtain the right value, b , we proceed in analogous way, starting with a plus a small positive quantity, which is increasing, with a tiny step, until it is satisfying

$$\mathcal{S}(\tilde{T}) < \min \left(\sum_{i \equiv 3} \nu^i n^i, \sum_{i \equiv 4} \nu^i n^i \right);$$

last value fulfilling this inequality is taken as right value b .

The analytical proofs performed in Sections 3 and 4 hold independently from the choice of collision frequencies ν^i involved in the BGK operator. On the other hand, in numerical simulations relaxation parameters ν^i are essential quantities which measure the rate at which BGK equations drive distributions towards equilibrium, hence they should be somehow related to the rate of convergence predicted by the original Boltzmann equations. As already assumed in numerical simulations relevant to different BGK models for mixtures [15, 3], we impose here that averaged loss terms of Boltzmann equations equal the BGK ones. More precisely, for a non reacting mixture we impose

$$\frac{1}{n^i} \sum_{(j,h,k) \in D_i} \iiint (K_i^{ijhk})^- [f](\mathbf{v}, \mathbf{w}, \hat{\mathbf{n}}') d\mathbf{v} d\mathbf{w} d\hat{\mathbf{n}}' = \frac{1}{n^i} \nu^i \int f^i(\mathbf{v}) d\mathbf{v}, \quad 1 \leq i \leq QN$$

where $(K_i^{ijhk})^-$ denotes the second (negative) addend in K_i^{ijhk} given in (2), hence

$$\nu^i = \frac{1}{n^i} \sum_{(j,h,k) \in D_i} \iiint \Theta(g^2 - \delta_{ij}^{hk}) B_{ij}^{hk}(g, \hat{\mathbf{n}} \cdot \hat{\mathbf{n}}') f^i(\mathbf{v}) f^j(\mathbf{w}) d\mathbf{v} d\mathbf{w} d\hat{\mathbf{n}}', \quad 1 \leq i \leq QN. \quad (92)$$

For all exothermic collisions, namely for all encounters $A^i + A^j \rightarrow A^h + A^k$ such that $\Delta E_{ij}^{hk} \leq 0$, we assume that differential cross sections are of Maxwell molecule type:

$$\int B_{ij}^{hk}(g, \hat{\mathbf{n}} \cdot \hat{\mathbf{n}}') d\hat{\mathbf{n}}' = \text{constant} = \nu_{ij}^{hk}, \quad (93)$$

and, for symmetry reasons, $\nu_{ji}^{kh} = \nu_{ij}^{hk}$. The differential cross sections B_{hk}^{ij} relevant to the reverse (endothermic) collisions are related to the exothermic ones by means of the micro-reversibility condition [16]

$$(\mu^{ij})^2 g B_{ij}^{hk}(g, \hat{\mathbf{n}} \cdot \hat{\mathbf{n}}') = (\mu^{hk})^2 g_{ij}^{hk} \Theta(g^2 - \delta_{ij}^{hk}) B_{hk}^{ij}(g_{ij}^{hk}, \hat{\mathbf{n}} \cdot \hat{\mathbf{n}}'),$$

hence it can be easily checked that

$$\int B_{hk}^{ij}(g, \hat{\mathbf{n}} \cdot \hat{\mathbf{n}}') d\hat{\mathbf{n}}' = \left(\frac{\mu^{ij}}{\mu^{hk}} \right)^{3/2} \sqrt{1 - \frac{\delta_{hk}^{ij}}{g^2}} \nu_{ij}^{hk}. \quad (94)$$

Therefore, the integrals appearing in (92) result immediately in $\nu_{ij}^{hk} n^j$ for the exothermic collisions, while the endothermic ones have to be managed numerically; however, an explicit solution is possible if we replace distributions by Maxwellian shapes characterized by actual number densities n^i , mass velocity \mathbf{u} and temperature T , and this will be the choice adopted here. Skipping all intermediate details, if we set

$$\begin{aligned} D_i^{\text{ex}} &= \left\{ j, h, k \leq Q N : h \equiv i, \quad k \equiv j, \quad \Delta E_{ij}^{hk} \leq 0 \right\}, \\ D_i^{\text{en}} &= \left\{ j, h, k \leq Q N : h \equiv i, \quad k \equiv j, \quad \Delta E_{ij}^{hk} > 0 \right\}, \end{aligned} \quad (95)$$

collision frequencies in our numerical examples for inert mixtures will be

$$\nu^i = \sum_{(j, h, k) \in D_i^{\text{ex}}} \nu_{ij}^{hk} n^j + \sum_{(j, h, k) \in D_i^{\text{en}}} \nu_{hk}^{ij} n^j e^{-\frac{\Delta E_{ij}^{hk}}{KT}} \quad (96)$$

(ratios between reduced masses simplify to 1 since there is no transfer of mass). Analogously, to analyze the BGK model with chemical reaction we set:

$$\begin{aligned} D_i^{\text{ex-mechanical}} &= \left\{ j, h, k \leq 4 N : h \equiv i, \quad k \equiv j, \quad \Delta E_{ij}^{hk} \leq 0 \right\}, \\ D_i^{\text{ex-chemical}} &= \left\{ j, h, k \leq 4 N : i \not\equiv j \not\equiv h \not\equiv k, \quad i + j \equiv 3, \quad h + k \equiv 3, \quad \Delta E_{ij}^{hk} \leq 0 \right\}, \\ D_i^{\text{en-mechanical}} &= \left\{ j, h, k \leq 4 N : h \equiv i, \quad k \equiv j, \quad \Delta E_{ij}^{hk} > 0 \right\}, \\ D_i^{\text{en-chemical}} &= \left\{ j, h, k \leq 4 N : i \not\equiv j \not\equiv h \not\equiv k, \quad i + j \equiv 3, \quad h + k \equiv 3, \quad \Delta E_{ij}^{hk} > 0 \right\}, \end{aligned} \quad (97)$$

and collision frequencies in our simulations will be

$$\begin{aligned} \nu^i &= \sum_{(j, h, k) \in D_i^{\text{ex-mechanical}}} \nu_{ij}^{hk} n^j + \sum_{(j, h, k) \in D_i^{\text{ex-chemical}}} \nu_{ij}^{hk} n^j \\ &+ \sum_{(j, h, k) \in D_i^{\text{en-mechanical}}} \nu_{hk}^{ij} n^j e^{-\frac{\Delta E_{ij}^{hk}}{KT}} + \sum_{(j, h, k) \in D_i^{\text{en-chemical}}} \nu_{hk}^{ij} n^j \left(\frac{\mu^{hk}}{\mu^{ij}} \right)^{3/2} e^{-\frac{\Delta E_{ij}^{hk}}{KT}}. \end{aligned} \quad (98)$$

In our examples we consider for simplicity a mixture of four gases, each one endowed with two energy levels (a fundamental state and an excited one); of course all could be

extended to an higher number of mechanically interacting species and of energy levels. Masses of the four gases are $m^1 = 11.7$, $m^2 = 3.6$, $m^3 = 8$ and $m^4 = 7.3$, while collision frequencies of the exothermic interactions are taken as $\nu_{ij}^{hk} = \frac{i+j}{20(h+k)}$. With this choice, several numerical tests have been done, and some illustrative ones are reported here below.

Reference Test:

In the reference test we consider, initial conditions are given by Maxwellian shapes characterized by velocities

$$\begin{array}{cccc} u_0^1 = 0.2 & u_0^2 = 0.1 & u_0^3 = 0.3 & u_0^4 = 0.4 \\ u_0^5 = 0.3 & u_0^6 = 0.1 & u_0^7 = 0.2 & u_0^8 = 0 \end{array}$$

and temperatures

$$\begin{array}{cccc} T_0^1 = 1 & T_0^2 = 3.5 & T_0^3 = 2 & T_0^4 = 2.5 \\ T_0^5 = 3 & T_0^6 = 1.5 & T_0^7 = 5 & T_0^8 = 4.5 \end{array}$$

while initial number densities and internal energies are reported in the following table:

$n_0^1 = 11$	$n_0^2 = 9$	$n_0^3 = 10$	$n_0^4 = 7$	$n_0^5 = 10$	$n_0^6 = 8$	$n_0^7 = 9$	$n_0^8 = 6$
$E^1 = 3$	$E^2 = 2$	$E^3 = 4$	$E^4 = 7$	$E^5 = 5$	$E^6 = 4$	$E^7 = 6$	$E^8 = 9$

Consequently, $u_0 \approx 0.23$ and $T_0 \approx 2.8$. Figure 1 shows the evolution in time, until the steady state, of the unknowns Φ^8 and Ψ^8 describing the distribution of the second energy level (the most excited one) of the gas G^4 , and also the evolution of the densities and the temperatures for every gas at both energy levels. We see that equilibrium temperature holds $T_M \approx 3$ higher than the initial one, hence this mixture (with the chosen initial data) is macroscopically slightly exothermic, with transformation of internal energy into thermal energy.

We repeat then the reference test starting from initial distributions f_0^i given by sums of two Gaussians symmetric with respect to u_0^i , with the same macroscopic densities and temperatures reported above. Figure 2 shows the behaviour of Φ^8 and Ψ^8 in this case, and it compares the steady state (that of course is exactly the same) and the evolution of the entropy functional for initial data given by single Maxwellians or by sums of Gaussians. In this comparison and also in the other tests we will describe below, quantities relevant to the original reference case (with Maxwellian initial distributions) are denoted by a subscript t .

Test 1: We modify now the reference case considering different values for the internal energies:

$n_0^1 = 11$	$n_0^2 = 9$	$n_0^3 = 10$	$n_0^4 = 7$	$n_0^5 = 10$	$n_0^6 = 8$	$n_0^7 = 9$	$n_0^8 = 6$
$E^1 = 3$	$E^2 = 2$	$E^3 = 4$	$E^4 = 7$	$E^5 = 10$	$E^6 = 12$	$E^7 = 8$	$E^8 = 9$

Figure 3 illustrates the results relevant to this test, also in comparison with the reference test case. Steady states are again Maxwellian distributions with (constant) mean velocity $u \approx 0.23$, but equilibrium temperature and, consequently, number densities, change with respect to the reference plots. More precisely, since energies in the second level have

been increased, also equilibrium temperature increases to $T_M \approx 4.055$ providing thus equilibrium densities of the excited levels lower (and, because of conservation of global N^s , the ones of the fundamentals states higher) than the ones of the reference test. This mixture is thus really exothermic, since during the evolution a lot of particles de-excite, and transform their internal energy into thermal one.

Test 2: Now, with respect to the reference case, we modify (precisely, we increase) densities of the excited energy levels:

$n_0^1 = 11$	$n_0^2 = 9$	$n_0^3 = 10$	$n_0^4 = 7$	$n_0^5 = 13$	$n_0^6 = 11$	$n_0^7 = 12$	$n_0^8 = 9$
$E^1 = 3$	$E^2 = 2$	$E^3 = 4$	$E^4 = 7$	$E^5 = 5$	$E^6 = 4$	$E^7 = 6$	$E^8 = 9$

This test is described and compared to the reference one in Figure 4. Changing initial densities provides a different mass velocity $u \approx 0.22$, and a different global temperature, ranging from $T_0 \approx 2.9$ to $T_M \approx 3.18$. As noticed since Section 2 relevant to the Boltzmann description, in any equilibrium configuration for a mixture of polyatomic gases we have the the highest fraction of each gas G^s belongs to the fundamental (de-excited) level, and we show here that this fact is true even if we choose as initial situation the reverse one, in which highest number densities characterize the excited components.

Test 3: Finally, we consider the same initial conditions as for the reference test, but we assume that the four gases are subject also to the chemical reaction with transfer of mass described in Subsection 4.2. Simulations of this reactive case are shown in Figures 5 and 6. First, Figure 5 confirms numerically the Mass Action Law and the conservation of the sums of total densities $N^1 + N^3$, $N^1 + N^4$, $N^2 + N^4$ and of ρu ; moreover. it shows the evolution of the collision frequencies ν^i versus time. Last, in Figure 6 we present a comparison between the reference test, without chemical collisions, and the test 3. Mean velocity does not change, while equilibrium temperature is now $T_M \approx 3.2$. As concerns the evolution of number densities, we note that the chemical reaction can produce loss of monotony (see n^6). It would be of course interesting to extend such simulations of reactive polyatomic mixtures to several different situations, varying for instance the order of magnitude of the involved collision frequencies, changing thus the dominant processes in the evolution (elastic scattering, or excitation/de-excitation of interacting particles, or chemical reactions). Such investigation, together with comparisons with experimental data or with numerical simulations of the Boltzmann system, is left as future work.

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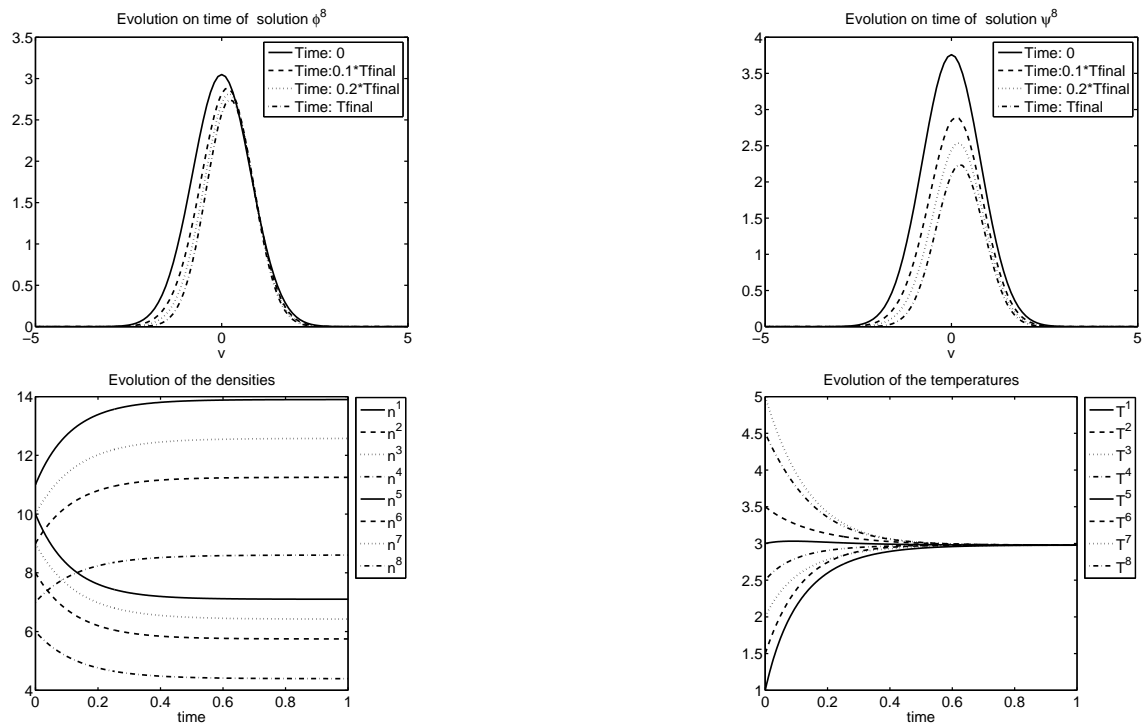


Figure 1: **Reference test, for Maxwellian initial data.**

Top: Time evolution of the distribution functions Φ^8 and Ψ^8 until the steady states.

Bottom: Left: Evolution of the number densities. Right: Evolution of the temperatures.

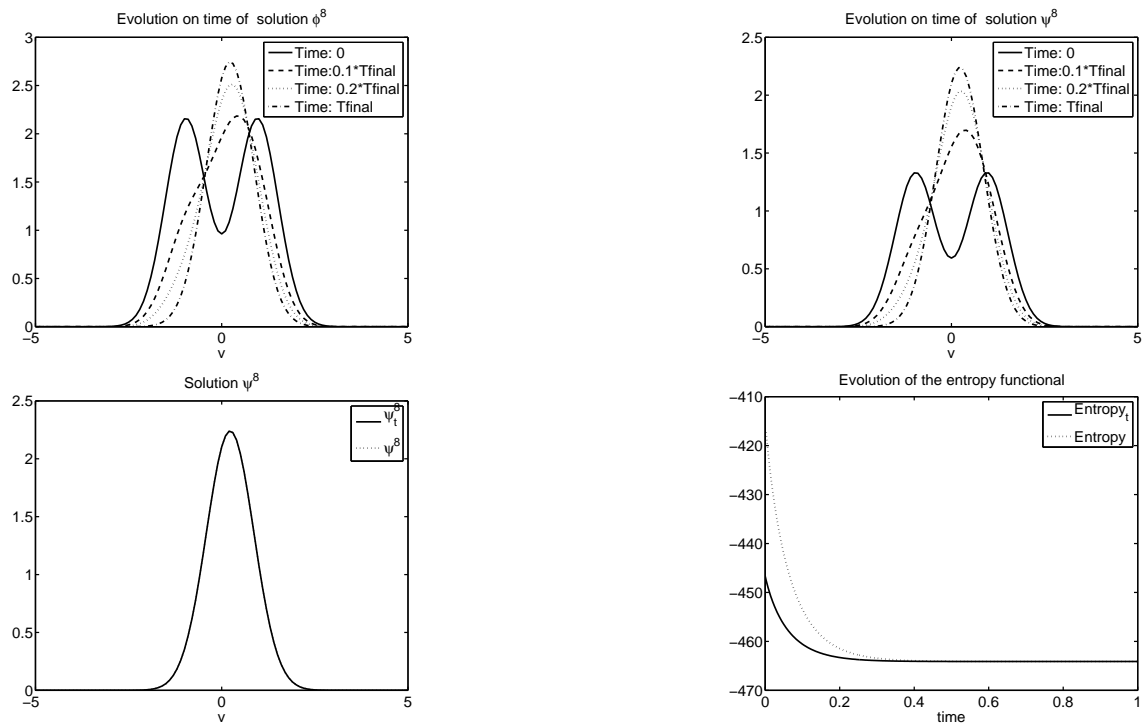


Figure 2: **Reference test, for initial data given by sums of Maxwellians.**

Top: Time evolution of the distribution functions Φ^8 and Ψ^8 until the steady states, for the reference test with initial data given by sums of Maxwellians.

Bottom: Left: Steady state of Ψ^8 ; Right: Entropy functional: comparison between the reference test with Maxwellian initial data and the test with initial data given by sums of Maxwellians. Lines relevant to the original reference case are denoted by a subscript t .

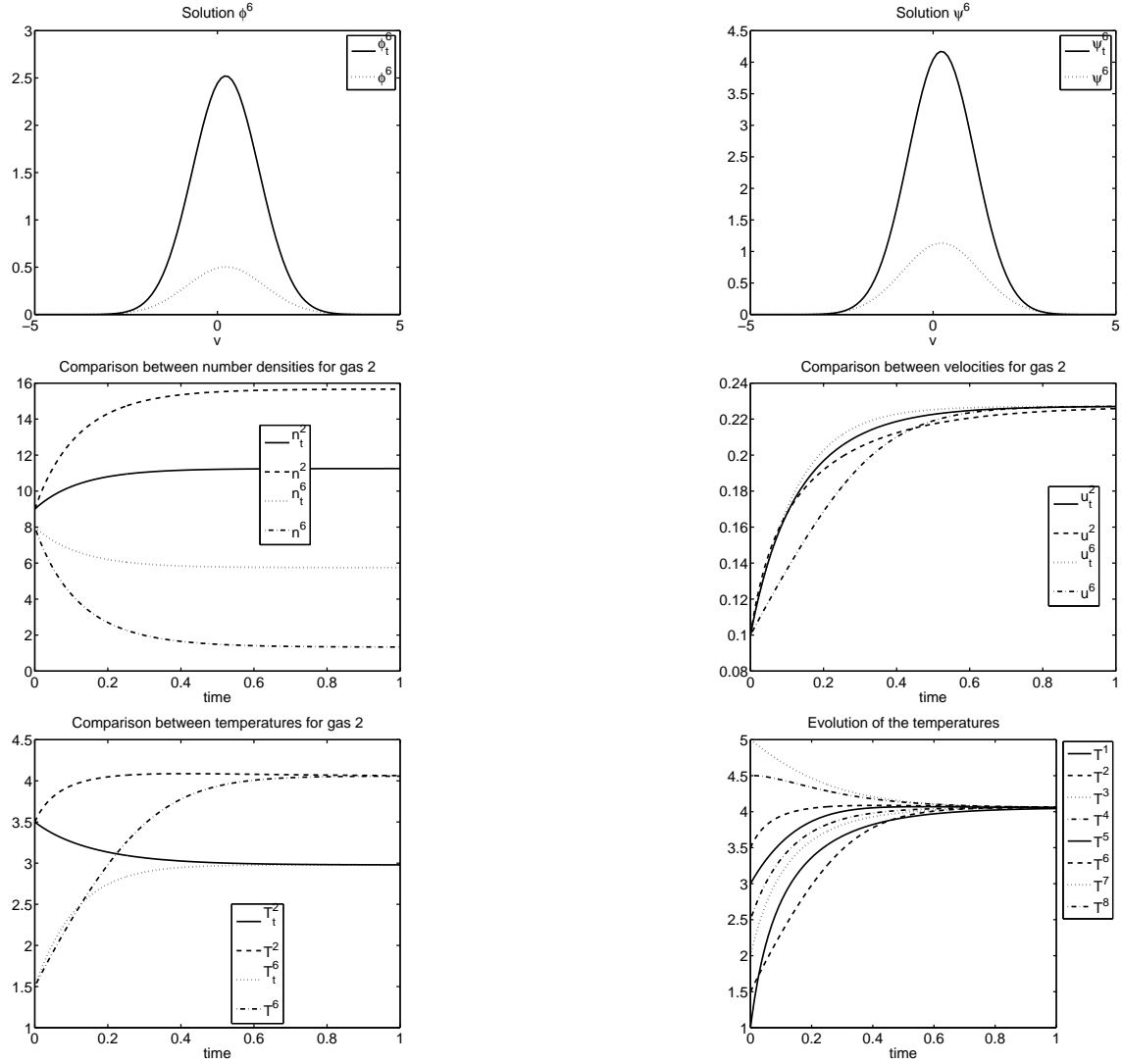


Figure 3: **Test 1.**

Top: Comparison between the steady states, for the gas G^2 at level 2, of the reference test and the test 1.

Middle: Comparison between the densities and the velocities of the reference test and the test 1.

Bottom: Left: Comparison between the temperatures of the reference test and the test 1.

Right: Evolution of the temperatures for the test 1.

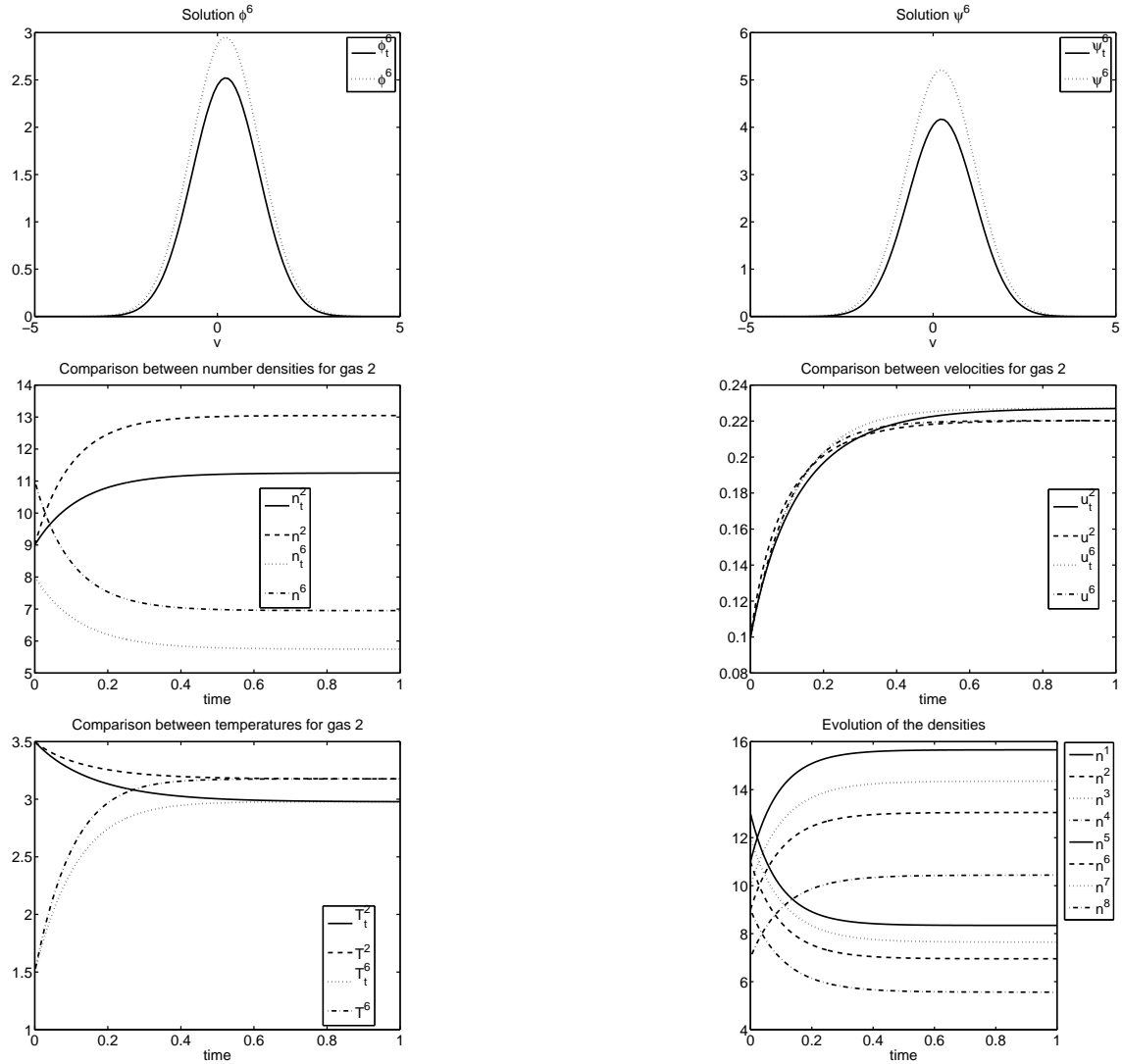


Figure 4: **Test 2.**

Top: Comparison between the steady states, for the gas G^2 at level 2, of the reference test and the test 2.

Middle: Comparison between the densities and the velocities of the reference test and the test 2.

Bottom: Left: Comparison between the temperatures of the reference test and the test 2.

Right: Evolution of the densities for the test 2.

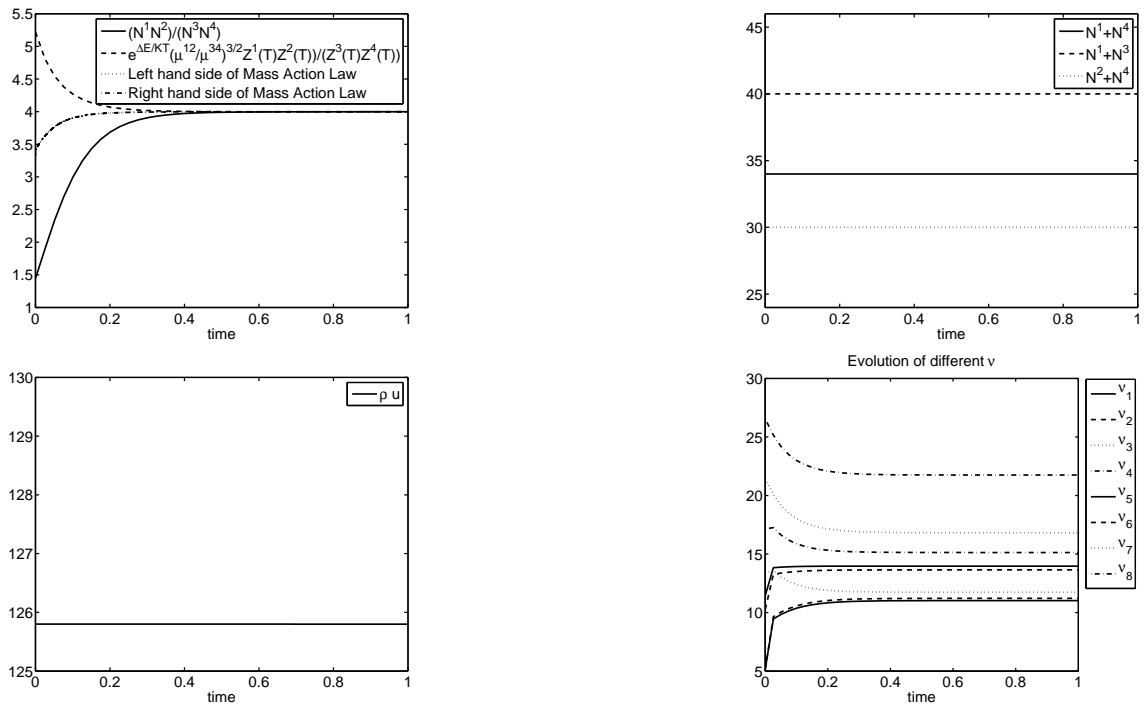


Figure 5: **Test 3.**

Top: Left: Mass Action Law: RHS and LHS of (56) and of (38). Right: Conservation of sum of total densities.

Bottom: Left: Conservation of ρu . Right: Evolution of ν^i .

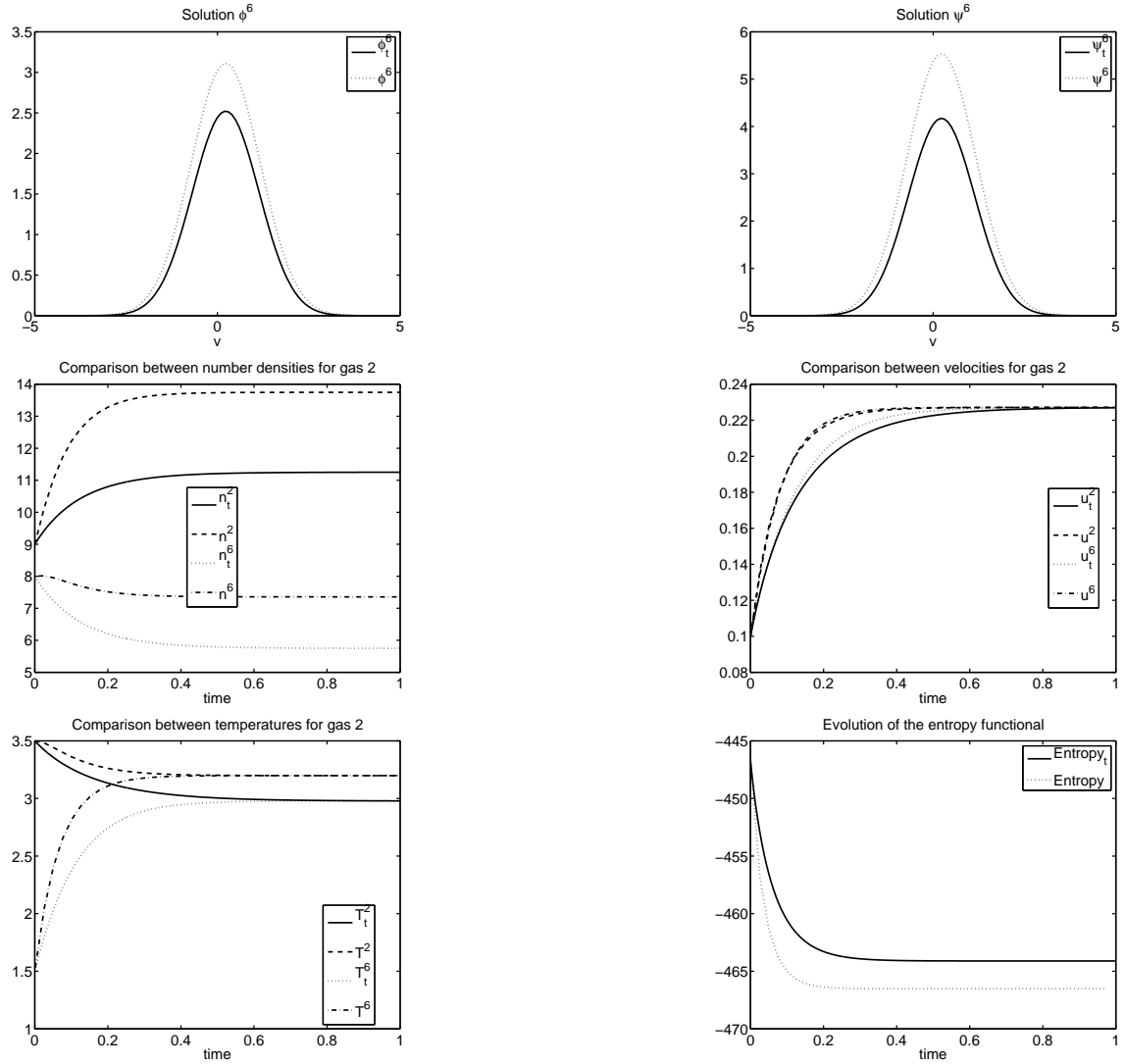


Figure 6: **Test 3.**

Top: Comparison between the steady states, for the gas G^2 at level 2, of the reference test and the test 3.

Middle: Comparison between the densities and the velocities of the reference test and the test 3.

Bottom: Comparison between the temperatures and the entropy functional of the reference test and the test 3.

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