A KINETIC RELAXATION MODEL FOR BIMOLECULAR CHEMICAL REACTIONS

BY

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Dedicated to the memory of Francesco Premuda

Abstract

A recently proposed consistent BGK–type approach for chemically reacting gas mixtures is discussed, which accounts for the correct rates of transfer for mass, momentum and energy, and recovers the exact conservation equations and collision equilibria, including mass action law. In particular, the hydrodynamic limit is derived by a Chapman–Enskog procedure, and compared to existing results for the reactive and non–reactive cases. In addition, numerical results are presented for non–isotropic space–homogeneous problems in which physical conditions allow reduction of the integrations over the three–dimensional velocity space to only one dimension.

1. Introduction

Kinetic approaches to chemically reacting gas mixtures constitute the proper tool of investigation in several circumstances, and allow a rigorous derivation and justification for the most common macroscopic descriptions used in the hydrodynamic regime [1, 2]. On the other hand, nonlinear chemical collision integrals of Boltzmann type are definitely not easy to deal with

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[3] and simpler approximate models would be convenient for practical applications. Following the experience of gas kinetic theory, relaxation time approximations of the type proposed by Bhatnagar, Gross, and Krook [4] and by Welander [5] (usually denoted as BGK models) seem to be the first candidates in that direction. Typically, the fine structure of the collision operator is replaced by a blurred image which retains only its qualitative and average properties, and prescribes relaxation towards a local equilibrium with a strength determined by a suitable characteristic time. The procedure must be carefully devised in order to avoid well known drawbacks which arise for a multi–species gas [6, 7], as unavoidable when dealing with a bimolecular chemical reaction

$$A^1 + A^2 \rightleftharpoons A^3 + A^4 \tag{1}$$

as we shall do in this work. Some relaxation models for the chemical collision operator have been introduced quite recently in the literature [8, 9]. In particular, the latter paper follows the consistent BGK strategy proposed in [7] for inert mixtures, which preserves positivity and indifferentiability principles, and resorts to a single BGK collision term for each species s ($s = 1, 2, 3, 4$), describing both mechanical (elastic) and chemical encounters, and drifting the distribution function f^s towards a suitable local Maxwellian $\mathcal{M}_s$. Indeed, the macroscopic parameters relevant to such equilibrium are not the actual fields, moments of f^s (number density n^s, drift velocity $\mathbf{u}^s$, temperature T^s), but some other fictitious fields $n_s, \mathbf{u}_s, T_s$, constructed "ad hoc" in order to recover the exact exchange rates for mass, momentum and energy, as given by the whole Boltzmann-like collision operator. The machinery is of course heavier than for chemically inert mixtures, since it has to account for transfer of mass and for energies of chemical link, but it is made possible by the explicit knowledge (for Maxwell–type interactions) of the moments of the chemical collision integrals [10]. It has been shown in [9] that such relaxation model of BGK type is a consistent approximation of the Boltzmann kinetic description, which reproduces in particular the correct macroscopic conservation equations and the correct collision equilibria, as Maxwellians at a common mass velocity and temperature, and with number densities related by the well known mass action law.

The present paper is aimed at proceeding further along the lines proposed in [9] by investigating some aspects that were left there as a future work. We shall focus in particular on two points here. The first is the hydrodynamic limit for small collision times of the present BGK equations

(via an asymptotic Chapman–Enskog expansion) in the collision dominated regime, when the reactive collision times are of the same order as the mechanical collision times, and both thermal and chemical equilibrium are reached eventually. This regime has been already introduced by Ludwig and Heil [11], and investigated in particular by Ern and Giovangigli [12] for arbitrary reactive gas mixtures of polyatomic species using Enskog expansions and Boltzmann-type collision terms. The second point is the extension of illustrative numerical calculations to non–isotropic situations, like those which are symmetric around one space direction (of interest for instance in the classical evaporation–condensation problem). At this still preliminary stage we consider only a single bimolecular reaction between monoatomic species and with Maxwell–type interactions, but the BGK strategy can be extended to more general situations, where the advantages related to the availability of explicit formulas for coefficients and to the much easier numerical approach become even more significant. It might be noticed that reaction (1) includes as a special case three–atoms reactions like

$$AB + C \rightleftharpoons B + AC, \tag{2}$$

for which a slightly simpler treatment would be in order [12].

The article is organized as follows. After presenting in Section 2 the main features of the considered BGK model, Section 3 is devoted to a detailed asymptotic analysis of the Chapman–Enskog type leading to closed macroscopic equations at the Navier–Stokes level, which are compared to analogous results obtained both in the chemically inert case from BGK equations [7] and in the chemically reactive case via Grad's expansion technique [13]. Section 4 deals instead with the specialization of the relaxation model to non-isotropic in velocity and one-dimensional in space physical problems, in which, following a procedure proposed in [14], the computational machinery becomes lighter thanks to the reduction of the three–fold velocity integrals to integrations on the real line. Finally numerical results for some illustrative space-homogeneous test cases are presented and briefly discussed.

2. BGK Equations

We recall and discuss here the main features of the relaxation time approximation introduced in [9] for the chemical reaction model worked out

in [3, 15]. Model kinetic equations read as

$$\frac{\partial f^s}{\partial t} + \mathbf{v} \cdot \frac{\partial f^s}{\partial \mathbf{x}} = \nu_s \big(\mathcal{M}_s - f^s \big) \qquad s = 1, \ldots, 4, \tag{3}$$

where $\mathcal{M}_s$ is a local Maxwellian with 5 disposable scalar parameters

$$\mathcal{M}_s(\mathbf{v}) = n_s \left(\frac{m^s}{2\pi K T_s} \right)^{\frac{3}{2}} \exp\left[-\frac{m^s}{2K T_s}(\mathbf{v} - \mathbf{u}_s)^2 \right] \qquad s = 1, \ldots, 4 \tag{4}$$

and ν_s is the inverse of the sth relaxation time, possibly depending on macroscopic fields, but independent of $\mathbf{v}$. The above auxiliary fields n_s, $\mathbf{u}_s$, T_s are determined by requiring that the exchange rates for mass, momentum and total (kinetic plus chemical) energy following from (3) coincide with those deduced from the corresponding Boltzmann equations. The latter rates are known analytically for Maxwell molecules [10], even in the chemical frame, and may be expressed in terms of some physical parameters like masses m^s (with $m^1 + m^2 = m^3 + m^4 = M$), reduced masses μ^{sr}, energies of chemical link E^s, and energy difference between reactants and products $\Delta E = -\sum_{s=1}^4 \lambda^s E^s$ (with $\lambda^1 = \lambda^2 = -\lambda^3 = -\lambda^4 = 1$), conventionally assumed to be positive. Other essential parameters are the microscopic collision frequencies (constant with respect to the impact speed g in our assumptions)

$$\nu_k^{sr}(g) = \nu_k^{rs}(g) = 2\pi g \int_0^\pi \sigma^{sr}(g, \chi)(1 - \cos\chi)^k \sin\chi \, d\chi \qquad k = 0, 1, \tag{5}$$

and

$$\nu_{12}^{34}(g) = 2\pi g \int_0^\pi \sigma_{12}^{34}(g, \chi) \sin\chi \, d\chi, \tag{6}$$

where σ stands for differential cross section, and $0 \leq \nu_1^{sr} \leq 2\nu_0^{sr}$. The above constraints on the exchange rates result in

$$n_s = n^s + \frac{\lambda^s}{\nu_s} Q$$

$$m^s n_s \mathbf{u}_s = m^s n^s \mathbf{u}^s + \frac{1}{\nu_s} \sum_{r=1}^4 \phi^{sr} \mathbf{u}^r + \frac{\lambda^s}{\nu_s} m^s \mathbf{u} \, Q \tag{7}$$

$$n_s \frac{3}{2} K T_s = n^s \frac{3}{2} K T^s - \frac{1}{2} m^s [n_s \mathbf{u}_s^2 - n^s (\mathbf{u}^s)^2] + \frac{1}{\nu_s} \sum_{r=1}^4 \psi^{sr} T^r$$

$$+\frac{1}{\nu_s}\sum_{r=1}^{4}\nu_1^{sr}\frac{\mu^{sr}}{m^s+m^r}n^sn^r(m^s\mathbf{u}^s+m^r\mathbf{u}^r)\cdot(\mathbf{u}^r-\mathbf{u}^s)$$

$$+\frac{\lambda^s}{\nu_s}Q\left[\frac{1}{2}m^s\mathbf{u}^2+\frac{3}{2}KT+\frac{M-m^s}{M}KT\frac{\left(\dfrac{\Delta E}{KT}\right)^{\frac{3}{2}}e^{-\frac{\Delta E}{KT}}}{\Gamma\left(\dfrac{3}{2},\dfrac{\Delta E}{KT}\right)}\right.$$

$$\left.-\frac{1-\lambda^s}{2}\frac{M-m^s}{M}\Delta E\right],$$

where Γ is an incomplete gamma function [16] and

$$Q=\nu_{12}^{34}\frac{2}{\sqrt{\pi}}\Gamma\left(\frac{3}{2},\frac{\Delta E}{KT}\right)\left[n^3n^4\left(\frac{m^1m^2}{m^3m^4}\right)^{\frac{3}{2}}e^{\frac{\Delta E}{KT}}-n^1n^2\right].\tag{8}$$

In addition, the symmetric singular matrices $\mathbf{\Phi}$ and $\mathbf{\Psi}$ are defined by

$$\phi^{sr}\ =\ \nu_1^{sr}\mu^{sr}n^sn^r-\delta^{sr}\sum_{l=1}^{4}\nu_1^{sl}\mu^{sl}n^sn^l\tag{9}$$

$$\psi^{sr}\ =\ 3K\nu_1^{sr}\frac{\mu^{sr}}{m^s+m^r}n^sn^r-\delta^{sr}3K\sum_{l=1}^{4}\nu_1^{sl}\frac{\mu^{sl}}{m^s+m^l}n^sn^l,\tag{10}$$

and global macroscopic parameters (including mass density ρ, viscosity tensor $\mathbf{p}$ and heat flux $\mathbf{q}$) are expressed in terms of single component parameters by

$$n\ =\ \sum_{s=1}^{4}n^s,\qquad\rho=\sum_{s=1}^{4}m^sn^s,\qquad\mathbf{u}=\frac{1}{\rho}\sum_{s=1}^{4}m^sn^s\mathbf{u}^s,$$

$$nKT\ =\ \sum_{s=1}^{4}n^sKT^s+\frac{1}{3}\sum_{s=1}^{4}\rho^s\left(u_k^su_k^s-u_ku_k\right),$$

$$p_{ij}\ =\ \sum_{s=1}^{4}p_{ij}^s+\sum_{s=1}^{4}\rho^s\left[\left(u_i^su_j^s-u_iu_j\right)-\frac{1}{3}\delta_{ij}\left(u_k^su_k^s-u_ku_k\right)\right],\tag{11}$$

$$q_i\ =\ \sum_{s=1}^{4}q_i^s+\sum_{s=1}^{4}p_{ij}^s\left(u_j^s-u_j\right)+\frac{5}{2}\sum_{s=1}^{4}n^sKT^s\left(u_i^s-u_i\right)$$

$$+\frac{1}{2}\sum_{s=1}^{4}\rho^s\left(u_k^s-u_k\right)\left(u_k^s-u_k\right)\left(u_i^s-u_i\right).$$

Actual conserved quantities in the Boltzmann collision process are in number

of seven, and may be chosen as three combinations of number densities like $n^1 + n^3$, $n^1 + n^4$, $n^2 + n^4$, the three components of the mass velocity $\mathbf{u}$, and the total internal (thermal + chemical) energy $\frac{3}{2}nKT + \sum_{s=1}^{4} E^s n^s$. This yields a set of 7 scalar exact non-closed macroscopic conservation equations

$$\frac{\partial}{\partial t}(n^s + n^r) + \frac{\partial}{\partial \mathbf{x}} \cdot (n^s \mathbf{u}^s + n^r \mathbf{u}^r) = 0 \quad (s,r) = (1,3), (1,4), (2,4)$$

$$\frac{\partial}{\partial t}(\rho \, \mathbf{u}) + \frac{\partial}{\partial \mathbf{x}} \cdot (\rho \, \mathbf{u} \otimes \mathbf{u} + \mathbf{P}) = \mathbf{0}$$

$$\frac{\partial}{\partial t}\left(\frac{1}{2}\rho \, u^2 + \frac{3}{2}nKT + \sum_{s=1}^{4} E^s n^s\right) + \frac{\partial}{\partial \mathbf{x}} \cdot \left[\left(\frac{1}{2}\rho u^2 + \frac{3}{2}nKT + \sum_{s=1}^{4} E^s n^s\right)\mathbf{u}\right.$$

$$\left. + \mathbf{P} \cdot \mathbf{u} + \mathbf{q} + \sum_{s=1}^{4} E^s n^s (\mathbf{u}^s - \mathbf{u})\right] = 0 \tag{12}$$

where $\mathbf{P} = nKT\mathbf{I} + \mathbf{p}$ is the pressure tensor. Notice that the three independent density combinations conserved by collisions would represent the atomic densities in the case of reaction (2). The set (12) of exact conservation equations is correctly reproduced by the relaxation model (3) [9], and another indication of the robustness of this approximation is the fact, proved again in [9], that collision equilibria also coincide with the actual ones, and are provided by a seven–parameter family of Maxwellians

$$\mathcal{M}^s(\mathbf{v}) = n^s \left(\frac{m^s}{2\pi KT}\right)^{\frac{3}{2}} \exp\left[-\frac{m^s}{2KT}(\mathbf{v} - \mathbf{u})^2\right], \qquad s = 1, \ldots, 4, \tag{13}$$

with equilibrium densities related by the well known mass action law of chemistry

$$\frac{n^1 n^2}{n^3 n^4} = \left(\frac{\mu^{12}}{\mu^{34}}\right)^{\frac{3}{2}} \exp\left(\frac{\Delta E}{KT}\right). \tag{14}$$

Other interesting features are in order for these BGK equations, but are less crucial for the present purposes, and will not be discussed here; the interested reader is referred to [9] for details. Another point that was left open in [9] is the most convenient choice of the inverse relaxation times ν_s, which in fact will be matter of future investigation. In this paper we will stick to the option of reproducing the actual average number of collisions (regardless if mechanical or chemical) taking place for each species, which

leads to

$$
\begin{aligned}
\nu_1 &= \sum_{r=1}^{4} \nu_0^{1r} n^r + \frac{2}{\sqrt{\pi}} \Gamma\left(\frac{3}{2}, \frac{\Delta E}{KT}\right) \nu_{12}^{34} n^2 \\
\nu_2 &= \sum_{r=1}^{4} \nu_0^{2r} n^r + \frac{2}{\sqrt{\pi}} \Gamma\left(\frac{3}{2}, \frac{\Delta E}{KT}\right) \nu_{12}^{34} n^1 \\
\nu_3 &= \sum_{r=1}^{4} \nu_0^{3r} n^r + \frac{2}{\sqrt{\pi}} \Gamma\left(\frac{3}{2}, \frac{\Delta E}{KT}\right) \left(\frac{\mu^{12}}{\mu^{34}}\right)^{\frac{3}{2}} e^{\frac{\Delta E}{KT}} \nu_{12}^{34} n^4 \\
\nu_4 &= \sum_{r=1}^{4} \nu_0^{4r} n^r + \frac{2}{\sqrt{\pi}} \Gamma\left(\frac{3}{2}, \frac{\Delta E}{KT}\right) \left(\frac{\mu^{12}}{\mu^{34}}\right)^{\frac{3}{2}} e^{\frac{\Delta E}{KT}} \nu_{12}^{34} n^3 .
\end{aligned}
\tag{15}
$$

3. Hydrodynamic Regime

Equations (3) may be scaled, measuring all quantities in terms of some typical values in order to make them dimensionless. Using macroscopic scales for space and time variables, and measuring relaxation times in units of a typical microscopic value, leads to equations which look exactly the same as (3), if the same symbol is retained for dimensionless variables, with only the appearance of the Knudsen number ε, ratio of the microscopic to the macroscopic time scales, downstairs on the right hand side

$$
\frac{\partial f^s}{\partial t} + \mathbf{v} \cdot \frac{\partial f^s}{\partial \mathbf{x}} = \frac{1}{\varepsilon} \nu_s \left(\mathcal{M}_s - f^s\right) \qquad s = 1, \ldots, 4.
\tag{16}
$$

The parameter ε is small in collision dominated regime, and tends to zero in the continuum limit we are interested in. We shall perform a formal Chapman–Enskog asymptotic analysis with respect to such small parameter, to first order accuracy, in order to achieve Navier–Stokes–like hydrodynamic equations as a closure of the conservation equations (12). To this end the distribution functions f^s are expanded as

$$
f^s = f^{s(0)} + \varepsilon f^{s(1)},
\tag{17}
$$

and consequently similar expansions hold for n^s, $\mathbf{u}^s$, T^s. However, hydrodynamic variables must remain unexpanded [17], namely

$$
n^s + n^r = n^{s(0)} + n^{r(0)} \qquad (s,r) = (1,3), (1,4), (2,4)
$$

$$\mathbf{u} \;=\; \frac{1}{\rho}\sum_{s=1}^{4} m^s n^{s(0)} \mathbf{u}^{s(0)} \tag{18}$$

$$\frac{3}{2}nT \;+\; \sum_{s=1}^{4} E^s n^s = \frac{3}{2}nT^{(0)} + \sum_{s=1}^{4} E^s n^{s(0)}$$

(with $n = \sum_{s=1}^{4} n^{s(0)}$ and $\rho = \sum_{s=1}^{4} m^s n^{s(0)}$ not expanded either), yielding the constraints

$$n^{1(1)} = n^{2(1)} = -n^{3(1)} = -n^{4(1)} = \frac{3n}{2\Delta E}T^{(1)}$$

$$\sum_{s=1}^{4} m^s n^{s(0)} \mathbf{u}^{s(1)} + \sum_{s=1}^{4} m^s n^{s(1)} \mathbf{u}^{s(0)} = \mathbf{0}. \tag{19}$$

Notice that internal energy is, as usual, an hydrodynamic field, but, contrary to classical (non–reactive) gas dynamics for monoatomic particles, it is not amenable only to the gas temperature T, so that the latter must be also expanded, as $T^{(0)} + \varepsilon T^{(1)}$.

These expansions induce of course similar expansions for all variables, in particular for the auxiliary fields and for the Maxwellians $\mathcal{M}_s$. The macroscopic collision frequencies ν_s, depending on the densities n^s, must be expanded as well. Equating finally equal powers of ε in (16) yields to leading order (ε^{-1})

$$\mathcal{M}_s^{(0)}(\mathbf{v}) - f^{s(0)}(\mathbf{v}) = 0, \tag{20}$$

and to the next order (ε^0)

$$\nu_s^{(0)}\left[\mathcal{M}_s^{(1)}(\mathbf{v}) - f^{s(1)}(\mathbf{v})\right] = \frac{\partial_0 f^{s(0)}}{\partial t} + \mathbf{v}\cdot\frac{\partial f^{s(0)}}{\partial \mathbf{x}} \tag{21}$$

where $\dfrac{\partial_0}{\partial t}$ is the first term of a formal expansion of the time derivative operator, to be considered as an unknown of the problem.

3.1. Zero order solution

Equations (20), (21) are uneasy, highly nonlinear, integro–functional equations in the unknowns $f^{s(i)}$, since their integral moments are needed in the definition of the parameters determining the auxiliary Maxwellians $\mathcal{M}_s^{(i)}$. However, equations (20) yield, in cascade, $n_s^{(0)} = n^{s(0)}$, $\mathbf{u}_s^{(0)} = \mathbf{u}^{s(0)}$,

$T_s^{(0)} = T^{s(0)}$, then

$$Q^{(0)} = \nu_{12}^{34} \frac{2}{\sqrt{\pi}} \Gamma\left(\frac{3}{2}, \frac{\Delta E}{T^{(0)}}\right) \left[n^{3(0)}n^{4(0)} \left(\frac{m^1 m^2}{m^3 m^4}\right)^{\frac{3}{2}} e^{\frac{\Delta E}{T^{(0)}}} - n^{1(0)}n^{2(0)}\right] = 0,$$

(22)

from which the zero–order mass action law follows

$$\frac{n^{1(0)}n^{2(0)}}{n^{3(0)}n^{4(0)}} = \left(\frac{\mu^{12}}{\mu^{34}}\right)^{\frac{3}{2}} \exp\left(\frac{\Delta E}{T^{(0)}}\right).$$

(23)

We have further on

$$\sum_{s=1}^{4} \phi^{sr(0)} \mathbf{u}^{r(0)} = \mathbf{0}, \qquad s = 1, \dots, 4$$

(24)

from which, due to the properties of matrix $\phi^{sr(0)}$ [13], $\mathbf{u}^{s(0)} = \mathbf{u}$ for all s and

$$\sum_{s=1}^{4} m^s n^{s(0)} \mathbf{u}^{s(1)} = \mathbf{0},$$

(25)

and finally

$$\sum_{s=1}^{4} \psi^{sr(0)} T^{r(0)} = 0, \qquad s = 1, \dots, 4$$

(26)

implying, again for the properties of matrix $\psi^{sr(0)}$ [13], $T^{s(0)} = T^{(0)}$ for all s. Notice that all species share, to leading order, the same drift velocity, equal to the global mass velocity $\mathbf{u}$, and the same temperature, equal to the leading term of the global temperature T, in agreement with the fact that $\mathbf{u}$ is an hydrodynamic variable, whereas T is not, and must be expressed as $T^{(0)} + \varepsilon T^{(1)}$. In conclusion we have

$$f^{s(0)}(\mathbf{v}) = \mathcal{M}^{s(0)}(\mathbf{v}) = n^{s(0)} \left(\frac{m^s}{2\pi T^{(0)}}\right)^{\frac{3}{2}} \exp\left[-\frac{m^s}{2T^{(0)}}(\mathbf{v} - \mathbf{u})^2\right], \quad (27)$$

for $s = 1, \dots, 4$, with seven free parameters, since the $n^{s(0)}$ and $T^{(0)}$ must be bound together by (23). Equations (27) yield immediately $p_{ij}^{s(0)} = 0$ and $q_i^{s(0)} = 0$ for all s, from which also $p_{ij}^{(0)} = 0$ and $q_i^{(0)} = 0$ for the leading terms of viscosity tensor and heat flux.

Before going on to the next step, we can select as unknowns for the

sought Navier–Stokes type equations the seven scalar variables $n^{s(0)}, s = 1, \ldots, 4$, and $\mathbf{u}$, and express $T^{(0)}$, wherever needed, by means of (23). Conservation equations may be rewritten as

$$\frac{\partial}{\partial t}\left(n^{s(0)} + n^{r(0)}\right) + \frac{\partial}{\partial \mathbf{x}} \cdot \left[(n^{s(0)} + n^{r(0)})\mathbf{u}\right] + \varepsilon\frac{\partial}{\partial \mathbf{x}} \cdot \left(n^{s(0)}\mathbf{u}^{s(1)} + n^{r(0)}\mathbf{u}^{r(1)}\right) = 0$$
$$(s,r) = (1,3),\ (1,4),\ (2,4)$$

$$\frac{\partial}{\partial t}(\rho\,\mathbf{u}) + \frac{\partial}{\partial \mathbf{x}} \cdot (\rho\,\mathbf{u} \otimes \mathbf{u}) + \frac{\partial}{\partial \mathbf{x}}(nT^{(0)}) + \varepsilon\frac{\partial}{\partial \mathbf{x}}(nT^{(1)}) + \varepsilon\frac{\partial}{\partial \mathbf{x}} \cdot \mathbf{p}^{(1)} = \mathbf{0}$$

$$\frac{\partial}{\partial t}\left(\frac{1}{2}\,\rho\,u^2 + \frac{3}{2}\,nT^{(0)} + \sum_{s=1}^{4} E^s n^{s(0)}\right)$$

$$+ \frac{\partial}{\partial \mathbf{x}} \cdot \left[\left(\frac{1}{2}\,\rho\,u^2 + \frac{5}{2}\,nT^{(0)} + \sum_{s=1}^{4} E^s n^{s(0)}\right)\mathbf{u}\right] + \varepsilon\frac{\partial}{\partial \mathbf{x}} \cdot \left(nT^{(1)}\mathbf{u}\right)$$

$$+ \varepsilon\frac{\partial}{\partial \mathbf{x}}\left(\mathbf{p}^{(1)} \cdot \mathbf{u}\right) + \varepsilon\frac{\partial}{\partial \mathbf{x}} \cdot \mathbf{q}^{(1)} + \varepsilon\frac{\partial}{\partial \mathbf{x}} \cdot \left(\sum_{s=1}^{4} E^s n^{s(0)}\mathbf{u}^{s(1)}\right) = 0$$

$$(28)$$

and their closure is achieved if we are able to determine, resorting to (21), constitutive equations for the quantities $\mathbf{u}^{s(1)}$, $T^{(1)}$, $p_{ij}^{(1)}$, and $q_i^{(1)}$, for which we have further

$$nT^{(1)} = \sum_{s=1}^{4} n^{s(0)}T^{s(1)}, \ \ p_{ij}^{(1)} = \sum_{s=1}^{4} p_{ij}^{s(1)}, \ \ q_i^{(1)} = \sum_{s=1}^{4} q_i^{s(1)} + \frac{5}{2}T^{(0)}\sum_{s=1}^{4} n^{s(0)}u_i^{s(1)}.$$

$$(29)$$

3.2. First order correction

Standard manipulations allow to evaluate the time and space derivatives of $f^{s(0)}$, and to express $\mathcal{M}_s^{(1)}$ as the derivative of $\mathcal{M}_s$ with respect to ε at $\varepsilon = 0$; in this way we obtain a formal solution of (21) as

$$f^{s(1)} = f^{s(0)}\left\{\frac{1}{n^{s(0)}}n_s^{(1)} + \frac{m^s}{T^{(0)}}\mathbf{u}_s^{(1)} \cdot (\mathbf{v} - \mathbf{u}) + \frac{1}{T^{(0)}}T_s^{(1)}\left[\frac{m^s}{2T^{(0)}}(\mathbf{v} - \mathbf{u})^2 - \frac{3}{2}\right]\right\}$$

$$- \frac{1}{\nu_s^{(0)}}f^{s(0)}\left\{\frac{1}{n^{s(0)}}\frac{\partial_0 n^{s(0)}}{\partial t} + \frac{m^s}{T^{(0)}}\frac{\partial_0 \mathbf{u}}{\partial t} \cdot (\mathbf{v} - \mathbf{u}) + \frac{1}{T^{(0)}}\frac{\partial_0 T^{(0)}}{\partial t}\left[\frac{m^s}{2T^{(0)}}(\mathbf{v} - \mathbf{u})^2 - \frac{3}{2}\right]\right\}$$

$$- \frac{1}{\nu_s^{(0)}}f^{s(0)}\left\{\frac{1}{n^{s(0)}}\frac{\partial n^{s(0)}}{\partial \mathbf{x}} \cdot \mathbf{v} + \frac{m^s}{T^{(0)}}\frac{\partial \mathbf{u}}{\partial \mathbf{x}} : \mathbf{v} \otimes (\mathbf{v} - \mathbf{u})\right.$$

$$\left. + \frac{1}{T^{(0)}}\frac{\partial T^{(0)}}{\partial \mathbf{x}} \cdot \left[\frac{m^s}{2T^{(0)}}(\mathbf{v} - \mathbf{u})^2 - \frac{3}{2}\right]\mathbf{v}\right\}$$

$$(30)$$

where

$$n_s^{(1)} = n^{s(1)} + \frac{\lambda^s}{\nu_s^{(0)}} Q^{(1)}$$

$$m^s n^{s(0)} \mathbf{u}_s^{(1)} = m^s n^{s(0)} \mathbf{u}^{s(1)} + \frac{1}{\nu_s^{(0)}} \sum_{r=1}^{4} \phi^{sr(0)} \mathbf{u}^{r(1)} \tag{31}$$

$$n^{s(0)} \frac{3}{2} T_s^{(1)} = n^{s(0)} \frac{3}{2} T^{s(1)} + \frac{1}{\nu_s^{(0)}} \sum_{r=1}^{4} \psi^{sr(0)} T^{r(1)}$$

$$+ \frac{\lambda^s}{\nu_s^{(0)}} Q^{(1)} \left[\frac{M - m^s}{M} T^{(0)} \frac{\left(\frac{\Delta E}{T^{(0)}}\right)^{\frac{3}{2}} e^{-\frac{\Delta E}{T^{(0)}}}}{\Gamma\left(\frac{3}{2}, \frac{\Delta E}{T^{(0)}}\right)} - \frac{1 - \lambda^s}{2} \frac{M - m^s}{M} \Delta E \right],$$

and $Q^{(1)} = -n^{1(1)} \tilde{Q}$, with

$$\tilde{Q} = \nu_{12}^{34} \frac{2}{\sqrt{\pi}} \Gamma\left(\frac{3}{2}, \frac{\Delta E}{T^{(0)}}\right)$$

$$\times \left\{ \left[n^{3(0)} + n^{4(0)} + \frac{2}{3} \frac{n^{3(0)} n^{4(0)}}{n} \left(\frac{\Delta E}{T^{(0)}}\right)^2 \right] \left(\frac{m^1 m^2}{m^3 m^4}\right)^{\frac{3}{2}} e^{\frac{\Delta E}{T^{(0)}}} + n^{1(0)} + n^{2(0)} \right\}. \tag{32}$$

A patient algebra allows now to recompute the auxiliary fields $n_s^{(1)}$, $\mathbf{u}_s^{(1)}$, $T_s^{(1)}$ from the distribution functions (30) and to make this solution effective by using (31) and (32). Skipping technical details, density fields provide the compatibility conditions

$$\frac{\partial_0 n^{s(0)}}{\partial t} + \frac{\partial}{\partial \mathbf{x}} \cdot (n^{s(0)} \mathbf{u}) = -\lambda^s n^{1(1)} \tilde{Q} \qquad s = 1, \ldots, 4. \tag{33}$$

Velocity fields yield the compatibility conditions

$$\frac{\partial_0 \mathbf{u}}{\partial t} + \mathbf{u} \cdot \frac{\partial \mathbf{u}}{\partial \mathbf{x}} = -\frac{1}{\rho} \frac{\partial}{\partial \mathbf{x}} (n T^{(0)}) \tag{34}$$

and the algebraic equations

$$\sum_{s=1}^{4} \phi^{sr(0)} \mathbf{u}^{r(1)} = \frac{\partial}{\partial \mathbf{x}} (n^{s(0)} T^{(0)}) - \frac{\rho^{s(0)}}{\rho} \frac{\partial}{\partial \mathbf{x}} (n T^{(0)}), \qquad s = 1, \ldots, 4. \tag{35}$$

This set of equations is the same which arises when the Chapman–Enskog algorithm is applied to the reactive Grad 13–moment equations [13], and, at the same time, it coincides with the results obtained in [7] for a chemically

inert mixture (apart from the superscript (0), not necessary there). The matrix $\phi^{sr(0)}$ is singular, but (35) is uniquely solvable when coupled to the constraint (25). The solution, *mutatis mutandis*, goes through the same steps of either [7] or [13], and may be cast as

$$\mathbf{u}^{s(1)} = -\sum_{r=1}^{4} L^{sr(0)} \frac{1}{\rho^{s(0)} \rho^{r(0)}} \frac{\partial}{\partial \mathbf{x}} (n^{r(0)} T^{(0)}) \qquad (36)$$

where $L^{sr(0)}$ is a suitable matrix, depending on the $n^{s(0)}$, which can be proved to be symmetric [7], reproducing thus the Onsager relations [18]. The expressions given by (36) also coincide with classical expressions for diffusion velocities of inert mixtures [19, 20], the only difference being the presence of $n^{s(0)}$ instead of the actual densities n^s. Indeed, matrix $L^{sr(0)}$ is contributed only by elastic scattering and is independent from the chemical reaction and from ΔE, and number densities would be hydrodynamic fields in the non–reactive case. Finally, temperature fields recomputed from (30) yield, after some algebra, a set of linear algebraic equations for the $T^{s(1)}$ with matrix coefficients $\psi^{sr(0)}$ (not shown here for brevity, since useless for our purposes) plus the compatibility condition

$$\frac{\partial_0 T^{(0)}}{\partial t} + \mathbf{u} \cdot \frac{\partial T^{(0)}}{\partial \mathbf{x}} + \frac{2}{3} T^{(0)} \frac{\partial}{\partial \mathbf{x}} \cdot \mathbf{u} = -\frac{2}{3n} \tilde{Q} \, \Delta E \, n^{1(1)}. \qquad (37)$$

Now $T^{(0)}$ can be evaluated from (23) and $\dfrac{\partial_0 T^{(0)}}{\partial t}$ may be cast in terms of the derivatives $\dfrac{\partial_0 n^{s(0)}}{\partial t}$, as

$$\frac{\partial_0 T^{(0)}}{\partial t} = -\frac{(T^{(0)})^2}{\Delta E} \sum_{s=1}^{4} \lambda^s \frac{1}{n^{s(0)}} \frac{\partial_0 n^{s(0)}}{\partial t}, \qquad (38)$$

which implies an additional compatibility condition between (33) and (37), determining $n^{1(1)}$ in terms of the chosen unknowns and of their spatial gradients. Bearing the first of (19) in mind, and resorting to (23) in order to eliminate unnecessary spatial gradients, the calculation yields

$$T^{(1)} = -\frac{2}{3} T^{(0)} \left\{ \tilde{Q} \left[1 + \frac{3}{2} n \left(\frac{T^{(0)}}{\Delta E} \right)^2 \sum_{s=1}^{4} \frac{1}{n^{s(0)}} \right] \right\}^{-1} \frac{\partial}{\partial \mathbf{x}} \cdot \mathbf{u}, \qquad (39)$$

and it is interesting to remark that it coincides with the temperature correction found in [13] for the same physical problem by resorting to the Grad

13–moment method. Of course this correction is specific for the chemical reaction (1) and would not appear in any non–reactive gas mixture. In particular, $T^{(1)}$ would vanish in the limit $\Delta E \to 0$.

3.3. Viscous stress and heat flux

In principle, the asymptotic problem to first order for the distribution functions is solved, since it is easy to see that the algebraic system for the $T^{s(1)}$ is uniquely solvable as well, and that also all zero–order time derivatives can be made explicit. However, in order to achieve the desired hydrodynamic equations from (28), it suffices to compute $p_{ij}^{(1)}$ and $q_i^{(1)}$ by suitable integrations of the distribution functions. More precisely we have

$$P_{ij}^{s(1)} = m^s \int_{\mathbb{R}^3} (v_i - u_i)(v_j - u_j) f^{s(1)}(\mathbf{v}) \, d_3\mathbf{v}, \ \ p_{ij}^{s(1)} = P_{ij}^{s(1)} - \delta_{ij} \frac{1}{3} \operatorname{tr} \mathbf{P}^{s(1)} \quad (40)$$

and

$$q_i^{s(1)} = -\frac{5}{2} T^{(0)} n^{s(0)} u_i^{s(1)} + \frac{1}{2} m^s \int_{\mathbb{R}^3} (v_i - u_i)(\mathbf{v} - \mathbf{u})^2 f^{s(1)} \, d_3\mathbf{v} \quad (41)$$

to be used then in (29). When computing $P_{ij}^{s(1)}$, it is not difficult to check that the addend of $f^{s(1)}$ involving the first order corrections yields a tensor proportional to the identity, which contributes nothing to the deviatoric part $p_{ij}^{s(1)}$, and the same occurs to the second addend, involving the $\frac{\partial_0}{\partial t}$ operator. For the third addend, involving spatial gradients, the same feature is in order for the gradients of $n^{s(0)}$ and $T^{(0)}$, whereas the rate of strain tensor contributes a term

$$-\frac{n^{s(0)} T^{(0)}}{\nu_s^{(0)}} \left[\delta_{ij} \left(2 \frac{\partial u_i}{\partial x_i} + \frac{\partial}{\partial \mathbf{x}} \cdot \mathbf{u} \right) + (1 - \delta_{ij}) \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right) \right] \quad (42)$$

where the square bracket is the sum of $\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i}$ and of an isotropic tensor. Going on and computing $p_{ij}^{s(1)}$ and $p_{ij}^{(1)}$, one ends up with

$$p_{ij}^{(1)} = -T^{(0)} \sum_{s=1}^{4} \frac{n^{s(0)}}{\nu_s^{(0)}} \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} - \frac{2}{3} \frac{\partial}{\partial \mathbf{x}} \cdot \mathbf{u} \, \delta_{ij} \right). \quad (43)$$

This Newtonian constitutive equation corresponds to a viscosity coefficient

$$\mu = T^{(0)} \sum_{s=1}^{4} \frac{n^{s(0)}}{\nu_s^{(0)}}, \quad (44)$$

exactly the same obtained in [7] from the BGK equations for a chemically inert gas mixture. An expression of the same type was obtained for the reactive case in [13] by the Grad method, but with a different viscosity coefficient, that was provided there by formal inversion of suitable matrices. Passing to (41), we may split again $f^{s(1)}$ in three different addends and evaluate separately the relevant contributions. The first one, with first order corrections, leaves after integration only the term $\frac{5}{2}T^{(0)}n^{s(0)}u_{is}^{(1)}$. In a similar fashion, from the second addend we have only $-\frac{5}{2}T^{(0)}\frac{n^{s(0)}}{\nu_s^{(0)}}\frac{\partial_0 u_i}{\partial t}$. More contributions come from the spatial gradients, and they can be put together as

$$-\frac{5}{2}\frac{T^{(0)}}{m^s}\frac{T^{(0)}}{\nu_s^{(0)}}\frac{\partial n^{s(0)}}{\partial x_i} - \frac{5}{2}T^{(0)}\frac{n^{s(0)}}{\nu_s^{(0)}}\mathbf{u}\cdot\frac{\partial u_i}{\partial\mathbf{x}} - 5\frac{n^{s(0)}T^{(0)}}{m^s\nu_s^{(0)}}\frac{\partial T^{(0)}}{\partial x_i},$$

so that there results

$$\begin{aligned}q_i^{s(1)} &= -\frac{5}{2}\frac{n^{s(0)}T^{(0)}}{\nu_s^{(0)}}\left[\frac{\partial_0 u_i}{\partial t} + \mathbf{u}\cdot\frac{\partial u_i}{\partial\mathbf{x}} + \frac{1}{\rho^{s(0)}}\frac{\partial}{\partial x_i}(n^{s(0)}T^{(0)})\right] \\ &\quad -\frac{5}{2}\frac{n^{s(0)}T^{(0)}}{m^s\nu_s^{(0)}}\frac{\partial T^{(0)}}{\partial x_i} + \frac{5}{2}T^{(0)}n^{s(0)}(u_{is}^{(1)} - u_i^{s(1)})\end{aligned} \tag{45}$$

and, upon using the second of (31) for $u_i^{s(1)}$, and (34) and (35) for the square bracket, we end up simply with

$$q_i^{s(1)} = -\frac{5}{2}T^{(0)}\frac{n^{s(0)}}{m^s\nu_s^{(0)}}\frac{\partial T^{(0)}}{\partial x_i}. \tag{46}$$

In conclusion, from (29)

$$q_i^{(1)} = -\frac{5}{2}T^{(0)}\sum_{s=1}^{4}\frac{n^{s(0)}}{m^s\nu_s^{(0)}}\frac{\partial T^{(0)}}{\partial x_i} + \frac{5}{2}T^{(0)}\sum_{s=1}^{4}n^{s(0)}u_i^{s(1)}, \tag{47}$$

a Fourier conduction law with a thermal conductivity

$$\lambda = \frac{5}{2}T^{(0)}\sum_{s=1}^{4}\frac{n^{s(0)}}{m^s\nu_s^{(0)}}. \tag{48}$$

Once more, this result coincides with the corresponding one for the same BGK strategy applied to a non–reactive mixture [7], and reproduces the structure of heat flux for the reactive case as obtained in [13], where again conductivity was given by the inversion of certain matrices.

3.4. Conclusions

Summarizing our results, hydrodynamic equations of Navier–Stokes type for the present relaxation model of the chemical reaction (1) in a gas mixture is provided by the set (28) of seven partial differential equations for the seven scalar unknowns $n^{s(0)}$ and $\mathbf{u}$, coupled to the transcendental algebraic equation (23) for $T^{(0)}$, and to the constitutive equations (36) for $u_i^{s(1)}$, (39) for $T^{(1)}$, (43) for $p_{ij}^{(1)}$, and (47) for $q_i^{(1)}$. All together, they read as

$$\frac{\partial}{\partial t}\Big(n^{s(0)} + n^{r(0)}\Big) + \frac{\partial}{\partial \mathbf{x}}\Big[\big(n^{s(0)} + n^{r(0)}\big)\mathbf{u}\Big] + \varepsilon\frac{\partial}{\partial \mathbf{x}}\Big(n^{s(0)}\mathbf{u}^{s(1)} + n^{r(0)}\mathbf{u}^{r(1)}\Big) = 0$$

$$(s, r) = (1, 3),\ (1, 4),\ (2, 4)$$

$$\frac{\partial}{\partial t}(\rho\,\mathbf{u}) + \frac{\partial}{\partial \mathbf{x}}(\rho\,\mathbf{u}\otimes\mathbf{u}) + \frac{\partial}{\partial \mathbf{x}}(nT^{(0)}) + \varepsilon\frac{\partial}{\partial \mathbf{x}}(nT^{(1)}) + \varepsilon\frac{\partial}{\partial \mathbf{x}}\cdot\mathbf{p}^{(1)} = \mathbf{0}$$

$$\frac{\partial}{\partial t}\Big(\frac{1}{2}\rho u^2 + \frac{3}{2}nT^{(0)} + \sum_{s=1}^{4} E^s n^{s(0)}\Big) + \frac{\partial}{\partial \mathbf{x}}\cdot\Big[\Big(\frac{1}{2}\rho u^2 + \frac{5}{2}nT^{(0)} + \sum_{s=1}^{4} E^s n^{s(0)}\Big)\mathbf{u}\Big]$$

$$+\varepsilon\frac{\partial}{\partial \mathbf{x}}\cdot\big(nT^{(1)}\mathbf{u}\big) + \varepsilon\frac{\partial}{\partial \mathbf{x}}\cdot\big(\mathbf{p}^{(1)}\cdot\mathbf{u}\big) + \varepsilon\frac{\partial}{\partial \mathbf{x}}\cdot\mathbf{q}^{(1)} + \varepsilon\frac{\partial}{\partial \mathbf{x}}\cdot\Big(\sum_{s=1}^{4} E^s n^{s(0)}\mathbf{u}^{s(1)}\Big) = 0$$

$$\frac{n^{1(0)}n^{2(0)}}{n^{3(0)}n^{4(0)}} = \Big(\frac{\mu^{12}}{\mu^{34}}\Big)^{\frac{3}{2}}\exp\Big(\frac{\Delta E}{T^{(0)}}\Big)$$

$$\mathbf{u}^{s(1)} = -\sum_{r=1}^{4} L^{sr(0)}\frac{1}{\rho^{s(0)}\rho^{r(0)}}\frac{\partial}{\partial \mathbf{x}}(n^{r(0)}T^{(0)})$$

$$T^{(1)} = -\frac{2}{3}T^{(0)}\Big\{\tilde{Q}\Big[1 + \frac{3}{2}\,n\Big(\frac{T^{(0)}}{\Delta E}\Big)^2\sum_{s=1}^{4}\frac{1}{n^{s(0)}}\Big]\Big\}^{-1}\frac{\partial}{\partial \mathbf{x}}\cdot\mathbf{u}$$

$$p_{ij}^{(1)} = -T^{(0)}\sum_{s=1}^{4}\frac{n^{s(0)}}{\nu_s^{(0)}}\Big(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} - \frac{2}{3}\frac{\partial}{\partial \mathbf{x}}\cdot\mathbf{u}\,\delta_{ij}\Big)$$

$$q_i^{(1)} = -\frac{5}{2}T^{(0)}\sum_{s=1}^{4}\frac{n^{s(0)}}{m^s\nu_s^{(0)}}\frac{\partial T^{(0)}}{\partial x_i} + \frac{5}{2}T^{(0)}\sum_{s=1}^{4} n^{s(0)}u_i^{s(1)}. \tag{49}$$

Euler equations correspond to the limiting case $\varepsilon = 0$. This BGK asymptotic limit has the same form of the Boltzmann asymptotic limit worked out in [13] via a Grad 13–moment expansion, and only the definition of viscosity coefficient and thermal conductivity differ in the two approaches. The present result differs instead substantially from the BGK asymptotic limit that would be in order if the chemical reaction were switched off, that was

thoroughly derived and discussed in [7]. In such a case in fact the kernel
of the collision operator is eight–dimensional, and all densities, as well as
the temperature, are hydrodynamic variables, so that Navier–Stokes equa-
tions are made up by eight partial differential equations, including continuity
equations for each species. In other words, also with Boltzmann models, the
linearized collision operator in the present regime contains terms account-
ing for reactive collisions, as opposed to the one that would be obtained if
chemical reactions were absent, or were considered a much slower process. It
is remarkable however that all first order corrections needed for the closure
(except, of course, the temperature correction, or additional reactive scalar
pressure, which is peculiar of the chemical reaction [2, 21]) are expressed by
constitutive equations which are, *mutatis mutandis*, the same in the reactive
and in the non–reactive case. This fact reproduces known results established
at the Boltzmann level [12]. At the BGK level, there are additionally reac-
tive contributions in the transport coefficients through the factors ν_s in (15),
which are affected by the reactive collision frequency ν_{12}^{34}. These contribu-
tions however affect only viscosity and thermal conductivity through $\nu_s^{(0)}$ in
(44) and (48).

4. Axially Symmetric Problems

As stated in the Introduction, we specialize now our BGK equations
(3), (4), (7) to problems with axial symmetry with respect to an axis (say,
$x_1 \equiv x$), in the sense that all transverse spatial gradients vanish, and the
gas is drifting only in the axial direction. In other words, distribution func-
tions f^s depend on the full velocity vector $\mathbf{v}$ (molecular trajectories are
three–dimensional) but dependence on the azimuthal direction around the
symmetry axis is such that all transverse components of the macroscopic ve-
locities $\mathbf{u}^s$ vanish. This occurs, for instance, when the distribution functions
depend on $\mathbf{v}$ only through its modulus and its latitudinal angle with respect
to that axis. As well known in the literature [14], this allows a sensible sim-
plification of the calculational apparatus, and a practical reduction to a fully
one–dimensional problem, though describing still a three–dimensional veloc-
ity space. On the other hand, this kind of problem is not only important for
theoretical investigation, but also quite frequent in practical applications: it
suffices to recall here the classical evaporation–condensation problems [22].
It is immediately seen that the previous assumptions imply $u_2^s = u_3^s = 0$,

and then $u_2 = u_3 = 0$ and $u_{2s} = u_{3s} = 0$ (for all s). It is convenient to introduce new unknowns

$$\phi^s = \iint f^s dv_2 dv_3, \qquad\qquad \psi^s = \iint (v_2^2 + v_3^2) f^s dv_2 dv_3, \qquad (50)$$

(integrations range from $-\infty$ to $+\infty$), each depending only on one space and one velocity variable. Of course, ϕ^s and ψ^s provide a reduced description of the velocity distributions, if compared to f^s, but they suffice for several purposes, as shown below. Dropping the subscript 1 also from velocities, the fundamental macroscopic parameters are in fact determined by ϕ^s and ψ^s as

$$
\begin{aligned}
n^s &= \int \phi^s \, dv, \qquad u^s = \frac{1}{n^s} \int v\phi^s dv, \\
\frac{3KT^s}{m^s} &= \frac{1}{n^s} \left[\int (v - u^s)^2 \phi^s dv + \int \psi^s dv \right].
\end{aligned}
\qquad (51)
$$

Setting

$$M_s(v) = n_s \left(\frac{m^s}{2\pi K T_s} \right)^{1/2} \exp\left[-\frac{m^s}{2KT_s}(v - u_s)^2 \right], \qquad (52)$$

multiplication of (3) by 1 and $(v_2^2 + v_3^2)$ and integration with respect to $(v_2, v_3) \in \mathbb{R}^2$ yields then the pair of BGK equations

$$
\begin{aligned}
\frac{\partial \phi^s}{\partial t} + v\frac{\partial \phi^s}{\partial x} &= \nu_s(M_s - \phi^s) \\
\frac{\partial \psi^s}{\partial t} + v\frac{\partial \psi^s}{\partial x} &= \nu_s \left(\frac{2KT_s}{m^s} M_s - \psi^s \right),
\end{aligned}
\qquad (53)
$$

which are actually coupled, since parameters n_s, u_s, T_s appearing in (52) follow from (7) and from (51). Collision equilibria are given by $\phi^s = M^s$, $\psi^s = \dfrac{2KT}{m^s} M^s$, where

$$M^s(v) = n^s \left(\frac{m^s}{2\pi K T} \right)^{1/2} \exp\left[-\frac{m^s}{2KT}(v - u)^2 \right]. \qquad (54)$$

It is now a five–parameter family of Maxwellians, with densities related by the mass action law (14).

We have processed numerically equations (53) in some simple space–homogeneous test case, mainly for illustrative purposes, without having in mind a specific reactive mixture, all quantities being measured in suit-

able scales. Moments of the distribution functions ϕ^s and ψ^s appearing in (51) have been numerically evaluated by means of the composite trapezoidal quadrature rule on a sufficiently large bounded velocity interval $[-R, R]$.

As reference problem (Problem A) we have taken an isotropically scattering mixture (then $\nu_1^{sr} = \nu_0^{sr}$) where the microscopic pair collision frequencies ν_0^{sr} are given by Table 1.

Table 1. Elastic collision frequencies ν_0^{sr}.

ν_0^{sr}	1	2	3	4
1	0.3	0.4	0.1	0.4
2	0.4	0.3	0.4	0.6
3	0.1	0.4	0.3	0.2
4	0.4	0.6	0.2	0.4

The reactive endothermic chemical collision frequency is instead $\nu_{12}^{34} = 0.01$, namely the typical chemical collision time is about one order of magnitude larger than the typical scattering collision time. This is done merely in order to possibly separate in the numerical outputs the effects due to mechanical encounters from those due to chemical reaction, and it is understood that we remain in the physical regime described in the Introduction [11, 12]. Masses take the values

$$m^1 = 11.7, \qquad m^2 = 3.6, \qquad m^3 = 8, \qquad m^4 = 7.3, \qquad (55)$$

chosen just as an illustrative example, and the energy difference in the chemical bonds is $\Delta E = 10$. Initial conditions have been selected as Maxwellian shapes characterized by the parameters

$$
\begin{aligned}
&n^1(0) = 9 \ \ n^2(0) = 12 \ \ n^3(0) = 13 \ \ n^4(0) = 11 \\
&u^1(0) = 1 \ \ u^2(0) = 2 \ \ \ u^3(0) = 3 \ \ \ u^4(0) = 6 \\
&T^1(0) = 1 \ \ T^2(0) = 5 \ \ \ T^3(0) = 4 \ \ \ T^4(0) = 2.
\end{aligned}
\qquad (56)
$$

These values determine uniquely, via the five disposable independent first integrals $(n^1 + n^3, \ n^1 + n^4, \ n^2 + n^4, \ u, \ \text{and} \ \frac{3}{2}nT + \sum_{s=1}^{4} E^s n^s)$ and the mass action law (14), the unique Maxwellian equilibrium, described by (54), with parameters which turn out to be

$$
\begin{aligned}
&n^1 = 10.688 \ \ n^2 = 13.687 \ \ n^3 = 11.312 \ \ \ n^4 = 9.312 \\
&\qquad\qquad u = 2.9614 \ \ \ T = 12.2145.
\end{aligned}
\qquad (57)
$$

Evolution of all macroscopic parameters can be deduced from (51) upon integration of the numerically computed ϕ^s and ψ^s. As discussed in [9], such evolution is correctly reproduced by the present BGK equations, and indeed our results coincide to computer accuracy with the ones of [10]. Typical trends are shown in Figures 1 and 2. Equalization of velocities and temperatures is due to elastic scattering, and it actually occurs on the short (mechanical) scale. Relaxation of densities n^s and temperature T (non–conserved quantities) is due instead to chemical interactions, and is ruled
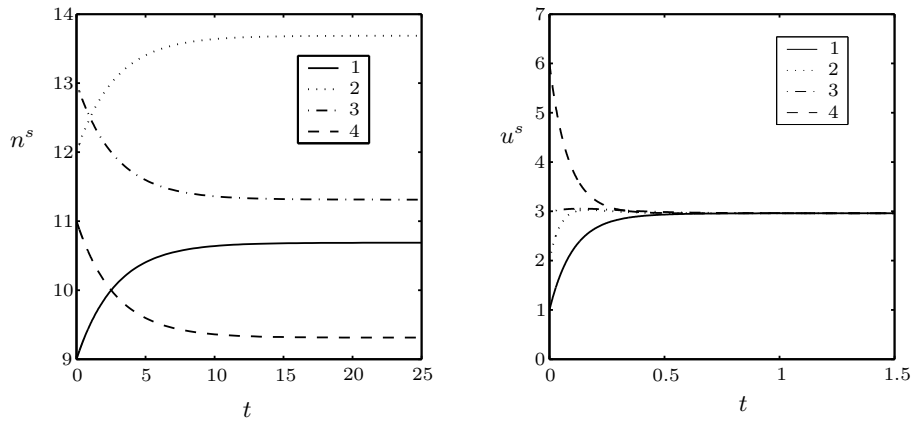
Figure 1. Trends of densities n^s (left) and of velocities u^s (right) versus time for problem A.
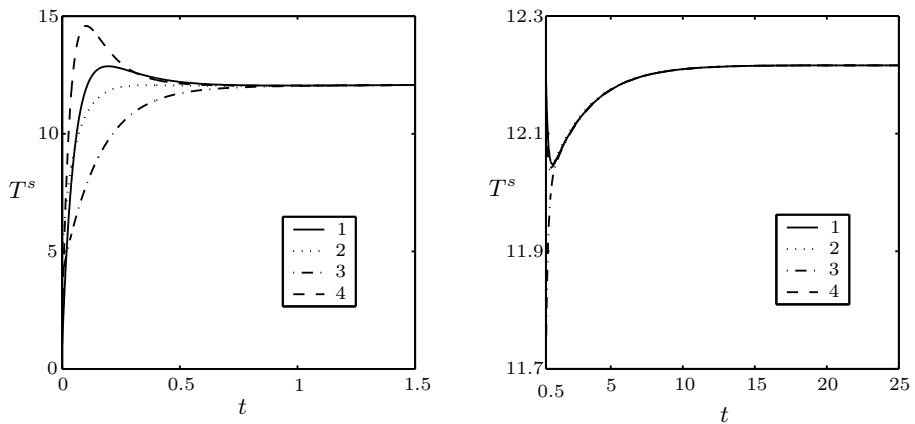
Figure 2. Time evolution of temperature T^s on the short (left) and on the long (right) time scale for Problem A.

by the longer reactive characteristic time. In the considered problem we observe an overall transformation of products into reactants, and a corresponding temperature increase due to transformation of energy from chemical to thermal. In general, overshoot or undershoot of some species temperature can occur, as indicated by Figure 2.
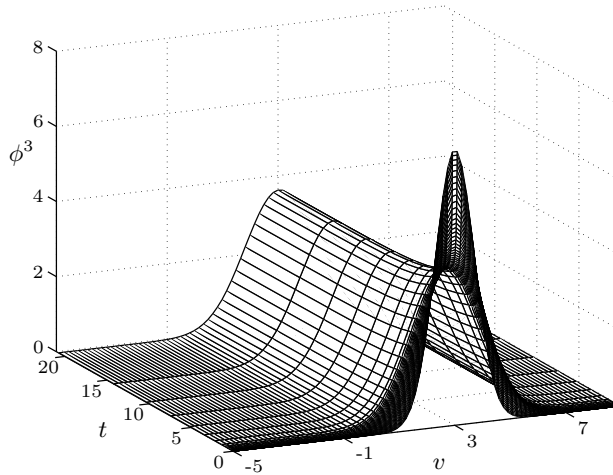

Figure 3. Function ϕ^3 versus t and v for Problem A.

Relaxation of the distribution functions ϕ^s towards the equilibria (54) is illustrated by Figure 3, relevant to $s = 3$, on the (v, t) plane. As expected, the initial shape gets strongly modified in a first short initial time–layer, dominated by mechanical encounters, then a restored, but different, Maxwellian evolves smoothly, at the chemical pace, towards the equilibrium M^3, following the slow time variations of n^3 and T^3, and with a practically constant u^3. The approach of ϕ^s to the associated local Maxwellian

$$\mathsf{M}^s = n^s \left(\frac{m^s}{2\pi K T^s} \right)^{1/2} \exp \left[-\frac{m^s}{2K T^s} (v - u^s)^2 \right], \tag{58}$$

where n^s, u^s, T^s are the actual time–dependent macroscopic parameters, is well depicted by the deviation $\phi^s - \mathsf{M}^s$ versus v and t, shown in Figure 4 for $s = 2$. The deviation is zero initially, because of the initial Gaussian shape, then undergoes positive and negative variations, which remain confined however both in amplitude (order one tenth) and in domain (a neighborhood of

the varying macroscopic velocity). In addition, the deviation vanishes iden-
tically in a very short time, of the order of the mechanical relaxation time,
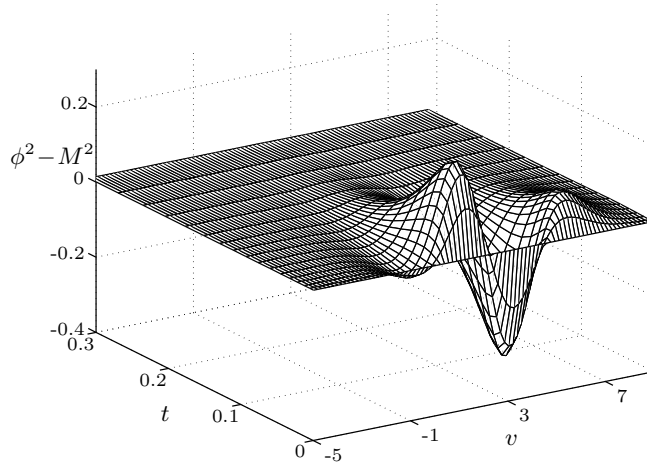and even smaller than the velocity or temperature equalization time.

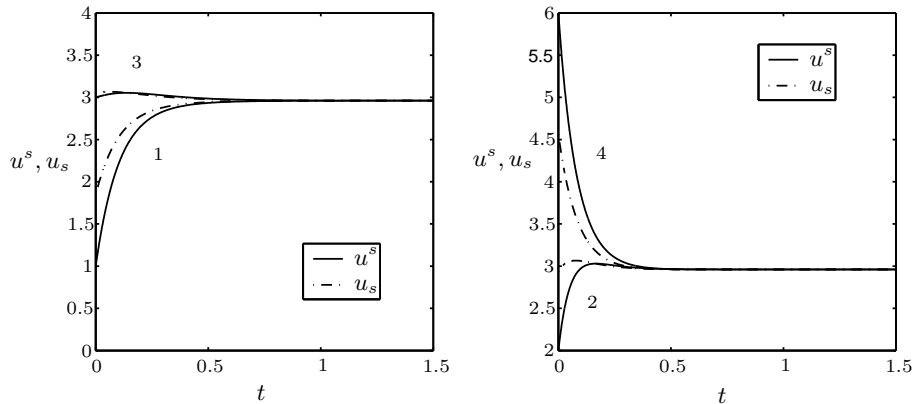**Figure 4.** Zoom of the deviation $\phi^2 - \mathsf{M}^2$ versus t and v for Problem A.

Figure 5. Difference between actual and auxiliary mean velocities (u^s and
u_s respectively) versus time: $s = 1, 3$ (left), $s = 2, 4$ (right) for Problem A.

Finally, a measure of the approach to equilibrium is provided also by
the difference between the actual and the auxiliary macroscopic fields, which
must relax to zero for increasing time. We exhibit here the trend of the
velocities u^s and u_s in Figure 5. Differences are again rather modest, and
tend quickly to vanish, on the fast mechanical scale. As predicted by the

BGK equations themselves, we have $\dot{u}^s < 0$ ($\dot{u}^s > 0$) for $u_s < u^s$ ($u_s > u^s$); in particular, we can observe that crossing of the actual and fictitious curves may occur only for the species with a non–monotonic trend for u^s (i.e., $s = 2, 3$), and it actually occurs when $\dot{u}^s = 0$.
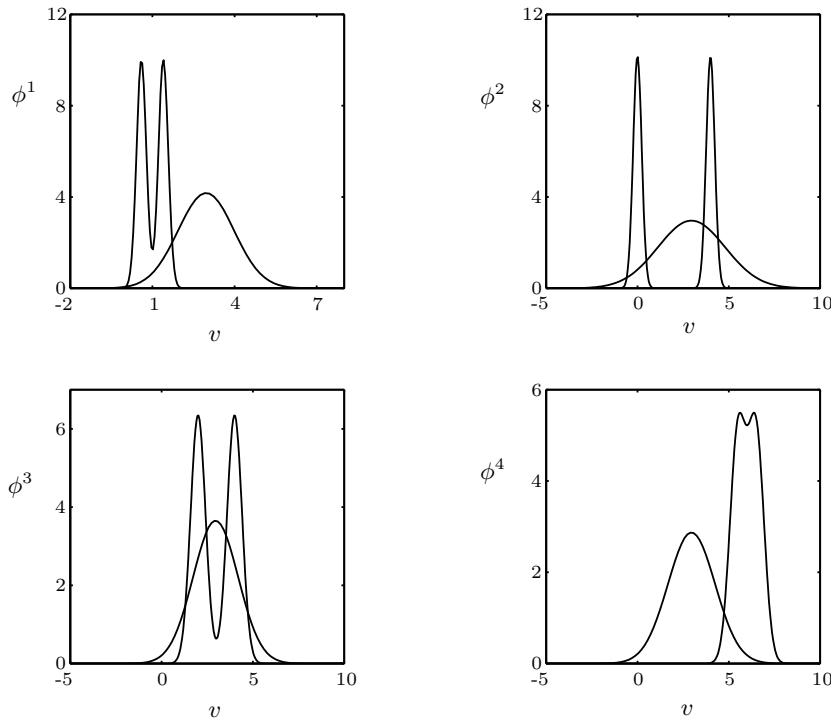

Figure 6. Initial and final velocity profiles for ϕ^s in Problem B.

We next examine the response of our relaxation model to a change of initial shape from a Gaussian to a bimodal distribution, as depicted in Figure 6 (Problem B). Such distributions are made up by two identical symmetrically displaced Maxwellians, chosen in such a way that the macroscopic initial conditions remain the same of Problem A, as given by (56). This requirement determines them uniquely, once the peak separation Δu is assigned. We have taken here

$$\Delta u^1 = 0.8 \qquad \Delta u^2 = 4 \qquad \Delta u^3 = 2 \qquad \Delta u^4 = 1. \qquad (59)$$

Since equations (56) are unchanged with respect to Problem A, evolution of all macroscopic variables remains the same, as well as the final equilibrium distributions M^s, which are also given in Figure 6. The three–dimensional

plot of Figure 7 shows ϕ^3 versus v and t; after a rapid transition to a unimodal shape, it evolves essentially in the same way as for Problem A (see Figure 3). Figure 8, to be compared to Figure 4, reports on the deviation of ϕ^2 from the local Maxwellian M^2 for Problem B on the short time scale. It can be noticed that relaxation to local thermodynamical equilibrium occurs essentially on the same time scale as for Problem A, but differences are larger by almost two orders of magnitude, due to strong deviation of the initial shape from a Gaussian (it is almost a double stream distribution for this species).
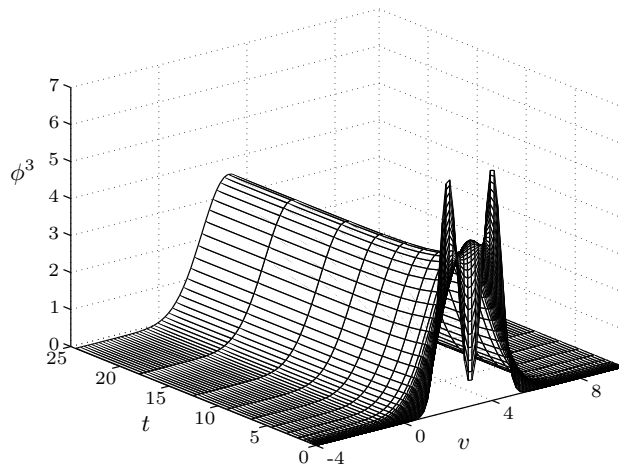

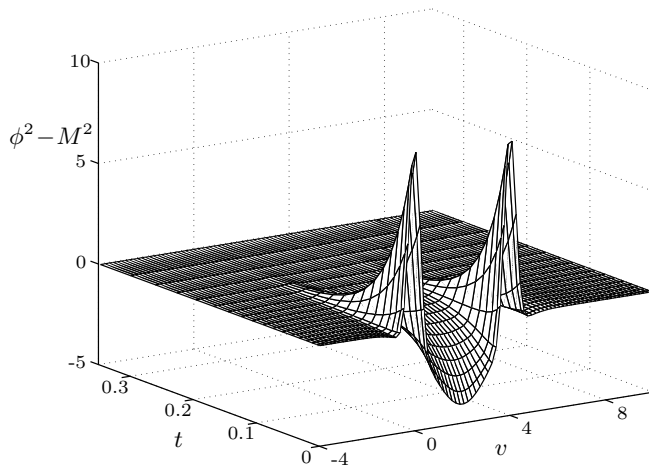**Figure 7.** Function ϕ^3 versus t and v for Problem B.

Figure 8. Zoom of the deviation $\phi^2 - \mathsf{M}^2$ versus t and v for Problem B.
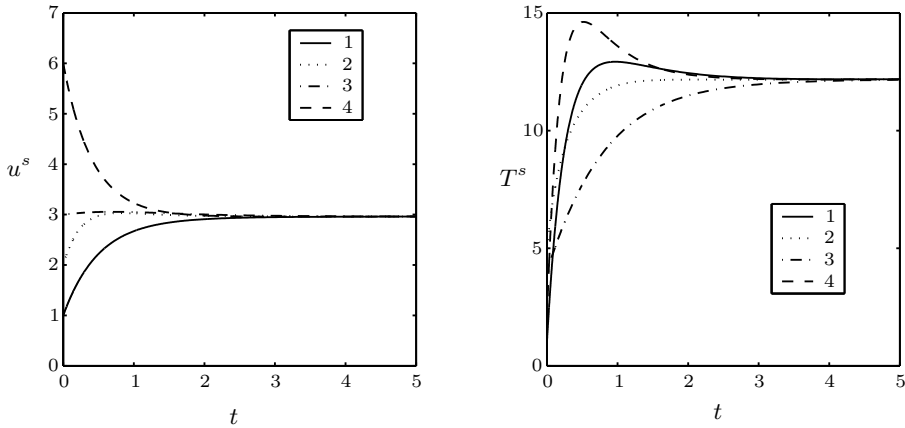
Figure 9. Trends of velocities u^s (left) and of temperatures T^s (right) versus time for problem C.

Finally, we have considered a third test case (Problem C) in order to see the response of our model to anisotropy of scattering. For this purpose we change, with respect to Problem A, only the microscopic collision frequencies for momentum transfer ν_1^{sr}, by taking a uniform reduction factor, i.e. $\nu_1^{sr} = \frac{1}{5}\nu_0^{sr}$, $\forall (s,r)$, which replaces the equality $\nu_1^{sr} = \nu_0^{sr}$ relevant to isotropic scattering. In this way, scattering is quite forwardly peaked (mainly grazing collisions), which means that, though mechanical encounters are still much more frequent than chemical reactions, momentum and energy transfer in elastic scattering becomes much less effective, and then all relaxation phenomena driven by mechanical collisions become slower and almost comparable to chemical relaxations. This is indeed what we actually verified numerically, and is illustrated by Figure 9, where we plot velocities and temperatures versus time, and realize that equalization times have increased, roughly speaking, by a factor of 5 with respect to the Problem A (see Figures 1 and 2). The slower rate of variation of macroscopic parameters has then interesting implications at the kinetic level. In fact, in agreement with a lower magnitude of time derivatives, we observe a sensible decrease of the differences between actual and auxiliary macroscopic fields. An example is provided by Figure 10, where we plot for comparison the temperatures T^s and T_s for Problem A and for Problem C (notice again the different time scales for the two problems). As a consequence of the much smaller deviations of fictitious fields from the actual ones, the auxiliary Maxwellians M_s towards which our collision relaxation model forces particle distributions are much closer now to the actual local Maxwellians M^s than for the reference
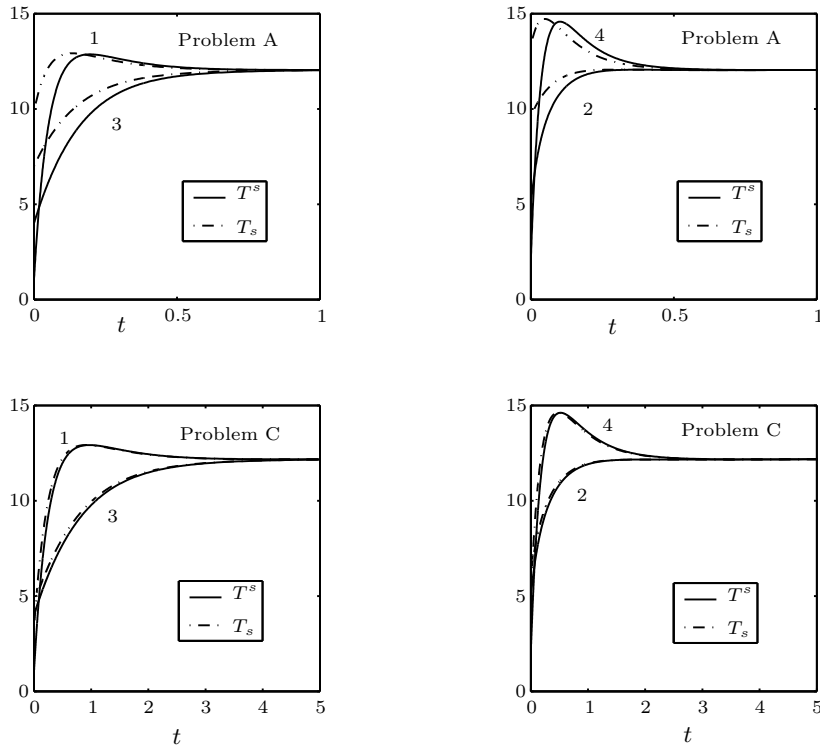
Figure 10. Comparison of actual and auxiliary temperatures (T^s and T_s respectively) versus time for problem A (above) and Problem C (below).
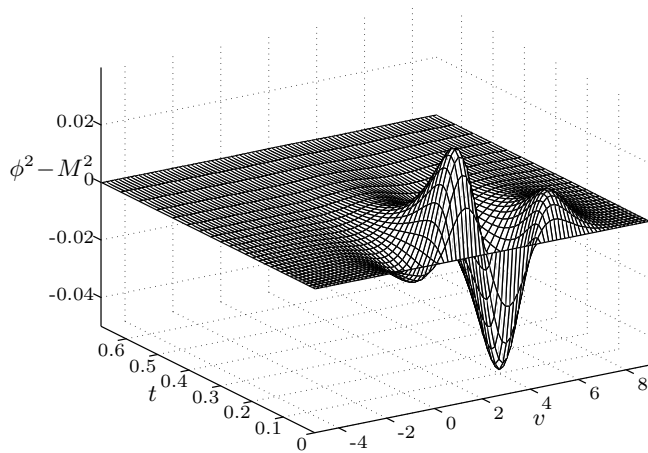

Figure 11. Zoom of the deviation $\phi^2 - \mathsf{M}^2$ versus t and v for Problem C.

problem. Deviations of distribution functions ϕ^s from the corresponding local Maxwellians are then smaller than for Problem A. This is shown, for $s = 2$, in Figure 11, where the differences, initially zero because of the Gaussian initial shape, tend again to zero (corresponding to local equilibrium) on a short time scale which is slightly longer than for Problem A, but undergo fluctuations that remain at least one order of magnitude smaller than in Figure 4.

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