

A Note on a Kinetic Relaxation Model for a Reactive Gas Mixture

M. Groppi, G. Spiga

Dipartimento di Matematica e Informatica, Università di Parma,

Parco Area delle Scienze 53/A - 43124 Parma, Italy

maria.groppi@unipr.it, giampiero.spiga@unipr.it

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Abstract

A reactive BGK-type model is proposed for a binary mixture of rarefied gases, by resorting to a simple Boltzmann collision operator for a slow irreversible de-excitation reaction, in a process driven by mechanical encounters. The hydrodynamic limit is worked out by a Chapman-Enskog asymptotic procedure up to the Navier-Stokes equations, and can fit exactly Fick's law for diffusion velocities and Newton's law for the viscous stress, which is traceless in the present scaling. Transport coefficients are not affected by the chemical reaction, whereas reactive effects are described by additional source terms (integrals involving the chemical cross sections), vanishing at chemical equilibrium, which in turn are not affected by mechanical relaxation parameters.

1 Introduction

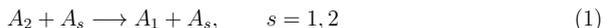
Relaxation time approximations of BGK type [1, 2] constitute probably the most ancient and yet the most popular and flexible simplified kinetic models of the true integro-differential Boltzmann equation in Rarefied Gas Dynamics [3, 4], retaining the most significant mathematical and physical features of the actual Boltzmann equation. On the other hand, BGK approaches have been extended to more complex physical scenarios, like gas mixtures [5, 6] and reversible bimolecular chemical reactions [7–9], considered in a kinetic framework [10].

As well known, one of the main shortcomings of the BGK approach is the partial reliability of its hydrodynamic regime in the asymptotic continuum limit. Even for a single

monoatomic gas, it is impossible to fit simultaneously, by a single relaxation parameter, viscosity coefficient and thermal conductivity, so that the Prandtl number is incorrect. This crucial drawback can be overcome by resorting to the so called ellipsoidal BGK (ES-BGK) model [11], which, in more recent times, has been cast in a consistent and elegant mathematical frame, also for polyatomic gases [12, 13]. Such a statistical model allows for different scales of relaxation, and introduces then additional disposable parameters, to be used in order to fit the required transport coefficients.

On the other hand, quite severe difficulties are encountered when trying to apply the BGK strategy to a gas made up by different species, like the ones occurring in any real-world application. A significant breakthrough in this direction, aimed mainly at fitting the Fick's matrix for diffusion velocities, has been performed in recent years, for the simple case of a binary mixture [14] as well as for a general number of components [15]. It is worth to mention that the same algorithm as in [15] can be successfully applied in order to deal with reversible reactions in multicomponent mixtures [16, 17]. These last generalized BGK models might be considered as "ellipsoidal", in some broad sense. In fact, they allow to quantitatively improve the hydrodynamic limit, in the spirit of the pioneering work on the subject [11], but entail typically an isotropic Gaussian attractor, leading eventually to a correct representation of diffusion velocities, but not of the Prandtl number.

The present note is aimed at generalizing the results of [14] to a reactive frame. The quoted article presented explicit results for the simplest conceivable case of a binary inert mixture of monoatomic gases, in which the additional constraint was a faster equalization of drift velocities of the two species in the relaxation to equilibrium, introducing thus a second relaxation parameter. It was shown that all conservation and variational properties are fulfilled, and positivity requirements of the macroscopic fields can be controlled. Here we assume that one of the two species (say, the second) is an excited state of the other, sharing then the same mass, and the mixture is reactive in the sense that the de-excitation process occurs via the irreversible binary interaction (without mass exchange)



which is of interest in several combustion problems, like for instance in flame structure [18], and motivates thus the present investigation. This model is probably the simplest way to mimic a polyatomic gas as a mixture of (identical) monoatomic gases, corresponding to two different energy levels of the internal structure. Reaction (1) takes place together

with all possible mechanical (elastic) encounters between the two species, with probability determined by the relevant microscopic differential cross sections σ , depending as usual on impinging relative speed g and deflection angle χ [4]. The common mass will be denoted by m , and the energies of chemical bond may be normalized as 0 for the ground state and $E > 0$ for the excited one (exothermic reaction).

The mechanical (elastic) collision operator is constructed in terms of different isotropic non-equilibrium attractors, with suitable drift velocities and temperatures, ensuring all pertinent mathematical requirements (conservation laws, collision equilibria, H -theorem). The model satisfies a maximum entropy principle and displays two disposable relaxation parameters for fitting transport coefficients. The reactive collision operator is taken to be slow with respect to the mechanical one (which plays the dominant role in driving the overall evolution problem) with typical relaxation time of the same order as the macroscopic time scale. Such a physical two-scale scenario is typical when interactions of some resonant type play an important role in the evolution, making collision between particles of the same species the leading process in the mixture. The present approach can be useful, for instance, in aerothermodynamics, where one is interested in rate coefficients in case of thermochemical non-equilibrium. Similar approaches in different contexts lead generally to multitemperature descriptions (such as occurrence of translational and vibrational temperatures) at macroscopic level [19]. We shall construct the reactive collision integral along the lines of the kinetic Boltzmann model proposed in [20] for a classical problem of extended thermodynamics [21], in whose frame polyatomic gases have been also dealt with [22]. The collision operator is defined in terms of the reactive cross sections σ_{21}^{11} and σ_{22}^{12} relevant to the encounters (1). Other scalings, as well as other problems, will be hopefully matter of future research.

The physical problem under investigation is then driven by purely elastic events, rather than by all energy-preserving encounters. In other words, these events do not realize that the two components are different states of the same species. In addition, the slower interactive mechanism linking together the two components of the mixture in a single gas is microscopically irreversible, peculiarities which constitute another motivation of the present work. While the dominant (mechanical) operator preserves number of particles in each species, total momentum, and total kinetic energy, the presence of reaction, no matter how slow, reduces the number of conserved quantities to total number of particles,

total momentum, and overall (mechanical plus chemical) total energy, making the problem singular from a mathematical point of view in the asymptotic continuum limit.

The paper is organized as follows. In the next Section we shall write down, in dimensionless form, the proposed generalized BGK model with chemical reaction, and, after analyzing, for the readers' convenience, its main features, we shall establish the main properties to be used in the Chapman-Enskog asymptotic expansion. In Section 3 we shall perform the hydrodynamic limit up to first order corrections (Navier-Stokes fluid-dynamic level) and achieve the sought reaction diffusion equations with proper reaction rates and transport coefficients. Results are finally briefly commented on, emphasizing the chemical corrections with respect to the non-reacting frame.

2 The kinetic reactive BGK model

The re-scaled (dimensionless) kinetic equations governing the evolution of the distribution functions f_s in the reactive binary mixture described in the Introduction read as

$$\frac{\partial f_s^\varepsilon}{\partial t} + \mathbf{v} \cdot \nabla_{\mathbf{x}} f_s^\varepsilon = \frac{\nu}{\varepsilon} (G_s[f_1^\varepsilon, f_2^\varepsilon] - f_s^\varepsilon) + J_s[f_1^\varepsilon, f_2^\varepsilon], \quad s = 1, 2 \quad (2)$$

where ε is the small positive parameter, Knudsen-like number, ratio of the fast to the slow time scales, $\nu > 0$ is a (constant) relaxation parameter, and where, as usual, $\mathbf{x} \in \mathbb{R}^3$ is space variable and $\mathbf{v} \in \mathbb{R}^3$ molecular velocity. Denoting by n_s, \mathbf{u}_s, T_s the standard number density, drift velocity, and temperature of species s , the generalized BGK attractor takes the Gaussian form [14]

$$G_s[f_1^\varepsilon, f_2^\varepsilon](\mathbf{v}) = n_s \left(\frac{m}{2\pi T^*} \right)^{\frac{3}{2}} \exp \left[-\frac{m}{2T^*} (\mathbf{v} - \mathbf{u}_s^*)^2 \right], \quad s = 1, 2 \quad (3)$$

where the fictitious parameters \mathbf{u}_s^* and T^* are determined by the actual mass velocity \mathbf{u} and gas temperature T and by an additional relaxation parameter η , with $\nu \leq \eta \leq 2\nu$, as

$$\mathbf{u}_s^* = \left(1 - \frac{\eta}{\nu} \right) \mathbf{u}_s + \frac{\eta}{\nu} \mathbf{u}, \quad T^* = T - \frac{1}{3n} \left(1 - \frac{\eta}{\nu} \right)^2 \sum_{s=1}^2 \rho_s (\mathbf{u}_s - \mathbf{u})^2 > \frac{1}{n} \sum_{s=1}^2 n_s T_s > 0, \quad (4)$$

with $\rho_s = mn_s$ for mass density. We remark that the attractor (3) is made up by Gaussians which are isotropic with respect to different auxiliary drift velocities, and that it allowed to fit Fick's diffusion law in the inert case. We also recall for convenience the definition of the higher order macroscopic fields in terms of the corresponding species quantities

(defined in the standard way), including pressure tensor \mathbf{P} and heat flux vector \mathbf{q} , namely

$$\begin{aligned}\mathbf{u} &= \frac{1}{\rho} \sum_{s=1}^2 \rho_s \mathbf{u}_s, & nT &= \sum_{s=1}^2 n_s T_s + \frac{1}{3} \sum_{s=1}^2 \rho_s (\mathbf{u}_s - \mathbf{u})^2 \\ \mathbf{P} &= \sum_{s=1}^2 \mathbf{P}_s + \sum_{s=1}^2 \rho_s (\mathbf{u}_s - \mathbf{u}) \otimes (\mathbf{u}_s - \mathbf{u}) \\ \mathbf{q} &= \sum_{s=1}^2 \mathbf{q}_s + \sum_{s=1}^2 (\mathbf{u}_s - \mathbf{u}) \cdot \mathbf{P}_s + \frac{3}{2} \sum_{s=1}^2 n_s T_s (\mathbf{u}_s - \mathbf{u}) + \frac{1}{2} \sum_{s=1}^2 \rho_s (\mathbf{u}_s - \mathbf{u}) (\mathbf{u}_s - \mathbf{u})^2.\end{aligned}\tag{5}$$

The collision invariants of the mechanical (elastic) collision operator $\nu(G_s - f_s)$ are the test functions pairs

$$(1, 0) \quad (0, 1) \quad (m\mathbf{v}, m\mathbf{v}) \quad \left(\frac{1}{2}mv^2, \frac{1}{2}mv^2\right),\tag{6}$$

and its collision equilibrium is given by the six-parameter family of Maxwellian distributions

$$f_s^M(\mathbf{v}) = n_s \left(\frac{m}{2\pi T}\right)^{\frac{3}{2}} \exp\left[-\frac{m}{2T}(\mathbf{v} - \mathbf{u})^2\right], \quad s = 1, 2\tag{7}$$

at common macroscopic velocity and temperature.

The chemical collision operator J_s , according to the kinetic model [23], takes, in the present irreversible scenario, the rather complicated form

$$\begin{aligned}J_1[f_1, f_2](\mathbf{v}) &= 2 \int_{\mathbb{R}^3 \times \mathbb{S}^2} \Theta\left(g^2 - \frac{4E}{m}\right) \frac{g^2}{g} \sigma_{21}^{11}(g-, \chi) f_2(\mathbf{v}_{11}^{21}) f_1(\mathbf{w}_{11}^{21}) d_3\mathbf{w} d_2\hat{n}' \\ &\quad + \int_{\mathbb{R}^3 \times \mathbb{S}^2} \Theta\left(g^2 - \frac{4E}{m}\right) \frac{g^2}{g} \sigma_{22}^{12}(g-, \chi) f_2(\mathbf{v}_{12}^{22}) f_2(\mathbf{w}_{12}^{22}) d_3\mathbf{w} d_2\hat{n}' \\ &\quad - \int_{\mathbb{R}^3 \times \mathbb{S}^2} g \sigma_{21}^{11}(g, \chi) f_1(\mathbf{v}) f_2(\mathbf{w}) d_3\mathbf{w} d_2\hat{n}' \\ J_2[f_1, f_2](\mathbf{v}) &= \int_{\mathbb{R}^3 \times \mathbb{S}^2} \Theta\left(g^2 - \frac{4E}{m}\right) \frac{g^2}{g} \sigma_{22}^{12}(g-, \chi) f_2(\mathbf{v}_{12}^{22}) f_2(\mathbf{w}_{12}^{22}) d_3\mathbf{w} d_2\hat{n}' \\ &\quad - \int_{\mathbb{R}^3 \times \mathbb{S}^2} g \sigma_{21}^{11}(g, \chi) f_2(\mathbf{v}) f_1(\mathbf{w}) d_3\mathbf{w} d_2\hat{n}' \\ &\quad - 2 \int_{\mathbb{R}^3 \times \mathbb{S}^2} g \sigma_{22}^{12}(g, \chi) f_2(\mathbf{v}) f_2(\mathbf{w}) d_3\mathbf{w} d_2\hat{n}'\end{aligned}\tag{8}$$

where \mathbf{x} and t dependence are omitted for brevity, Θ stands for unit step (Heaviside) function, and the auxiliary velocities are defined by

$$\mathbf{v}_{ij}^{hk} = \frac{1}{2}(\mathbf{v} + \mathbf{w} + g_{ij}^{hk} \hat{n}'), \quad \mathbf{w}_{ij}^{hk} = \frac{1}{2}(\mathbf{v} + \mathbf{w} - g_{ij}^{hk} \hat{n}')\tag{9}$$

where

$$g_{12}^{22} = g_{11}^{21} = g_- = \left(g^2 - \frac{4E}{m}\right)^{\frac{1}{2}}, \quad g = |\mathbf{v} - \mathbf{w}|, \quad \cos \chi = \hat{n} \cdot \hat{n}'. \quad (10)$$

Here and below it is implicitly understood that integrations with respect to velocity variables range all over \mathbb{R}^3 , and integrations with respect to unit vectors like $\hat{n} = (\mathbf{v} - \mathbf{w})/g$ or \hat{n}' range all over the unit sphere \mathbb{S}^2 . The operator J_s is better represented in a weak form of more direct physical meaning, namely, for any pair of smooth test functions $\varphi_s(\mathbf{v})$, we have

$$\begin{aligned} & \sum_{s=1}^2 \int \varphi_s(\mathbf{v}) J_s[f_1, f_2](\mathbf{v}) d_3 \mathbf{v} = \\ & = \iiint g \sigma_{21}^{11}(g, \chi) [\varphi_1(\mathbf{v}_{21}^{11}) + \varphi_1(\mathbf{w}_{21}^{11}) - \varphi_2(\mathbf{v}) - \varphi_1(\mathbf{w})] f_2(\mathbf{v}) f_1(\mathbf{w}) d_3 \mathbf{v} d_3 \mathbf{w} d_2 \hat{n}' \\ & + \iiint g \sigma_{22}^{12}(g, \chi) [\varphi_1(\mathbf{v}_{22}^{12}) + \varphi_2(\mathbf{w}_{22}^{12}) - \varphi_2(\mathbf{v}) - \varphi_2(\mathbf{w})] f_2(\mathbf{v}) f_2(\mathbf{w}) d_3 \mathbf{v} d_3 \mathbf{w} d_2 \hat{n}', \end{aligned} \quad (11)$$

where again auxiliary (post-collision) velocities are defined by (9), with now

$$g_{21}^{11} = g_{22}^{12} = g_+ = \left(g^2 + \frac{4E}{m}\right)^{\frac{1}{2}}. \quad (12)$$

By the same technique as in [20] it is not difficult to prove that collision invariants for the whole (mechanical plus reactive) collision operator in (2) are provided by the pairs

$$(1, 1) \quad (m\mathbf{v}, m\mathbf{v}) \quad \left(\frac{1}{2}mv^2, \frac{1}{2}mv^2 + E\right), \quad (13)$$

and the overall collision equilibrium for the reactive mixture is given by

$$f_1^{eq}(\mathbf{v}) = n \left(\frac{m}{2\pi T}\right)^{\frac{3}{2}} \exp\left[-\frac{m}{2T}(\mathbf{v} - \mathbf{u})^2\right], \quad f_2^{eq}(\mathbf{v}) = 0, \quad (14)$$

with only five free scalar parameters (n, \mathbf{u}, T). Moreover, exact (non-closed) macroscopic conservation equations read as

$$\begin{aligned} & \frac{\partial n}{\partial t} + \nabla_{\mathbf{x}} \cdot (n\mathbf{u}) = 0 \\ & \frac{\partial}{\partial t}(\rho\mathbf{u}) + \nabla_{\mathbf{x}} \cdot (\rho\mathbf{u} \otimes \mathbf{u}) + \nabla_{\mathbf{x}}(nT) + \nabla_{\mathbf{x}} \cdot \mathbf{\Pi} = \mathbf{0} \\ & \frac{\partial}{\partial t} \left(\frac{1}{2}\rho u^2 + \frac{3}{2}nT + En_2\right) + \nabla_{\mathbf{x}} \cdot \left[\left(\frac{1}{2}\rho u^2 + \frac{5}{2}nT + En_2\right)\mathbf{u} \right. \\ & \quad \left. + \mathbf{\Pi} \cdot \mathbf{u} + \mathbf{q} + En_2(\mathbf{u}_2 - \mathbf{u})\right] = 0 \end{aligned} \quad (15)$$

with appearance of the viscous stress tensor $\mathbf{\Pi} = \mathbf{P} - nT\mathbf{I}$ (deviatoric part of the pressure tensor \mathbf{P}), of the heat flux \mathbf{q} and of the diffusion velocity $\mathbf{u}_2 - \mathbf{u}$. For later use, we need also the weak forms of the kinetic equations (2) corresponding to the collision invariants (6) of the mechanical operator only, which drives the evolution. They may be cast as a set of six scalar partial differential equations made up by the set (15) of five actual conservations, plus an additional balance equation, accounting for the fact that particle number in each species is not preserved by reaction (1), namely

$$\frac{\partial n_2}{\partial t} + \nabla_{\mathbf{x}} \cdot (n_2 \mathbf{u}) = -\nabla_{\mathbf{x}} \cdot [n_2(\mathbf{u}_2 - \mathbf{u})] - \sum_{r=1}^2 S_{2r} \quad (16)$$

with reactive rates (source contributions)

$$S_{2r} = \iint g \sigma_{2r}^{ch}(g) f_2(\mathbf{v}) f_r(\mathbf{w}) d_3 \mathbf{v} d_3 \mathbf{w}, \quad \sigma_{2r}^{ch} = 2\pi \int_0^\pi \sigma_{2r}^{1r}(g, \chi) \sin \chi d\chi, \quad r = 1, 2, \quad (17)$$

which obviously vanish at chemical equilibrium, since that corresponds to depletion of the excited species. According to the Chapman-Enskog singular asymptotic expansion [3, 24] for $\varepsilon \rightarrow 0$, hydrodynamic variables to be kept unexpanded are then n_1, n_2, \mathbf{u}, T (and then also n, ρ_1, ρ_2 and ρ), whereas constitutive equations are needed for $\mathbf{\Pi}, \mathbf{q}, \mathbf{u}_2 - \mathbf{u}, S_{2r}$ ($r = 1, 2$).

Notice how the present facts are at variance with respect to the usual kinetic theory with reversible chemistry [8, 10], where kinetic energy is not a conserved quantity for the dominant operator, and consequently temperature is not hydrodynamic variable, so that it is affected (together with scalar pressure) to higher order corrections in the asymptotic expansion. In the present frame transfer of energy between its kinetic and internal forms is taken to be a seldom one-directional event, so that excitation energy actually gets entirely transformed into kinetic energy, but only on the slow scale.

Species velocities \mathbf{u}_s and temperatures T_s have then to be expanded in powers of ε . They are related however by the constraints following from their definition

$$\sum_{s=1}^2 \rho_s (\mathbf{u}_s - \mathbf{u}) = 0, \quad \sum_{s=1}^2 n_s (T_s - T) + \frac{1}{3} \sum_{s=1}^2 \rho_s (\mathbf{u}_s - \mathbf{u})^2 = 0. \quad (18)$$

Being interested here only in a first order fluid-dynamic approximation (Navier-Stokes level), we shall set

$$f_s^\varepsilon = f_s^{(0)} + \varepsilon f_s^{(1)}, \quad s = 1, 2 \quad (19)$$

which implies

$$\mathbf{u}_s = \mathbf{u}_s^{(0)} + \varepsilon \mathbf{u}_s^{(1)}, \quad T_s = T_s^{(0)} + \varepsilon T_s^{(1)}, \quad S_{2r} = S_{2r}^{(0)} + \varepsilon S_{2r}^{(1)}, \quad r = 1, 2. \quad (20)$$

The first step in the procedure is

$$G_s[f_1^{(0)}, f_2^{(0)}] = f_s^{(0)}, \quad s = 1, 2 \quad (21)$$

which yields [14]

$$f_s^{(0)} = f_s^M = n_s \left(\frac{m}{2\pi T} \right)^{\frac{3}{2}} \exp \left[-\frac{m}{2T} (\mathbf{v} - \mathbf{u})^2 \right], \quad (22)$$

from which

$$\mathbf{u}_s^{(0)} = \mathbf{u}, \quad T_s^{(0)} = T, \quad S_{2r}^{(0)} = n_2 n_r \left(\frac{m}{2\pi T} \right)^3 \iint g \sigma_{2r}^{ch}(g) \exp \left[-\frac{m}{2T} (w^2 + w'^2) \right] d_3 \mathbf{v} d_3 \mathbf{w}. \quad (23)$$

Constraints (18) reduce then to

$$\sum_{s=1}^2 \rho_s \mathbf{u}_s^{(1)} = \mathbf{0}, \quad \sum_{s=1}^2 n_s T_s^{(1)} = 0, \quad (24)$$

and both $\mathbf{\Pi}$ and \mathbf{q} are $O(\varepsilon)$. All first order corrections needed for closing the exact equations (15) and (16) will be worked out in the next Section.

3 Hydrodynamic limit

Bearing (19) and (22) in mind, the kinetic generalized BGK equations for the unknowns f_s^ε may be ordered in the functional form

$$f_s^\varepsilon(\mathbf{v}) = G_s[f_1^\varepsilon, f_2^\varepsilon](\mathbf{v}) - \frac{\varepsilon}{\nu} \left(\frac{\partial f_s^M}{\partial t} + \mathbf{v} \cdot \nabla_{\mathbf{x}} f_s^M \right) + \frac{\varepsilon}{\nu} J_s[f_1^M, f_2^M] + O(\varepsilon^2). \quad (25)$$

Terms $J_s[f_1^M, f_2^M] \equiv J_s^{(0)}$ are explicit, though complicated, functions of the hydrodynamic variables, precisely, owing to (8) and (22),

$$\begin{aligned} J_1^{(0)}(\mathbf{v}) &= 2f_1^M(\mathbf{v}) e^{E/T} \int \Theta(g_-) \frac{g_-^2}{g} \sigma_{21}^{ch}(g_-) f_2^M(\mathbf{w}) d_3 \mathbf{w} \\ &+ f_2^M(\mathbf{v}) e^{E/T} \int \Theta(g_-) \frac{g_-^2}{g} \sigma_{22}^{ch}(g_-) f_2^M(\mathbf{w}) d_3 \mathbf{w} - f_1^M(\mathbf{v}) \int g \sigma_{21}^{ch}(g) f_2^M(\mathbf{w}) d_3 \mathbf{w} \\ J_2^{(0)}(\mathbf{v}) &= f_2^M(\mathbf{v}) e^{E/T} \int \Theta(g_-) \frac{g_-^2}{g} \sigma_{22}^{ch}(g_-) f_2^M(\mathbf{w}) d_3 \mathbf{w} \\ &- f_1^M(\mathbf{v}) \int g \sigma_{21}^{ch}(g) f_2^M(\mathbf{w}) d_3 \mathbf{w} - 2f_2^M(\mathbf{v}) \int g \sigma_{22}^{ch}(g) f_2^M(\mathbf{w}) d_3 \mathbf{w}. \end{aligned} \quad (26)$$

Closed form representation might be possible for simple expressions of the cross sections σ_{2r}^{ch} . However, all Maxwellians in the integrands are isotropic functions of $\mathbf{w} - \mathbf{u}$, and g

depends only on $|(\mathbf{v} - \mathbf{u}) - (\mathbf{w} - \mathbf{u})|$, so that all integrals, as well as the Maxwellians out of them, depend only on $|\mathbf{v} - \mathbf{u}|$. Therefore, an important implication of (26) is that both $J_s^{(0)}$ are isotropic functions of the peculiar velocity $\mathbf{c} = \mathbf{v} - \mathbf{u}$.

The derivatives of Maxwellians in (25) may be performed by lengthy but known manipulations, leading to

$$\begin{aligned} \frac{\partial f_s^M}{\partial t} + \mathbf{v} \cdot \nabla_{\mathbf{x}} f_s^M &= f_s^M \left[\frac{\partial n_s}{\partial t} \frac{1}{n_s} + \frac{m}{T} \mathbf{c} \cdot \frac{\partial \mathbf{u}}{\partial t} + \frac{1}{T} \left(\frac{m}{2T} c^2 - \frac{3}{2} \right) \frac{\partial T}{\partial t} \right. \\ &\quad \left. + \frac{1}{n_s} \nabla_{\mathbf{x}} n_s \cdot \mathbf{v} + \frac{m}{T} \mathbf{v} \cdot \nabla_{\mathbf{x}} \mathbf{u} \cdot \mathbf{c} + \frac{1}{T} \left(\frac{m c^2}{2T} - \frac{3}{2} \right) \nabla_{\mathbf{x}} T \cdot \mathbf{v} \right]. \end{aligned} \quad (27)$$

On the other hand, the exact balance equations (15) and (16), after some algebra, may be ordered as

$$\begin{aligned} \frac{\partial n_1}{\partial t} + \nabla_{\mathbf{x}} \cdot (n_1 \mathbf{u}) - \sum_{r=1}^2 S_{2r}^{(0)} &= O(\varepsilon) \\ \frac{\partial n_2}{\partial t} + \nabla_{\mathbf{x}} \cdot (n_2 \mathbf{u}) + \sum_{r=1}^2 S_{2r}^{(0)} &= O(\varepsilon) \\ \frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla_{\mathbf{x}} \mathbf{u} + \frac{1}{\rho} \nabla_{\mathbf{x}} (nT) &= O(\varepsilon) \\ \frac{\partial T}{\partial t} + \mathbf{u} \cdot \nabla_{\mathbf{x}} T + \frac{2}{3} T \nabla_{\mathbf{x}} \cdot \mathbf{u} - \frac{2E}{3n} \sum_{r=1}^2 S_{2r}^{(0)} &= O(\varepsilon), \end{aligned} \quad (28)$$

which, as usual, can be used in order to eliminate time derivatives from (27). In the result, we may separate mechanical and chemical contributions as

$$\frac{\partial f_s^M}{\partial t} + \mathbf{v} \cdot \nabla_{\mathbf{x}} f_s^M = \left(\frac{Df_s^M}{Dt} \right)_{ME} + \left(\frac{Df_s^M}{Dt} \right)_{CH} \quad (29)$$

where

$$\begin{aligned} \left(\frac{Df_s^M}{Dt} \right)_{ME} &= \left[\frac{1}{n_s} \left(\mathbf{c} \cdot (\nabla_{\mathbf{x}} n_s) - \frac{n_s}{n} \mathbf{c} \cdot (\nabla_{\mathbf{x}} n) \right) + \frac{m}{T} \left(\mathbf{c} \otimes \mathbf{c} - \frac{1}{3} c^2 \mathbf{I} \right) : \nabla_{\mathbf{x}} \mathbf{u} \right. \\ &\quad \left. + \frac{1}{T} \left(\frac{m c^2}{2T} - \frac{5}{2} \right) \mathbf{c} \cdot \nabla_{\mathbf{x}} T \right] f_s^M(\mathbf{v}) + O(\varepsilon) \end{aligned} \quad (30)$$

$$\left(\frac{Df_s^M}{Dt} \right)_{CH} = f_s^M(\mathbf{v}) \left[\frac{(-1)^{s-1}}{n_s} + \frac{2E}{3nT} \left(\frac{m c^2}{2T} - \frac{3}{2} \right) \right] \sum_{r=1}^2 S_{2r}^{(0)} + O(\varepsilon).$$

Finally, the relaxation terms G_s in (25) can be expanded versus ε , and, due to (3) and (4), one gets

$$G_s^\varepsilon(\mathbf{v}) \equiv G_s [f_1^\varepsilon, f_2^\varepsilon] = f_s^M(\mathbf{v}) + \varepsilon f_s^M(\mathbf{v}) \frac{m}{T} \left(1 - \frac{\eta}{\nu} \right) \mathbf{u}_s^{(1)} \cdot \mathbf{c} + O(\varepsilon^2). \quad (31)$$

Therefore, collecting results, one ends up with

$$f_s^{(1)}(\mathbf{v}) = f_{sME}^{(1)}(\mathbf{v}) + f_{sCH}^{(1)}(\mathbf{v}), \quad (32)$$

where

$$\begin{aligned} f_{sME}^{(1)}(\mathbf{v}) &= f_s^M(\mathbf{v}) \left\{ \frac{m}{T} \left(1 - \frac{\eta}{\nu} \right) \mathbf{u}_s^{(1)} \cdot \mathbf{c} - \frac{1}{\nu} \left[\frac{1}{n_s} \mathbf{c} \cdot \nabla_{\mathbf{x}} n_s - \frac{1}{n} \mathbf{c} \cdot \nabla_{\mathbf{x}} n \right] \right. \\ &\quad \left. + \frac{m}{T} \left(c_i c_j - \frac{1}{3} c^2 \delta_{ij} \right) \frac{\partial u_i}{\partial x_j} + \frac{1}{T} \left(\frac{mc^2}{2T} - \frac{5}{2} \right) \mathbf{c} \cdot \nabla_{\mathbf{x}} T \right\} \end{aligned} \quad (33)$$

$$f_{sCH}^{(1)}(\mathbf{v}) = \frac{1}{\nu} J_s^{(0)}(\mathbf{v}) - \frac{1}{\nu} f_s^M(\mathbf{v}) \left[\frac{(-1)^{s-1}}{n_s} + \frac{2E}{3nT} \left(\frac{mc^2}{2T} - \frac{3}{2} \right) \right] \sum_{r=1}^2 S_{2r}^{(0)}.$$

This result is not yet explicit, since the needed unknowns $f_s^{(1)}$ are expressed in terms of their moments

$$\mathbf{u}_s^{(1)} = \frac{1}{n_s} \int \mathbf{c} f_s^{(1)}(\mathbf{v}) d_3 \mathbf{c}. \quad (34)$$

In any case, it is evident that the mechanical contribution in (32) is orthogonal to any isotropic function of \mathbf{c} , whereas the chemical one is isotropic in \mathbf{c} . In order to complete the procedure we have now to re-compute $\mathbf{u}_s^{(1)}$ from (32) by taking moment with weight \mathbf{c} , and the solution of the resulting linear algebraic equation for it makes (32) fully explicit. Skipping details, this leads to

$$\begin{aligned} \mathbf{u}_1^{(1)} &= -\frac{1}{\eta} \frac{T}{\rho} \frac{n_2}{n_1} \nabla_{\mathbf{x}} n_1 + \frac{1}{\eta} \frac{T}{\rho} \nabla_{\mathbf{x}} n_2 \\ \mathbf{u}_2^{(1)} &= \frac{1}{\eta} \frac{T}{\rho} \nabla_{\mathbf{x}} n_1 - \frac{1}{\eta} \frac{T}{\rho} \frac{n_1}{n_2} \nabla_{\mathbf{x}} n_2 \end{aligned} \quad (35)$$

showing how diffusion velocities do not depend on the chemical reaction (reactive contributions in (32) disappear upon integration with weight function \mathbf{c}). Analogously, $f_{sCH}^{(1)}$ is orthogonal to weight functions like $c_i c_j - (1/3)c^2 \delta_{ij}$, or $\mathbf{c}c^2$, so that chemical contributions do not affect viscous stress $\mathbf{\Pi}$ and heat flux \mathbf{q} . Fick, Newton, and Fourier law are then the same as in the inert case of Ref. [14], a result which was, in some sense, expected, in view of the fact that reactive collisions are slow if compared to the mechanical ones.

In order to complete the hydrodynamic closure, we need only first order corrections to chemical sources, appearing in (16), which can be rewritten as

$$S_{2r}^{(1)} = \iint g \sigma_{2r}^{ch}(g) f_2^M(\mathbf{w}) f_r^{(1)}(\mathbf{v}) d_3 \mathbf{v} d_3 \mathbf{w} + \iint g \sigma_{2r}^{ch}(g) f_2^{(1)}(\mathbf{v}) f_r^M(\mathbf{w}) d_3 \mathbf{v} d_3 \mathbf{w}. \quad (36)$$

Here, by usual arguments, the \mathbf{w} integrations yield isotropic functions of \mathbf{c} , so that mechanical contributions $f_{sME}^{(1)}$ cancel out in the \mathbf{v} integration, and therefore elastic collisions do not affect the chemical terms of the reactive Navier-Stokes equations. This result resembles analogous conclusions on reversible slow chemistry [16, 25] and provides a new explicit result for the reactive fluid-dynamic contributions. Notice that $O(\varepsilon)$ chemical sources involve both leading reactive sources $S_{2r}^{(0)}$ through $f_s^{(1)}$ given in (32) and (33).

4 Conclusions

We may summarize results of this note as follows. The present kinetic model for a binary mixture of rarefied gases undergoing an irreversible chemical reaction features a mechanical collision operator of generalized BGK type with two relaxation parameters, aimed at fitting transport coefficients, coupled to a reactive integral operator of Boltzmann type, the process being driven by the mechanical part (slow reaction). First, we have proved that mechanical constitutive equations for diffusion velocities, viscous stress, and heat flux do not differ from those relevant to the same gas, considered as chemically inert [14]. Conversely, we have found that chemical contributions at fluid-dynamic level depend solely on reactive cross sections: they exhibit source terms which are even $O(1)$ with respect to the small scaling parameter, so that they would be present also at the Euler level. Such a rigid separation between mechanics and chemistry is expected to disappear at a higher level fluid-dynamics (Burnett), or if the chemical time scale were of the same order as the mechanical one; these investigations will be matter of future work. In any case, the present relaxation model with irreversible chemistry is in accordance with the standard scheme of non-equilibrium slowly reacting gas flows, for which the uncoupling between chemical and mechanical effects at fluid-dynamic level is known [25].

Reactive Navier-Stokes (reaction-diffusion) equations derived in this note for the generalized BGK model (2) follow from (15) and (16) bearing in mind that

$$\mathbf{\Pi} = \varepsilon \mathbf{\Pi}^{(1)}, \quad \mathbf{q} = \varepsilon \mathbf{q}^{(1)}, \quad \mathbf{u}_2 = \mathbf{u} + \varepsilon \mathbf{u}_2^{(1)}, \quad S_{2r} = S_{2r}^{(0)} + \varepsilon S_{2r}^{(1)}.$$

They read as

$$\begin{aligned}
 \frac{\partial n}{\partial t} + \nabla_{\mathbf{x}} \cdot (n\mathbf{u}) &= 0 \\
 \frac{\partial(\rho\mathbf{u})}{\partial t} + \nabla_{\mathbf{x}} \cdot (\rho\mathbf{u} \otimes \mathbf{u}) + \nabla_{\mathbf{x}}(nT) &= -\varepsilon \nabla_{\mathbf{x}} \cdot \mathbf{\Pi}^{(1)} \\
 \frac{\partial}{\partial t} \left(\frac{1}{2} \rho u^2 + \frac{3}{2} nT + En_2 \right) + \nabla_{\mathbf{x}} \cdot \left[\left(\frac{1}{2} \rho u^2 + \frac{5}{2} nT + En_2 \right) \mathbf{u} \right] &= -\varepsilon \nabla_{\mathbf{x}} \cdot \left(\mathbf{\Pi}^{(1)} \cdot \mathbf{u} + \mathbf{q}^{(1)} + En_2 \mathbf{u}_2^{(1)} \right) \\
 \frac{\partial n_2}{\partial t} + \nabla_{\mathbf{x}} \cdot (n_2 \mathbf{u}) + \sum_{r=1}^2 S_{2r}^{(0)} &= -\varepsilon \nabla_{\mathbf{x}} \cdot (n_2 \mathbf{u}_2^{(1)}) - \varepsilon \sum_{r=1}^2 S_{2r}^{(1)}
 \end{aligned} \tag{37}$$

where

$$\begin{aligned}
 \mathbf{\Pi}^{(1)} &= -\frac{1}{\nu} nT \left(\nabla_{\mathbf{x}} \mathbf{u} + (\nabla_{\mathbf{x}} \mathbf{u})^T - \frac{2}{3} \nabla_{\mathbf{x}} \cdot \mathbf{u} \mathbf{I} \right) \\
 \mathbf{q}^{(1)} &= -\frac{1}{\nu} \frac{5}{2} \frac{nT}{m} \nabla_{\mathbf{x}} T
 \end{aligned} \tag{38}$$

which correspond to Newton's law with viscosity $\frac{\varepsilon}{\nu} nT$ and to Fourier's law with thermal conductivity $\frac{\varepsilon}{\nu} \frac{5}{2} \frac{nT}{m}$, with no Dufour effect, in agreement with the fact that particles of the two species are essentially monoatomic and mechanically identical [3, 26]. Diffusion velocities $\varepsilon \mathbf{u}_s^{(1)}$ are provided by (35), which defines Fick's diffusion law, without thermal diffusion (Soret effect), for the same reasons as before. Leading reactive sources are given by (23), and first order corrections may be rewritten as

$$S_{2r}^{(1)} = \iint g \sigma_{2r}^{ch}(g) f_2^M(\mathbf{w}) f_{rCH}^{(1)}(\mathbf{v}) d_3 \mathbf{v} d_3 \mathbf{w} + \iint g \sigma_{2r}^{ch}(g) f_{2CH}^{(1)}(\mathbf{v}) f_r^M(\mathbf{w}) d_3 \mathbf{v} d_3 \mathbf{w}, \tag{39}$$

where f_s^M is the Maxwellian (7), and $f_{sCH}^{(1)}$ is the reactive correction (33), with (26) for $J_s^{(0)}$. The relaxation parameter η may be used to fit exactly any given Fick's diffusion matrix. The other relaxation parameter ν may be used to fit either viscosity or thermal conductivity, but not both transport coefficients simultaneously (Prandtl number can not be controlled). The quite complicated task of introducing a third relaxation parameter in order to overcome this drawback, rather typical in the BGK literature for mixtures [15], will hopefully be matter of future investigation.

Finally, it can be noticed that the viscous stress $\mathbf{\Pi}$ in (38) is traceless at the Navier-Stokes fluid-dynamic level, namely the so called chemical pressure [8, 10] (equivalent to the dynamical pressure for polyatomic gases [21]) is here vanishing, and would appear only as a higher order correction. This is a consequence of the assumed "resonant"

scaling by which particles of both components tend to keep their internal energy state in all encounters, so that no reactive mixing effects are present to leading order in the evolution of the mixture. Such effects show up, after an initial fast transient, at the slower time scale, where, as a consequence of irreversibility of reaction (1), the evolution leads eventually to a non-standard equilibrium with depletion of one of the components.

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