

Kinetic models for reactive mixtures: Problems and applications

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Summary. — Problems related to physical consistency and practical application of kinetic BGK models for reactive mixtures are investigated. In particular, two approximation strategies are discussed, relevant to the different physical scenarios of slow and fast chemical reactions, respectively. The former is tested *versus* the steady shock problem in comparison to available hydrodynamic results. For the latter, allowing for an explicit proof of the *H*-theorem, a preliminary sample is shown of the space homogeneous calculations in progress.

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1. – Introduction

Rarefied gas flows with chemical reactions arise in a wide range of applications, like for instance combustion processes, shock and detonation waves, chemical reactors, and space vehicles. Kinetic approaches [1] to the description of such problems, even though mathematically uneasy, represent a basis for a rigorous derivation of fluid-dynamic equations and also for the correct treatment of fundamental issues, such as surface phenomena, including evaporation/condensation and phase transition. Consequently, chemically reacting mixtures have been quite extensively dealt with from a kinetic point of view in recent scientific literature [2]. We shall consider the physical frame of a four-component gas mixture of species A^i , $i = 1, \dots, 4$, colliding among themselves and undergoing the reversible bimolecular chemical reaction $A^1 + A^2 \rightleftharpoons A^3 + A^4$. The gap in the energies of chemical bonds, $\Delta E = E^3 + E^4 - E^1 - E^2$, may be conventionally assumed to be positive. The evolution of the four distribution functions $f^i(\mathbf{x}, \mathbf{v}, t)$ is governed, according to the simplest model proposed in [3], by the set of nonlinear integro-differential Boltzmann-like equations

$$(1) \quad \frac{\partial f^i}{\partial t} + \mathbf{v} \cdot \frac{\partial f^i}{\partial \mathbf{x}} = Q^i[f] \quad i = 1, \dots, 4,$$

where \underline{f} is the vector of the four distributions, and the collision operator $Q^i[\underline{f}]$ describes the effects due to both elastic scattering and chemical reactions. The relevant fluid-dynamic equations (Euler and Navier-Stokes), typically obtained by Chapman-Enskog asymptotic expansion, crucially depend on the interplay of the orders of magnitude of the various phenomena which are accounted for, and in particular on how fast is chemical reaction with respect to mechanical scattering.

In any case, since reactive Boltzmann equations are quite heavy to deal with, it is worth considering simpler models, suitable for practical applications, as for instance relaxation approximations of BGK type. We shall adopt here the consistent model for multi-component gases proposed in [4], which avoids all typical drawbacks encountered when dealing with mixtures (see [5] and [4] itself for details and deeper discussion), and is based on the idea of only one collision operator per species

$$(2) \quad \frac{\partial f^i}{\partial t} + \mathbf{v} \cdot \frac{\partial f^i}{\partial \mathbf{x}} = \nu_i(\mathcal{M}_i - f^i) = \tilde{Q}^i, \quad i = 1, \dots, 4,$$

where ν_i are \mathbf{v} -independent collision frequencies and \mathcal{M}_i are suitable Maxwellian attractors. In order to extend such strategy to the much more complicated reactive frame, one must account for exchange of mass and of energy of chemical link, and has to build up an algorithm which preserves positivity, indifferentiability (see again [4]), and also reproduces the main features of the Boltzmann kinetic equations, like correct collision invariants, collision equilibria, and entropy principle (H -theorem) [6]. Once more, like for the hydro-dynamic limit, different BGK models should be devised according to the characteristic time of the reaction, in order to describe adequately the regimes of slow [7] and of fast [8] chemistry, respectively.

We briefly recall here the main features of the actual reactive Boltzmann equations. The interested reader is referred to [9] for proofs and details. Collision invariants constitute a seven-dimensional linear subspace of the continuous functions of \mathbf{v} , and represent three independent pairwise conservations of mass (*e.g.*, for species (1, 3), (1, 4), (2, 4)), conservation of momentum, and conservation of total (thermal plus chemical) internal energy. As a consequence, seven exact, but not closed, macroscopic conservation equations hold, including chemical contributions to internal energy and heat flux, and involving macroscopic observables, which are velocity moments of the distribution functions. An extended version of Boltzmann's lemma allows to determine collision equilibria as the seven parameter family of local Maxwellians

$$(3) \quad f_M^i(\mathbf{v}) = n^i \left(\frac{m^i}{2\pi KT} \right)^{3/2} \exp \left[-\frac{m^i}{2KT} (\mathbf{v} - \mathbf{u})^2 \right] \quad i = 1, \dots, 4$$

with \mathbf{u} and T standing for mass velocity and temperature of the mixture, and where number densities n^i must be related by the mass action law

$$(4) \quad \frac{n^1 n^2}{n^3 n^4} = \left(\frac{m^1 m^2}{m^3 m^4} \right)^{3/2} \exp \left[\frac{\Delta E}{KT} \right].$$

Another crucial property of the collision term \underline{Q} is that we can introduce, in space

homogeneous conditions, an H -functional

$$(5) \quad H[f] = \sum_{i=1}^4 \int_{\mathbb{R}^3} f^i \log \frac{f^i}{(m^i)^3} d\mathbf{v}$$

and prove an equivalent of the H -theorem, namely that H is a strict Lyapunov functional for stability of equilibria (3), quantifying entropy principle and second law of thermodynamics.

Relaxation time approximations for the above reactive setting have been introduced in recent times: we may quote, without pretending to be exhaustive, the papers [10] and [11]. We shall stick here, however, to the reactive extension of the line proposed in [4], discussing two different algorithms that seem to be well suited for two separate collision-dominated physical regimes: the first for slow chemical reactions (reactive time much longer than mechanical one), and the second for fast chemical reactions (comparable elastic and chemical characteristic times). This short paper is written at formal level and is aimed at commenting on response and performance of the proposed models in different physical scenarios.

2. – BGK model equations for slow reactions

In the case of slow chemistry, after a short initial transient on the elastic scale, distributions have approached a local mechanical equilibrium, and, in the hypothesis of Maxwellian collision model, exchange rates of mass, momentum and kinetic energy for each species (suitable weak forms of the corresponding collision integrals) may be approximated analytically in terms of the fundamental macroscopic fields [9]. Thus, one is able to repeat, *mutatis mutandis*, the same steps as in [4], and to build up accordingly a collision operator of the type (2). Specifically, the “attractors” \mathcal{M}_i are fictitious Maxwellians,

$$(6) \quad \mathcal{M}_i(\mathbf{v}) = n_i \left(\frac{m^i}{2\pi K T_i} \right)^{3/2} \exp \left[- \frac{m^i}{2K T_i} (\mathbf{v} - \mathbf{u}_i)^2 \right],$$

where the word fictitious means that they are defined in terms of twenty auxiliary quantities (n_i, \mathbf{u}_i, T_i) , which differ from the actual fundamental physical fields (n^i, \mathbf{u}^i, T^i) , power moments of the distribution functions f^i , and constitute rather a set of disposable parameters to be used for the purposes of the model itself. The idea is equating the twenty exchange rates for mass, momentum and energy of each species, which may be easily computed on using (6) into the BGK approximation (2) of the collision operator, to the actual corresponding exchange rates for the true Boltzmann collision operator in (1), available from [9]. In spite of the formidable machinery, the resulting twenty algebraic equations can be solved uniquely for the auxiliary parameters, which eventually can be cast in closed analytical form [6]. The resulting reactive BGK model can be shown to fulfill all previously mentioned consistency requirements [4], and to retain most of the essential features of the Boltzmann kinetic equations [6], in particular correct collision invariants, collision equilibria (3), and mass action law (4). The inverse relaxation times ν_i can be estimated on the basis of a count of the average number of collisions actually undergone by each species, thus by equating the velocity averaged kinetic loss terms at Boltzmann and BGK level.

As a test problem on which the performance of this model can be discussed, we choose the classical one-dimensional steady shock wave problem

$$(7) \quad v \frac{\partial f^i}{\partial x} = \nu_i (\mathcal{M}_i - f^i), \quad i = 1, \dots, 4, \quad \lim_{x \rightarrow \pm\infty} f^i(x, v) = M_{\pm}^i(v),$$

where x and v are the first components of position and velocity vectors, and where M_{\pm}^i denote families of equilibrium Maxwellians with upstream ($-$) and downstream ($+$) parameters n_{\pm}^i , u_{\pm} (T_{\pm} follow from mass action law). Such parameters are in a one-to-one correspondence via the reactive Rankine-Hugoniot relations, and the entropy inequality results in the expected condition $Ma_- > 1$, where Ma_- is the upstream Mach number (shock speed), plus the requirement on the change of chemical composition $\chi_+^1 - \chi_-^1 = \chi_+^2 - \chi_-^2 = -(\chi_+^3 - \chi_-^3) = -(\chi_+^4 - \chi_-^4) < 0$, where $\chi^i = n^i/n$ are the concentration fractions [12]. Notice that the reactive speed of sound is given by

$$(8) \quad c = c_0 \left\{ \left[\sum_{i=1}^4 \frac{1}{\chi^i} + \frac{2}{5} \left(\frac{\Delta E}{KT} \right)^2 \right] / \left[\sum_{i=1}^4 \frac{1}{\chi^i} + \frac{2}{3} \left(\frac{\Delta E}{KT} \right)^2 \right] \right\}^{1/2} = \alpha c_0,$$

and is thus smaller than the inert shock speed $c_0 = \sqrt{5nKT/(3\rho)}$, where ρ is the total mass density. This shock problem has been investigated in detail in [13], by a suitable upwind finite difference scheme. An example of the results is given in fig. 1, which is relevant to a physical situation where the microscopic mean reactive times are larger than the mean elastic times by one order of magnitude. It shows the structure for the number densities n^i , with values of masses and of energies of chemical link corresponding to the reaction $\text{NO} + \text{CO}_2 \rightleftharpoons \text{NO}_2 + \text{CO}$, for three different Mach numbers Ma_- . It is apparent how the very smooth, almost constant, profiles at low Ma_- steepen for increasing Mach, and present a slower tail downstream, sometimes with overshooting.

We want to discuss here such behavior, also in the light of the features of the proposed algorithm. In fact the model is suitable for situations in which chemical relaxation is much slower than mechanical relaxation and in regimes close to mechanical equilibrium, as imposed by the option (6), and in agreement with the fact that in such regimes the actual Boltzmann exchange rates are available. In conditions of this type, it is worth to examine also the results of a simpler hydro-dynamic approach, based on a closure in terms of mechanical equilibria, which are given again by (3), but without any additional constraint, thus without mass action law. There results a set of hyperbolic balance laws, with chemical source terms, which, for the steady shock problem, becomes an eight-dimensional dynamical system, with seven conservation laws. This much easier problem has been recently worked out in [14], to which we refer once more for technical details. The essential difference with respect to the kinetic BGK approach is that one has to consider two different cases, according to whether $M_{0-} < 1 < Ma_-$ ($1 < Ma_- < 1/\alpha_-$) or $M_{0-} > 1$ ($Ma_- > 1/\alpha_-$), where M_{0-} is the inert Mach number, always smaller than the reactive one Ma_- , as follows from (8). In the first quite restricted region (α_- is typically only slightly smaller than unity), a smooth solution exists, connecting the asymptotic limits, in spite of the absence of viscosity and thermal conductivity, just by dissipative effects of the reaction. Indeed, in this region of only slightly supersonic Mach numbers, an inert shock structure does not exist, since $M_{0-} < 1$. For Ma_- increasing and entering the second unbounded region only a weak solution exists, with a jump discontinuity, whose edges are related to the singularity present in the vector

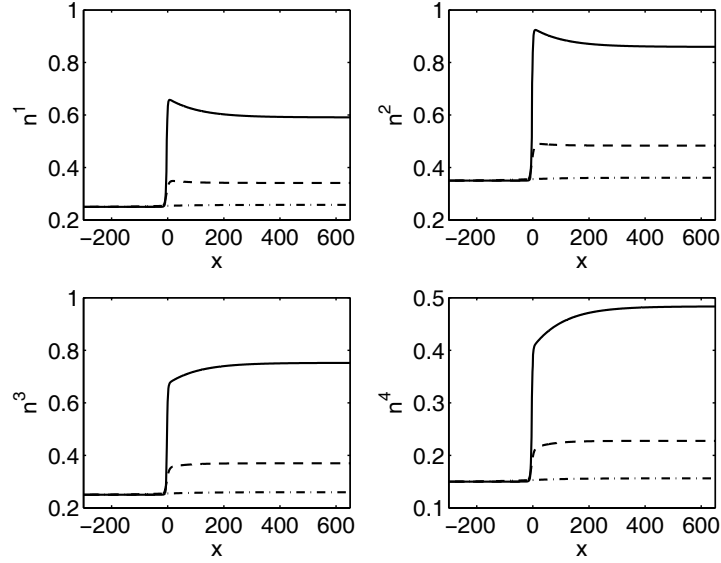


Fig. 1. – Kinetic shock profiles of the number densities n^i for three different Mach numbers: $Ma_- = 2.470$ (solid line), $Ma_- = 1.286$ (dashed line), and $Ma_- = 1.023$ (dot-dashed line).

field. In particular, the jump corresponds exactly to the discontinuity developed by the hyperbolic conservation laws of the inert mixture (now the inert shock does exist), and it is remarkable that only a constant trend is allowed ahead of the shock to join it to the upstream state, whereas a smooth tail towards the downstream state follows the shock. This tail joins together the downstream equilibria corresponding to the same upstream equilibrium via the inert and the reactive Rankine-Hugoniot conditions, respectively. All of the above features, encountered also in other macroscopic approaches [15], agree very well with the structure shown in fig. 1. In fact, BGK results show a very fast (but continuous) trend, corresponding to the transition that would occur if the mixture were non-reactive, followed by a much smoother tail, in which the slow chemical process drives the mixture itself towards the chemical equilibrium downstream, separating thus in practice the fast from the slow relaxation. Presence or not of overshooting for a specific quantity can be inferred from the comparison of the downstream/upstream differences for the inert and the reactive case. The agreement between the kinetic BGK profiles for number densities and the hydrodynamic results is shown by fig. 2, deduced from [14], merely with jump discontinuities replacing the stiff, but yet continuous, kinetic wave fronts. The different horizontal scales are due to different scalings when making equations dimensionless.

3. – BGK model equations for fast reactions

The previous discussion shows how appropriate is the BGK model [6] in dealing with slow chemical reactions. However, the need clearly emerges for an alternative relaxation model, adequate for fast chemistry. The question has been addressed in a recent paper [8], and a new idea has been proposed, whose developments are presently in progress. This different strategy still resorts to (2), but the “attractor” is now defined by the new

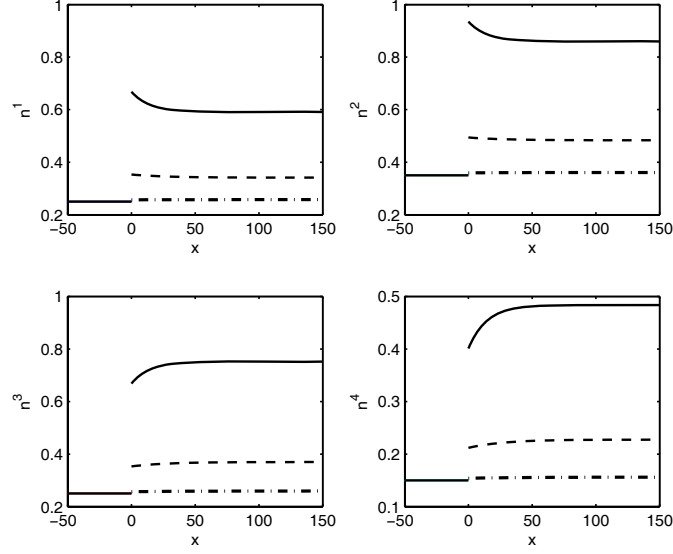


Fig. 2. – Discontinuous hydrodynamic shock profiles of the number densities n^i for three different Mach numbers: $Ma_- = 2.470$ (solid line), $Ma_- = 1.286$ (dashed line), and $Ma_- = 1.023$ (dot-dashed line).

fictitious Maxwellians

$$(9) \quad \mathcal{M}_i(\mathbf{v}) = \tilde{n}^i \left(\frac{m^i}{2\pi K\tilde{T}} \right)^{3/2} \exp \left[-\frac{m^i}{2K\tilde{T}} (\mathbf{v} - \tilde{\mathbf{u}})^2 \right],$$

with now only seven disposable parameters, \tilde{n}^i , $\tilde{\mathbf{u}}$, \tilde{T} , different again from the actual fields, which must be bound together by the mass action law

$$(10) \quad \frac{\tilde{n}^1 \tilde{n}^2}{\tilde{n}^3 \tilde{n}^4} = \left(\frac{m^1 m^2}{m^3 m^4} \right)^{3/2} \exp \left[\frac{\Delta E}{K\tilde{T}} \right].$$

The BGK operator drives then distribution functions towards a full (thermal and chemical) equilibrium, as it seems appropriate when the mechanical and reactive mechanisms have the same level of importance in driving the process. At this point, auxiliary parameters are determined in the standard way as in the pioneering papers on relaxation time approximation in kinetic theory, namely pretending that Boltzmann and BGK collision operators share “a priori” the same collision invariants

$$(11) \quad \int (\tilde{Q}^i + \tilde{Q}^j) d_3\mathbf{v} = 0, \quad (i, j) = (1, 3), (1, 4), (2, 4),$$

$$\sum_{i=1}^4 \int m^i \mathbf{v} \tilde{Q}^i d_3\mathbf{v} = \mathbf{0}, \quad \sum_{i=1}^4 \int \left(\frac{1}{2} m^i v^2 + E^i \right) \tilde{Q}^i d_3\mathbf{v} = 0.$$

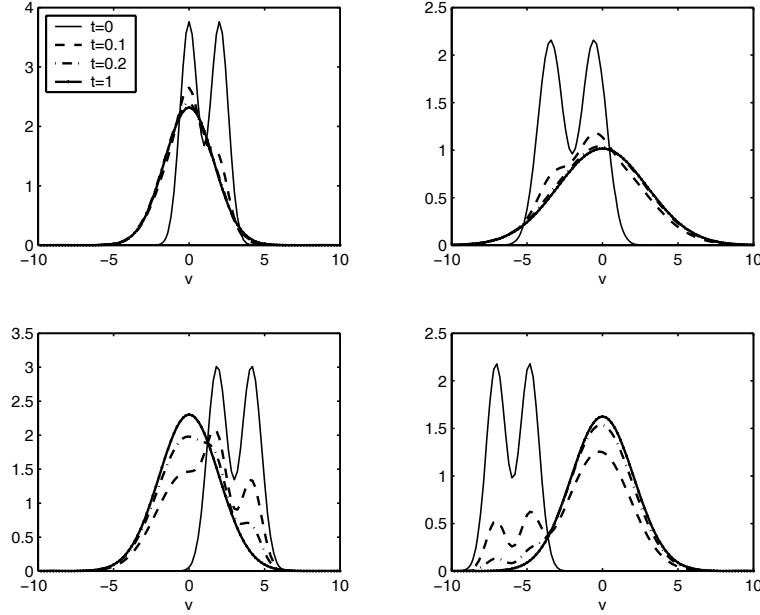


Fig. 3. – Time evolution of the reduced distribution functions for double humped initial distributions. (ϕ^1 : left top. ϕ^2 : right top. ϕ^3 : left bottom. ϕ^4 : right bottom.)

This leads to seven algebraic equations for the fictitious parameters, which can be worked out to express all of them in terms of the actual fields and of \tilde{n}^1 , and then the procedure is closed by enforcing the mass action law (10), yielding a transcendental equation for the single unknown \tilde{n}^1 , which can be shown to possess a unique physical solution [8].

A positive feature of this second model is that it is not affected by any restriction on differential cross-sections, which may have any dependence on relative speed, and may or not exhibit thresholds for the exothermic reaction. Moreover, the model recovers by definitions the correct collision invariants and conservation equations, and it is easy to show that also collision equilibria (3) with mass action law (4) are correctly reproduced. In addition, in space homogeneous conditions, equilibrium parameters are uniquely defined by initial conditions. However, the main new feature of this latter BGK model is probably the fact that it allows for an analytical proof of the H -theorem, a result that has not been possible to achieve for the reactive models we are aware of so far (however, in most cases, there is of course numerical evidence of it). This should provide an important tool of investigation for future mathematical research. Indeed, the Lyapunov functional for the present BGK equations is given by the actual Boltzmann H -functional (5), which, in a space homogeneous setting, is known to have its minimum exactly at the unique equilibrium compatible with the given initial conditions. Therefore, it suffices to prove Boltzmann's lemma, which follows from convexity

$$\begin{aligned} \dot{H}[f] &= \sum_{i=1}^4 \int \tilde{Q}^i[f] \log \frac{f^i}{(m^i)^3} d_3\mathbf{v} \\ &= - \sum_{i=1}^4 \nu_i \int (f^i - \mathcal{M}_i) \log \frac{f^i}{\mathcal{M}_i} d_3\mathbf{v} < 0 \quad \forall f \neq f_M \end{aligned}$$

by virtue of the crucial identity

$$\sum_{i=1}^4 \int \tilde{Q}^i[f] \log \frac{\mathcal{M}_i[f]}{(m^i)^3} d_3\mathbf{v} = \nu_1(\tilde{n}^1 - n^1) \left\{ \log \left[\frac{\tilde{n}^1 \tilde{n}^2}{\tilde{n}^3 \tilde{n}^4} \left(\frac{m^3 m^4}{m^1 m^2} \right)^{3/2} \right] - \frac{\Delta E}{K\tilde{T}} \right\} = 0 \quad \forall f,$$

following in turn from the combined exploitation of conservation properties (11) and of mass action law (10). Chemical equilibrium for the attractors is then a crucial ingredient in the proof, that was lacking for instance in [6] and [11]. Numerical applications of these fast BGK equations are now in progress [16]. As a sample we report here in fig. 3 on the space homogeneous relaxation problem towards the unique (mechanical and chemical) equilibrium. The figure is relevant to a situation where chemical and mechanical microscopic parameters are of the same order of magnitude. For a typical axially symmetric problem, the reduced (namely, integrated over the transverse components of velocity) distribution functions ϕ^i evolve from two-peaked initial distributions at different densities, velocities, and temperatures towards Maxwellians at a common velocity and a common temperature, with densities related by mass action law.

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REFERENCES

- [1] CERCIGNANI C., *The Boltzmann Equation and its Applications* (Springer, New York) 1988.
- [2] GIOVANGIGLI V. and MASSOT M., *Math. Meth. Appl. Sci.*, **27** (2004) 739.
- [3] ROSSANI A. and SPIGA G., *Physica A*, **272** (1999) 563.
- [4] ANDRIES P., AOKI K. and PERTHAME B., *J. Stat. Phys.*, **106** (2002) 993.
- [5] GARZÓ V., SANTOS A. and BREY J. J., *Phys. Fluids A*, **1** (1989) 380.
- [6] GROPPI M. and SPIGA G., *Phys. Fluids*, **16** (2004) 4273.
- [7] GROPPI M. and SPIGA G., *Bull. Inst. Math., Acad. Sin.*, **2** (2007) 609.
- [8] BISI M., GROPPI M. and SPIGA G., in *Rarefied Gas Dynamics: 26th International Symposium*, edited by ABE T. (A.I.P., New York) 2009, pp. 87–92.
- [9] BISI M., GROPPI M. and SPIGA G., in *Kinetic Methods for Nonconservative and Reacting Systems*, edited by TOSCANI G. (Quaderni di Matematica, Seconda Università di Napoli) 2005, pp. 1–145.
- [10] MONACO R., PANDOLFI BIANCHI M. and SOARES A. J., *J. Phys. A: Math. Gen.*, **38** (2005) 10413.
- [11] KREMER G., PANDOLFI BIANCHI M. and SOARES A. J., *Phys. Fluids*, **18** (2006) 037104.
- [12] GROPPI M., SPIGA G. and TAKATA S., *Bull. Inst. Math., Acad. Sin. (New Ser.)*, **2** (2007) 935.
- [13] GROPPI M., AOKI K., SPIGA G. and TRITSCH V., *Phys. Fluids*, **20** (2008) 117103.
- [14] GROPPI M., ROSSANI A. and SPIGA G., *Commun. Math. Sci.*, **7** (2009) 143.
- [15] CONFORTO F., MONACO R., SCHÜRRER F. and ZIEGLER I., *J. Phys. A*, **36** (2003) 5381.
- [16] BISI M., CÁCERES M. J. and SPIGA G., in preparation.