

Tests of a convergent numerical scheme for nonlinear Boltzmann-like models with chemical reactions: two, three and four species

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Abstract

We review recent tests of a convergent numerical scheme for space-homogeneous, nonlinear Boltzmann-like equations for fluids with two, three and four species of gas particles, respectively, with elastic and reactive binary collisions. The tests refer both to simpler exactly solvable models with elastic collisions, and to more complicated examples, involving chemical reactions, which present only exact expressions for certain low-order moments of the one-particle distribution functions. The results of the numerical tests appear to be in very good agreement with theoretical predictions.

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Key words: numerical scheme, numerical test, theoretical prediction, non-linear Boltzmann-like equations, energy, operators, Dirac measures.

1 Introduction

An accurate, computational method has been recently introduced [7], in order to solve numerically nonlinear Boltzmann-like equations [4], [5], [6] for reacting gas mixtures. The method represents a generalization of a rigorous numerical scheme proposed in [1], [2], which combines analytical and stochastic techniques to obtain numerical solutions of the classical Boltzmann equation.

As compared to the method of [1], [2], the numerical techniques developed in [7] have to face increased mathematical difficulties, essentially due to the presence of several species of gas particles and occurrence of reactions.

The usefulness of models with exact solutions for numerical tests is well known. In this respect, the simplest example is represented by the Krook-Wu model [8], corresponding to a system of Boltzmann equations describing nonreactive gas mixtures.

The numerical tests on the Krook-Wu equations have the merit to provide some insight in the effectiveness of the numerical method in dealing with models with

nonlinearities, and in handling several unknown distribution functions, corresponding to several species.

The scheme of [7] was tested in [10] on the exact Krook-Wu solutions of the multi-component Boltzmann equation [8], in order to study the effectiveness of the method in applications to gas mixtures.

However, the Krook-Wu equations refer only to non-reacting gases. Consequently, the results of [10] are of rather limited interest. In fact, they do not provide information on the applicability of the scheme of [7] to models with chemical reactions.

More realistic evaluations, based on the confrontation between numerical and analytical results, should require the knowledge of non-trivial, exact solutions of the non-linear Boltzmann-like equations for reacting flows. So far, analytical solutions to Boltzmann models with chemical reactions, have been obtained only for linear equations [12], or equations with collision terms defined by trivial (reaction) collision laws [3]. Unfortunately, such exact, simple solutions do not serve the purposes of the aforementioned evaluations.

On the other hand, one could perform useful, indirect tests on certain non-trivial Boltzmann models for reacting flows. Although the models cannot be solved analytically, they provide exactly solvable equations for the time evolution of certain macroscopic variables (e.g. concentration, energy). In that case, the one-particle distribution functions of the gas species can be obtained, solving numerically the Boltzmann model, by means of the techniques developed in [7]. Then the aforementioned macroscopic quantities (at various moments) can be calculated as averages with respect to the numerical one-particle distribution functions. The resulting values can be compared with those provided by the analytical solutions of the equations for macroscopic quantities. Moreover, the computed values of the macroscopic variables can serve to study the accuracy of the numerical scheme concerning the verification of the bulk conservation properties [4], [5], [6] of the model. Results of several tests on Boltzmann-like models with chemical reactions have been recently published in [11].

In this paper we review comparatively some of the results of the above numerical tests, and also present new results concerning the situation when exothermal reactions involving three species are included in the models investigated in [11]. Our aim is to give a first answer to the important question concerning the sensitivity of the method with respect to the change of the nature of the binary interactions and the number of components of the model, the main conclusion being that the accuracy of the numerical seems not to be affected by such changes (in the regime of reactions involving few particles).

2 Analytical Considerations

In this paper, we are interested in the kinetics of space-homogeneous gas mixtures consisting of $2 \leq N \leq 4$ chemical species, of gas particles with binary elastic collisions and binary reactions. The gas reactions conserve the total mass, momentum and energy of the reaction partners in the reaction channels [4].

We assume that each species X_i is composed of point particles with mass m_i , and one-internal state characterized by internal energy E_i , $1 \leq i \leq 4$. We consider the situation when the following kinds of gas interactions are possible:

(a) nonreactive (elastic) collisions

$$(2.1) \quad X_i + X_j \rightarrow X_i + X_j,$$

for $1 \leq i, j \leq 4$ and $\{i, j\} \neq \{3, 4\}$;

(b) reactions of the form

$$(2.2) \quad X_1 + X_2 \rightarrow X_3 + X_4$$

and the reverse reaction

$$(2.3) \quad X_3 + X_4 \rightarrow X_1 + X_2$$

Notice that reactions of the form

$$X_1 + X_2 \rightleftharpoons 2X_3$$

can be considered as particularization of (2.2), (2.3) to the case when $X_3 = X_4$.

To be precise, without loss of generality, we suppose reaction (2.2) to be endothermic ($E_1 + E_2 \leq E_3 + E_4$). This means that reaction (2.3) is exothermal.

In this case, the weak form of the Boltzmann-like model introduced in [5], reads

$$(2.4) \quad \left(\phi, \frac{\partial f_i}{\partial t} \right) = (\phi, P_i(\mathbf{f})) - (\phi, S_i(\mathbf{f})), \quad (\forall) 1 \leq i \leq 4; \phi \in C_b(\mathbb{R}^3).$$

for the unknown one-particle distribution functions $f_i = f_i(t, \mathbf{v})$ (depending on time t and velocity \mathbf{v}) and associated to the species X_i , $1 \leq i \leq 4$. Here $\mathbf{f} := (f_1, \dots, f_4)$

$$(2.5) \quad (\phi, P_i(\mathbf{f})) = \sum_{j,k,l=1}^4 \int_{\mathcal{D}_{kl;ij} \times \mathbb{S}} \phi(\mathbf{v}_{ij;kl}) \cdot r_{ij;kl}(\mathbf{v}, \mathbf{w}, \mathbf{n}) \cdot f_k(\mathbf{v}) f_l(\mathbf{w}) d\mathbf{v} d\mathbf{w} d\mathbf{n},$$

and

$$(2.6) \quad (\phi, S_i(\mathbf{f})) = \sum_{j,k,l=1}^4 \int_{\mathcal{D}_{ij;kl} \times \mathbb{S}} \phi(\mathbf{v}) \cdot r_{kl;ij}(\mathbf{v}, \mathbf{w}, \mathbf{n}) \cdot f_i(\mathbf{v}) f_j(\mathbf{w}) d\mathbf{v} d\mathbf{w} d\mathbf{n},$$

where $C_b(\mathbb{R}^3)$ denotes the space of continuous, bounded, real functions on \mathbb{R}^3 , $\mathbb{S} := \{\mathbf{n} \in \mathbb{R}^3 \mid |\mathbf{n}| = 1\}$,

$$(2.7) \quad \mathcal{D}_{ij;kl} := \{(\mathbf{v}, \mathbf{w}) \in \mathbb{R}^3 \times \mathbb{R}^3 \mid \bar{W}_{ij;kl}(\mathbf{v}, \mathbf{w}) \geq 0\},$$

with

$$(2.8) \quad \bar{W}_{ij;kl}(\mathbf{v}, \mathbf{w}) := \frac{m_i m_j}{2(m_i + m_j)} |\mathbf{v} - \mathbf{w}|^2 + E_i + E_j - E_k - E_l,$$

$$(2.9) \quad \begin{aligned} \mathbf{v}_{ij;kl} &= \mathbf{v}_{ij;kl}(\mathbf{v}, \mathbf{w}, \mathbf{n}) := \frac{m_i \mathbf{v} + m_j \mathbf{w}}{m_i + m_j} + \\ &+ \left[\frac{2 \cdot m_l}{m_k(m_i + m_j)} \bar{W}_{ij;kl}(\mathbf{v}, \mathbf{w}) \right]^{1/2} \cdot \mathbf{n}, \end{aligned}$$

Finally the collision law $r_{ij;kl}(\mathbf{v}, \mathbf{w}, \mathbf{n})$ characterizes the reaction $X_i + X_j \rightarrow X_k + X_l$. According to the hypotheses of the model, in formulae (2.4), (2.5) and (2.6), only the collision laws associated to reactions (2.1), (2.2), (2.3) do not vanish identically.

It is known [5], [7] that the Cauchy problem associated to (2.4) has, in some sense, unique positive global solutions (for details the reader is referred to [5], [6], [7]).

Following [10], [11], we consider collision laws similar to those introduced by Krook and Wu for nonreactive gaseous mixtures [8].

Assumption:

$$(2.10) \quad r_{12;12}(\mathbf{v}, \mathbf{w}, \mathbf{n}) = \begin{cases} \text{const} \geq 0 & \text{when } \bar{W}_{12;34}(\mathbf{v}, \mathbf{w}, \mathbf{n}) < 0, \\ 0 & \text{if } \bar{W}_{12;34}(\mathbf{v}, \mathbf{w}, \mathbf{n}) \geq 0; \end{cases}$$

the functions $r_{12;34}$, $r_{34;12}$ are nonnegative constants (on their domains); similarly $r_{ij;ij}$ is nonnegative and constant if $\{i, j\} \neq \{1, 2\}$ or $\{i, j\} \neq \{3, 4\}$.

Under hypothesis (2.10), isotropic initial conditions lead to isotropic solutions, i.e., $f_i(\mathbf{v}) = f_i(v)$ for $1 \leq i \leq 4$ (where $v := |\mathbf{v}|$ is the modulus of the velocity \mathbf{v}).

In that case, one can provide a more explicit form for Eq.(2.4). Indeed, define

$$(2.11) \quad F_i(v) := 4\pi v^2 f_i(v), \quad \text{for } 1 \leq i \leq 4.$$

Denote the concentration of the species i by

$$(2.12) \quad I_i := \int_0^\infty F_i(v) dv, \quad \text{for } 1 \leq i \leq 4.$$

Let $\lambda_{kl;ij} := 4\pi \cdot r_{ij;kl}$ ($1 \leq i, j, k, l \leq 4$). Using suitable changes of variables in (2.5), (2.6), one obtains

$$(2.13) \quad (\phi, P_i(\mathbf{f})) = \sum_{j,k,l=1}^4 \lambda_{kl;ij} \cdot I_k I_l \int_{\mathbb{D}_{kl;ij}} \phi(\tilde{v}) \cdot F_k(v) F_l(w) dv dw d\zeta d\eta,$$

$$(2.14) \quad (\phi, S_i(\mathbf{f})) = \sum_{j,k,l=1}^4 \lambda_{ij;kl} \cdot I_i I_j \int_{\mathbb{D}_{ij;kl}} \phi(v) \cdot F_i(v) F_j(w) dv dw d\zeta d\eta,$$

where

$$(2.15) \quad \mathbb{D}_{kl;ij} := \{(v, w, \zeta, \eta) \in \mathbb{R}_+^2 \times [0, 1]^2 \mid \tilde{v}_{kl;ij} \in \mathbb{R}\}$$

The post collision velocity of the species i , $\tilde{v}_{kl;ij}$ is given by

$$(2.16) \quad \tilde{v}_{kl;ij} = \tilde{v}_{kl;ij}(v, w, \zeta, \eta) := \left[V_{kl}^2 + \frac{gm_k}{m_l} \rho_{kl;ij}^2 + 2 \left(\frac{m_k}{m_l} \right)^{1/2} \rho_{kl;ij} V_{kl} (2\eta - 1) \right]^{1/2},$$

where

$$(2.17) \quad V_{kl} = V_{kl}(v, w, \zeta) := (m_k^2 v^2 + m_l^2 w^2 + 2m_k m_l v w (2\zeta - 1))^{1/2} / (m_k + m_l),$$

$$(2.18) \quad \begin{aligned} \rho_{kl;ij} = \rho_{kl;ij}(v, w, \zeta) &:= [m_k m_l (v^2 + w^2 + 2vw(2\zeta - 1)) / (m_k + m_l)^2 + \\ &+ 2(E_k + E_l - E_i - E_j) / (m_k + m_l)]^{1/2}. \end{aligned}$$

The simple particularization of the above model concerns the non-reactive gas with two species [10]: $N = 2$, $E_i = 0$ and $\lambda_{kl;ij} = 0$, for $k \neq i$ and $l \neq j$.

Let $\lambda_{ij;ij} = \lambda_{ij}$, $m_{ik} = m_i / (m_i + m_k)$

$$(2.19) \quad p_1 = \lambda_{22} - \lambda_{21}\mu(3 - 2\mu), \quad p_2 = \lambda_{11} - \lambda_{12}\mu(3 - 2\mu),$$

with $\mu = 4m_1 m_2 / (m_1 + m_2)^2$.

The constants λ_{ki} satisfy the condition

$$(2.20) \quad \lambda_{12}/I_1 = \lambda_{21}/I_2,$$

The Krook-Wu like solutions [8] are determined if either condition on parameters $p_1 = p_2$ or condition $2\mu^2(\lambda_{21}/p_1 - \lambda_{12}/p_2) = 1$ is fulfilled. Then the general solution has the form:

$$(2.21) \quad f_i(t, v) = \Phi(v; \alpha_i(t)) [1 - 3p_i R(t) + Q_i(t) v^2], \quad i = 1, 2,$$

where

$$(2.22) \quad \begin{aligned} \Phi(v; \alpha) &= (2\pi\alpha)^{-3/2} \exp(-v^2/2\alpha), \\ Q_i(t) &= m_i p_i R(t) / \xi(t), \\ \alpha_i(t) &= \xi(t) / m_i, \\ R(t) &= A / [A \cdot \exp(A(t - t_0)) - B], \\ \xi(t) &= (I_1 + I_2) / [I_1 + I_2 + 8\pi(I_1 p_1 + I_2 p_2) \cdot R(t)], \end{aligned}$$

with A and B constants defined by:

$$(2.23) \quad A = 4\pi[\lambda_{11} + \lambda_{21}\mu(3 - 2\mu p_2/p_1)]/6, \quad B = 16\pi^2[\lambda_{11} p_1 + \lambda_{21}\mu(3 - 2\mu) p_2]/3.$$

On the other hand, if reactions are present (under condition (2.10)), no nontrivial analytical solution of the model is known. However, as mentioned in the Introduction, in some particular cases, indirect tests can be done, because starting from (2.4) one can solve exactly the equations for chemical concentrations and energies.

Indeed, the internal energy can be expressed exactly in terms of concentrations.

$$(2.24) \quad E_{int}(t) = \sum_{i=1}^4 I_i(t) E_i.$$

By the global conservation of energy, the total (kinetic + internal) energy of the gas

$$(2.25) \quad E(t) = \sum_{i=1}^4 \frac{m_i \langle v_i^2 \rangle(t)}{2} + \sum_{i=1}^4 I_i(t) E_i = E(0),$$

From (2.25) the total kinetic energy of the particles can be written

$$(2.26) \quad E_{cin}(t) = \sum_{i=1}^4 \frac{m_i \langle v_i^2 \rangle(t)}{2} = \sum_{i=1}^4 \frac{m_i \langle v_i^2 \rangle(0)}{2} + \sum_{i=1}^4 [I_i^0 - I_i(t)] E_i.$$

Moreover, if species X_1 and X_2 interact only by elastic collisions, then

$$(2.27) \quad \begin{cases} \dot{I}_i &= \lambda \cdot I_3 I_4, & i = 1, 2 \\ \dot{I}_i &= -\lambda \cdot I_3 I_4, & i = 3, 4 \end{cases}$$

with $\lambda := \lambda_{34;12}$. These equations can be solved immediately.

Let $I_i^0 := I_i(0)$, $1 \leq i \leq 4$. If $I_3^0 \neq I_4^0$ then, the solutions of (2.27) are

$$(2.28) \quad \begin{cases} I_i(t) &= I_i^0 + \frac{I_3^0 I_4^0 \cdot [\exp(I_4^0 \cdot \lambda t) - \exp(I_3^0 \cdot \lambda t)]}{I_4^0 \cdot \exp(I_4^0 \cdot \lambda t) - I_3^0 \cdot \exp(I_3^0 \cdot \lambda t)}, & i = 1, 2 \\ I_i(t) &= \frac{I_i^0 (I_4^0 - I_3^0) \cdot \exp(I_i^0 \cdot \lambda t)}{I_4^0 \cdot \exp(I_4^0 \cdot \lambda t) - I_3^0 \cdot \exp(I_3^0 \cdot \lambda t)}, & i = 3, 4, \end{cases}$$

and when $I_3^0 = I_4^0$, the solutions of (2.27) are

$$(2.29) \quad \begin{cases} I_i(t) &= I_i^0 + \frac{(I_3^0)^2 \cdot \lambda t}{(1 + I_3^0 \cdot \lambda t)}, & i = 1, 2 \\ I_i(t) &= \frac{I_i^0}{(1 + I_i^0 \cdot \lambda t)}, & i = 3, 4. \end{cases}$$

3 Numerical Method and Results

One considers some time interval $[0, T]$ and some given time step $0 < \Delta t < T$. The time-discretized version of (2.4) has the following form

$$(3.30) \quad (\phi, F_i^{p+1}) = (\phi, Q_{ij}^p),$$

where $\{i, j\} = \{1, 2\}$ or $\{i, j\} = \{3, 4\}$, $p \in \{0, 1, \dots, \lceil T/\Delta t \rceil - 1\}$ ($\lceil x \rceil$ denoting the integer part of the real positive number x) and $\phi \in C_b(\mathbb{R}^3)$.

The operators Q_{ij}^p in (3.30) are defined through the following measures. For $\{i, j\} = \{1, 2\}$ and $\{k, l\} = \{3, 4\}$ let

$$(3.31) \quad \begin{aligned} d\overline{H}_{ij}(v, w, \zeta, \eta) &:= \frac{1}{\overline{J}_{ij}} F_i(v) F_j(w) dv dw d\zeta d\eta && \text{on } \mathbb{D}_{ij;kl}, \\ d\underline{H}_{ij}(v, w, \zeta, \eta) &:= \frac{1}{\underline{J}_{ij}} F_i(v) F_j(w) dv dw d\zeta d\eta && \text{on } \mathbb{R}_+^2 \times [0, 1]^2 \setminus \mathbb{D}_{ij;kl}. \end{aligned}$$

where

$$\begin{aligned}
 \bar{J}_{ij} &:= \int_{\mathbb{D}_{ij;kl}} F_i(v) F_j(w) dv dw d\zeta d\eta, \\
 \underline{J}_{ij} &:= \int_{\mathbb{R}_+^2 \times [0,1]^2 \setminus \mathbb{D}_{ij;kl}} F_i(v) F_j(w) dv dw d\zeta d\eta.
 \end{aligned}
 \tag{3.32}$$

For $\{i, j\} = \{1, 2\}$, let

$$dH_{ij}(v, w, \zeta, \eta) := \frac{1}{I_i I_j} F_i(v) F_j(w) dv dw d\zeta d\eta$$

on $\mathbb{R}_+^2 \times [0, 1]^2$.

The operators Q_{ij}^p have the following form.

$$\begin{aligned}
 (\phi, Q_{ij}^p) &:= \left[\sum_{k=1}^4 \left(\frac{m_k}{M_{tot}^p} - \lambda_{ik;ik} \Delta t \right) I_k^p - \lambda_{ii;ii} \Delta t I_i^p \right] I_i^p(\phi, F_i^p) + \\
 &+ \left[\left(\frac{m_j}{M_{tot}^p} - \lambda_{ij;ij} \Delta t \right) \underline{J}_{ij}^p(\phi, \underline{H}_{ij}^p) + \right. \\
 &+ \left. \left(\frac{m_j}{M_{tot}^p} - \lambda_{ij;34} \Delta t \right) \bar{J}_{ij}^p(\phi, \bar{H}_{ij}^p) \right] I_j^p I_i^p + \\
 &+ \left[\lambda_{ii;ii} (\tilde{\phi}_{ii;ii}, H_{ii}^p) I_i^p + \sum_{k=1}^4 \lambda_{ik;ik} (\tilde{\phi}_{ik;ik}, H_{ik}^p) I_k^p \right] \Delta t I_i^p + \\
 &+ \left[\lambda_{ij;ij} \underline{J}_{ij}^p(\tilde{\phi}_{ij;ij}, \underline{H}_{ij}^p) I_j^p I_i^p + \lambda_{34;ij} (\tilde{\phi}_{34;ij}, H_{34}^p) I_3^p I_4^p \right] \Delta t;
 \end{aligned}
 \tag{3.34}$$

when $\{i, j\} = \{1, 2\}$ and

$$\begin{aligned}
 (\phi, Q_{ij}^p) &:= \left[\sum_{k=1}^4 \left(\frac{m_k}{M_{tot}^p} - \lambda_{ik;ik} \Delta t \right) I_k^p - \lambda_{ii;ii} \Delta t I_i^p \right] I_i^p(\phi, F_i^p) + \\
 &+ \left[\lambda_{ii;ii} (\tilde{\phi}_{ii;ii}, H_{ii}^p) I_i^p + \sum_{k=1}^4 \lambda_{ik;ik} (\tilde{\phi}_{ik;ik}, H_{ik}^p) I_k^p \right] \Delta t I_i^p + \\
 &+ \lambda_{12;ij} \bar{J}_{12}^p(\tilde{\phi}_{12;ij}, \bar{H}_{12}^p) \Delta t I_1^p I_2^p.
 \end{aligned}
 \tag{3.35}$$

if $\{i, j\} = \{3, 4\}$.

Note that, in (3.34) and (3.35) the quantities I_i^p , \underline{H}_{ij}^p , \bar{H}_{ij}^p , \underline{J}_{ij}^p , \bar{J}_{ij}^p , H_{ij}^p are defined as in (2.12), (3.31), (3.32), (3.33), simply replacing F_i and F_j by F_i^p and F_j^p

respectively. Moreover,

$$(3.36) \quad M_{tot}^p := \sum_{i=1}^4 m_i I_i^p$$

and $\tilde{\phi}_{ij;kl} := \phi \circ \tilde{v}_{ij;kl}$, with $\tilde{v}_{ij;kl}$ given by (2.16).

We approximate the initial data $F_i^0(v)dv$ by sums of Dirac measures

$$(3.37) \quad d\mu_{i,N}^0(v) = \frac{1}{N} \sum_{n=1}^N \delta(v - v_{i,n}^0)dv$$

concentrated on N points $v_{i,n}^0$, (such that $d\mu_{i,N}^0(v)$ converges to $F_i^0(v)dv$ as $N \rightarrow \infty$ in the weak sense of measures) and we approximate the Lebesgue measure on the unit square $d\zeta d\eta$ by sums of Dirac measures concentrated on N points $\frac{1}{N} \sum_{n=1}^N \delta(\zeta - \zeta_n) \delta(\eta - \eta_n) d\zeta d\eta$.

As one knows [7], the product measures in the r.h.s. of (3.30), yields a power-like increasing computational effort. The decrease of the computational effort (preserving the convergence of the scheme) is accomplished by random selections, applying Theorems 7, 8 of [7].

In all our tests we used the mixed congruential method to generate sequences $\{\omega_n\}_{n \in \mathbb{N}}$ of pseudo-random numbers. The elements $\omega_n = z_n/b$, where z_n are given recursively by $z_n = \lambda z_{n-1} + r \pmod{b}$. In this relation $b > 1$, λ and r are fixed natural numbers and λ is relative prime with b . The initialization is made with some integer $0 \leq z_0 < b$. Here $b = 3 \cdot 10^{30}$, $r = 1987654321$, $\lambda = 19867917$. Each test starts with an arbitrary positive $z_0 < b$.

The approximation of the initial data by sums of Dirac measures was made by means of the Hamersley-Van der Corput sequences (see [9] for details).

The numerical results correspond to several tests as follows.

In the case of the model with elastic collisions which presents exact solutions, a typical result can be found in [10]: $m_1 = 5$, $m_2 = 1$, $n_1 = 2$, $t_0 = \ln(3p_2 + B/A)/A$, $T = 6$. (This choice of t_0 ensures the positivity of f_i given by (2.21) for each $t \geq 0$.)

In a first experiment we have obtained for each $i = 1, 2$ ten numerical solutions for $N = 1500$ approximation points, at $T = 6$ and $J = 16$ iteration steps. Denote $G_i(t, v) := 4\pi \int_0^v u^2 f_i(t, u) du$, for $i = 1, 2$. The numerical results are represented in Figure 1 and Figure 2.

In the case of the model with chemical reactions, our experiments consisted of three series of tests performed on the model introduced in Section 2, corresponding to the caricatures of three kinds of chemical reactions (the below quantities are expressed in conventional, dimensionless units):

Case A: three distinct chemical species without endothermal reactions (only processes (2.1) and (2.3) with $X_3 = X_4$ occur) e.g. gas mixtures consisting of N_2 , O_2 and NO , at sufficiently low temperature, undergoing binary elastic collisions, as well as reactive collision inducing the reverse reaction in the process $N_2 + O_2 \rightleftharpoons 2NO$.

Masses : $m_1 = 46.48 \cdot 10^{-7}$, $m_2 = 53.12 \cdot 10^{-7}$, $m_3 = m_4 = 49.80 \cdot 10^{-7}$.

Initial concentrations: $I_1^0 = 0$, $I_2^0 = 0.1$, $I_3^0 = I_4^0 = 0.45$.

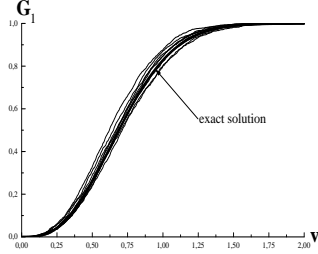


Figure 1: Exact solution of the first specie and ten numerical solutions for $N = 1500$, at $T = 6$ and $J = 16$.

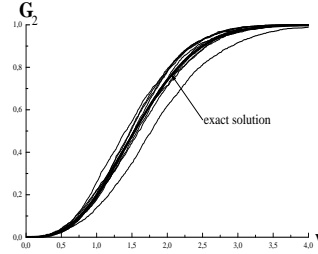


Figure 2: Exact solution of the second specie and ten numerical solutions for $N = 1500$, at $T = 6$ and $J = 16$.

Internal energies: $E_1 = -53.2344$, $E_2 = 19.6528$, $E_3 = E_4 = -2.9272$.

Values of λ : $\lambda_{11;11} = 1.2056$, $\lambda_{12;12} = \lambda_{33;33} = \lambda_{34;12} = \lambda_{44;44} = 1.3324$, $\lambda_{12;34} = 0$, $\lambda_{13;13} = \lambda_{14;14} = 1.2690$, $\lambda_{22;22} = 1.4592$, $\lambda_{23;23} = \lambda_{24;24} = 1.3958$.

Simulation time $T = 16$.

Initialization function in the time-discretized equations:

$$(3.38) \quad F_i^0(v) = 4\pi v^2 I_i^0 \left(\frac{m_i}{\pi} \right)^{3/2} \exp(-m_i v^2), \quad 1 \leq i \leq 4$$

Case B: four distinct species, without endothermic reaction (only processes (2.1), (2.3) occur and X_1, \dots, X_4 are different) e.g. gas mixtures consisting of HF, HCl, FCl and F_2 , at sufficiently low temperature, undergoing binary elastic collisions, as well as reactive collision inducing the direct reaction in the process $HF + FCl \rightleftharpoons F_2 + HCl$.

Masses: $m_1 = 33.20 \cdot 10^{-7}$, $m_2 = 90.47 \cdot 10^{-7}$, $m_3 = m_4 = 63.08 \cdot 10^{-7}$.

Initial concentrations: $I_1^0 = 0.02$, $I_2^0 = 0.08$, $I_3^0 = 0.4$, $I_4^0 = 0.5$.

Internal energies: $E_1 = -42.4750$, $E_2 = 9.3264$, $E_3 = 24.7642$, $E_4 = -20.7251$.

Values of λ : $\lambda_{11;11} = 1.2582$, $\lambda_{12;12} = \lambda_{34;12} = 2.1073$, $\lambda_{12;34} = 0$, $\lambda_{13;13} = 1.6091$, $\lambda_{14;14} = 1.7564$, $\lambda_{22;22} = 2.9564$, $\lambda_{23;23} = 2.4582$, $\lambda_{24;24} = 2.6055$, $\lambda_{33;33} = 1.9600$, $\lambda_{44;44} = 2.2547$.

Simulation time $T = 8.5$.

Initialization function in the time-discretized equations is the same as in Case A, (3.38)

Case C: four distinct species (2.1), (2.2), (2.3) occur and X_1, \dots, X_4 are different) e.g. gas mixtures consisting of BrF, FCl, BrCl, F_2 with elastic collisions and all reactions of the form in the process $BrF + FCl \rightleftharpoons F_2 + BrCl$.

Masses: $m_1 = 164.34 \cdot 10^{-7}$, $m_2 = 90.47 \cdot 10^{-7}$, $m_3 = 63.08 \cdot 10^{-7}$, $m_4 = 191.73 \cdot 10^{-7}$.

Initial concentrations: $I_1^0 = 0.35$, $I_2^0 = 0.6$, $I_3^0 = 0.05$, $I_4^0 = 0$.

Internal energies: $E_1 = -15.3415$, $E_2 = -15.6736$, $E_3 = -0.2328$, $E_4 = -10.1946$.

Values of λ : $\lambda_{11;11} = 3.6020$, $\lambda_{12;12} = \lambda_{34;12} = 3.2792$, $\lambda_{12;34} = 3.2792$, $\lambda_{13;13} = 2.7810$, $\lambda_{14;14} = 4.1002$, $\lambda_{22;22} = 2.9564$, $\lambda_{23;23} = 2.4582$, $\lambda_{24;24} = 3.7774$, $\lambda_{33;33} = 1.9600$, $\lambda_{44;44} = 4.5985$.

Simulation time $T = 1.75$.

Initialization function in the time-discretized equations:

$$(3.39) \quad F_i^0(v) = 4\pi v^2 I_i^0 \left(\frac{m_i}{20 \cdot \pi} \right)^{3/2} \exp \left(-\frac{m_i v^2}{20} \right), \quad 1 \leq i \leq 4$$

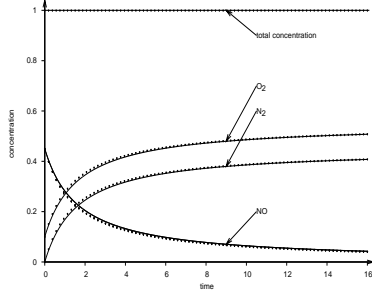


Figure 3: The evolution of the concentrations in Case A for 46000 points and 85 iteration steps.

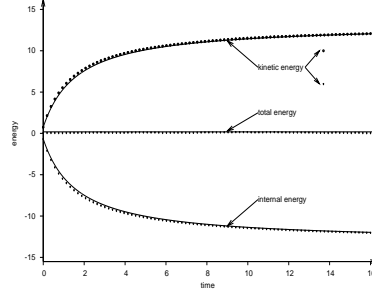


Figure 4: The evolution of the energies in Case A for 46000 points and 85 iteration steps.

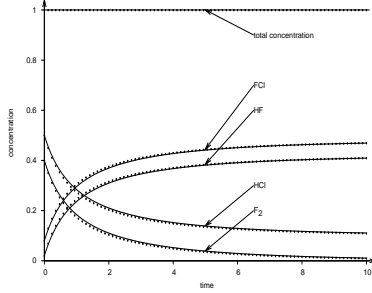


Figure 5: The evolution of the concentrations in Case B for 46000 points and 85 iteration steps.

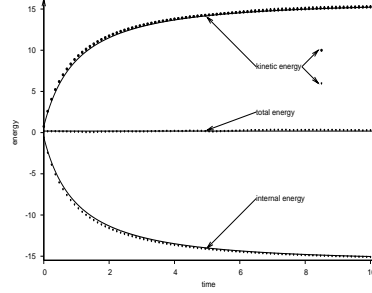


Figure 6: The evolution of the energies in Case B for 46000 points and 85 iteration steps.

The “support” of the initial datum is included in $[0, 2000]$ when F_i^0 is given by (3.38). It is included in $[0, 6000]$ if F_i^0 is given by (3.39). For details concerning the approximation of the initial data (3.38), (3.39), the interested reader is referred to [9], [10].

The above results present the evolution of concentrations and energies for several tests. The numerical results are indicated by dots. Each dot corresponds to a number given as the arithmetic mean of the values obtained as results of six simulations (corresponding to identical physical conditions). In addition to the numerical results, the values of the known exact solutions of the equations for the above macroscopic quantities are represented as lines, in the aforementioned figures.

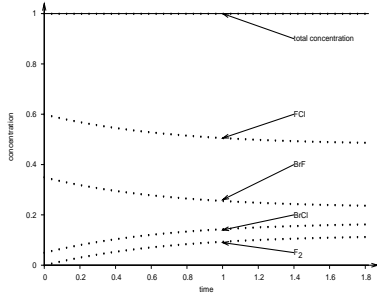


Figure 7: The evolution of the concentrations in Case C for 46000 points and 55 iteration steps.

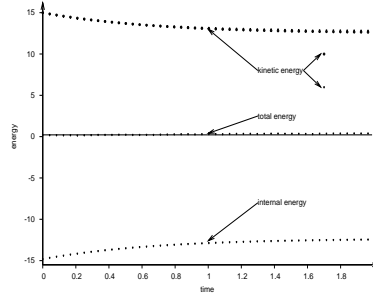


Figure 8: The evolution of the energies in Case C for 46000 points and 55 iteration steps.

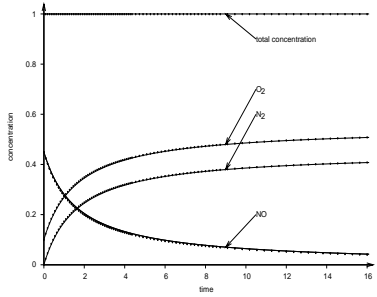


Figure 9: The evolution of the concentrations in Case A for 46000 points and 92 iteration steps with non-constant time step.

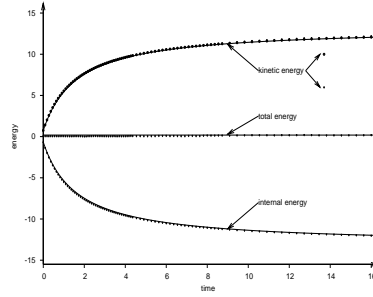


Figure 10: The evolution of the energies in Case A for 46000 points and 92 iteration steps with non-constant time step.

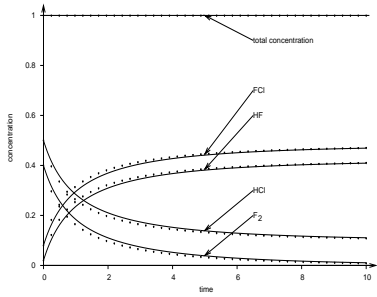


Figure 11: The evolution of the concentrations in Case B for 4600 points and 41 iteration steps.

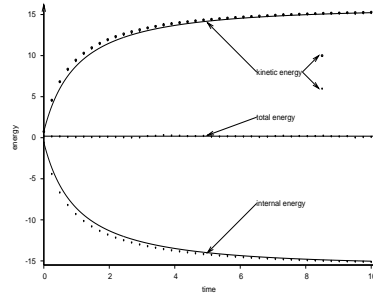


Figure 12: The evolution of the energies in Case B for 4600 points and 41 iteration steps.

Moreover, Figures 4, 6, 8, 10 and 12 detail the values of the kinetic energy, calculated by two different methods. Specifically, the first method evaluates the kinetic energy (kinetic energy 1, represented in our figures by circles) at each iteration step, as difference between the total energy (at $t = 0$) and the numerical value of internal energy (expressed in terms of concentrations as in (2.26)). The second method yields the kinetic energy (kinetic energy 2, represented in our figures by points) as an average with respect to the one-particle distribution functions.

Figures 3-6 present the evolution of concentrations and energies (simulated quantities and exact solutions) in Cases A and B for 85 iteration steps and 46000 concentration points. Figures 7-8 correspond to Case C for 46000 concentration points and 55 iteration steps. Figures 9-10 correspond to Case A where we used 46000 concentration points and a non-constant time step ($\Delta t = 1/11$ for the first 48 step, $\Delta t = 2/11$ for the next 24 steps and $\Delta t = 4/11$, for the last 20 steps). Figures 11-12 correspond to Case B for 4600 concentration points and 41 iteration steps.

A few remarks and critical considerations are in order:

The analysis of the results shows a good agreement between numerical and exact values.

The results described in Figures 3-8 are a little bit finer than those obtained in [11].

Figures 9-10 have no correspondent in literature. The time discretized method used in [7] is a first order Euler method. Our tests with non-constant time-step, Figures 9-10, suggest that, a high-order method seems to improve the precision, without increasing the computational effort of the numerical scheme. This could be very useful for computations in space non-homogeneous cases.

It appears from the analysis of Figures 11-12 that one can still obtain satisfactory results using less concentration points. However, we recall that, according to Theorem 10 in [7], the convergence of the numerical scheme, presented in this paper, requires the number of concentration points (of the measures) to be dependent on the length of time-step of the iteration. Indeed, taking the same number of concentration points, a very small iteration time-step may provide more inaccurate values of some estimated quantity (at a given moment) than a greater one. This numerical phenomenon was confirmed by tests in [10].

The main source of errors in the computation of the one-particle distribution function comes from the use of repeated random selections. Here it should be remarked that when the kinetic energy is calculated by means of the numeric values of concentrations ("kinetic energy 1"), the probabilistic selection appears only in the evaluation of the integrals (3.32). Then the estimation of "kinetic energy 1" is expected to be more accurate than for "kinetic energy 2". Indeed, Figure 12 shows clearly that "kinetic energy 1" is closer to the exact solution for energy than "kinetic energy 2".

Finally, we recall that the numerical method of [7] can be applied to more general models, with non constant collision kernels. However, in such situations, it is difficult to find exact solutions. Then the tests should rather be limited to comparing the data provided by the numerical scheme with those obtained from some relevant experiments.

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