

A kinetic model allowing to obtain the energy law of polytropic gases in the presence of chemical reactions

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Received 9 January 2004; accepted 17 July 2004

Available online 28 September 2004

Abstract

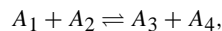
We propose a kinetic model which describes a mixture of reactive gases, in which a unique continuous internal energy parameter is present. This model enables to recover at the level of its hydrodynamical limit the Euler equations of a mixture of reactive polytropic gases.

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1. Introduction

In this paper we propose a kinetic model of Boltzmann type for a mixture of reactive gases. The originality of our model is that it satisfies the following requirements:

1. we wish to introduce *only one* internal energy parameter which has moreover to be *continuous* (that is, not discrete);
2. we wish to be able to write down precisely the kernels, and to rigorously prove the conservations laws and the H-theorem;
3. we wish to be able to take into account any chemical reversible reactions of type



in which the mass of the A_i may all be different, and which may be either endothermic or exothermic;

4. when looking at the hydrodynamical limit (that is, the limit when the Knudsen number goes to 0), we wish to be able to relate (in a simple and computable way) the cross sections at the Boltzmann level with the macroscopic parameters of the corresponding reactive Euler equations (that is, for example, the energy law of each specie, or the dependence of the reaction rate with respect to temperature). In particular, we want to be able to recover the energy law of polytropic gases.

Let us comment briefly on these requirements: the adjunction of only one parameter of internal energy which is moreover continuous will ensure that the numerical computations (under the form of particle methods) remain tractable (no need to take

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into account a large number of discrete energy levels). This is at variance with classical models such as those presented in [1–3] and [4], and constitutes the main originality of our work. The second and fourth requirements ensure that (at least at the formal level) the link between the microscopic and macroscopic description is rigorous. In particular, thanks to the fourth requirement, one has the possibility to couple numerical codes of both types (particle methods for the kinetic part, finite volumes for the Euler part). Finally, it is clear that one should be able to treat at least chemical reactions as described in the third requirement. Our model certainly can be extended to more complicated chemical situations, but in order to keep a readable paper, we shall not investigate in this direction. For very general models, cf. [8].

Our model is presented in the framework of the so-called Borgnakke–Larsen procedure (cf. [5]), and is a generalization of the models (which do not include chemical reactions) already introduced in [6] and [7].

For each specie A_i ($i = 1, \dots, 4$) of the mixture, we introduce a *number density function* f_i , which depends on the time t , the position (in space) x in \mathbb{R}^N (of course $N = 3$ in the applications, but we shall keep N in the sequel so that it is possible to see the dependence of the kernels with respect to the dimension), the velocity v (in \mathbb{R}^N), but also an *internal energy* I , which will vary in \mathbb{R}_+ (that is, as required, one unique continuous parameter). This last quantity will enable to get general energy laws at the level of the Euler equation.

If we denote by $n_i(x, t) dx$ the *number of particles* of the specie i at time t in an infinitesimal region of thickness dx centered in x , the physical meaning of the density f_i is the following:

$$n_i(t, x) = \int_{\mathbb{R}^N} \int_0^{+\infty} f_i(t, x, v, I) \varphi_i(I) dv dI, \quad (1)$$

where $\varphi_i(I) dI$ is a nonnegative measure which is a parameter of the model (typically, one can take $\varphi_i(I) = I^{\alpha_i}$ for some $\alpha_i \geq 0$).

As we shall see, the introduction of the functions $\varphi_i(I)$ is crucial, since it will permit to obtain a mass action law and a set of energy laws that are typical of polyatomic (polytropic) gases.

The paper is organized as follows: in Section 2, we write down the kernels corresponding to collisions between molecules of the same specie or of different species, but without chemical reactions. These kernels are close to that described in [6] and [7]. One of the differences (with the kernels presented in these papers) is that we take into account the mass of the molecules (which may be different for the different species) and the non-symmetric aspect of the bi-species kernel.

Then, in Section 3, we shall explain how to modify the previous description when chemical reactions are allowed. The main difficulty here is to include in the model the energy which is dissipated when a chemical reaction occurs.

Finally, in Section 4, we link our kinetic model with the fluid-dynamic (Euler) system corresponding to a mechanical (but not chemical) equilibrium.

2. Nonreactive collision kernels

We consider the (nonreactive) collision between two molecules of species i and j , with mass m_i and m_j , velocity v and v_* , and internal energy I and I_* respectively. After this collision, the molecules belong to the same specie, they still have mass m_i and m_j , but their velocities and internal energies have changed, and are now denoted by v' , v'_* , I' and I'_* (as a matter of fact, the kernel that we shall write use the inverse (and traditional) convention: the primed quantities correspond to the state of the molecules before the collision).

The conservations of momentum and total energy write:

$$m_i v' + m_j v'_* = m_i v + m_j v_*, \quad (2)$$

$$\frac{1}{2} m_i |v'|^2 + \frac{1}{2} m_j |v'_*|^2 + I' + I'_* = \frac{1}{2} m_i |v|^2 + \frac{1}{2} m_j |v_*|^2 + I + I_*. \quad (3)$$

Since we shall systematically work in the reference frame of the center of mass, we introduce the reduced mass

$$\mu_{ij} = \frac{m_i m_j}{m_i + m_j}. \quad (4)$$

The Borgnakke–Larsen procedure, which we shall use throughout this paper, is one of the simplest (and most natural) way to describe the evolution of the different energies (kinetic, internal) in the process of collision (from the mathematical point of view, it can also be seen as a simple way of parametrizing equations (2) and (3)). The idea of this procedure can be described as follows: one first computes the total energy ε of the incoming molecules in the center of mass reference frame (thanks to Eqs. (2) and (3), this is also the total energy of the outgoing molecules in the center of mass reference frame):

$$\varepsilon = \frac{1}{2} \mu_{ij} |v - v_*|^2 + I + I_* = \frac{1}{2} \mu_{ij} |v' - v'_*|^2 + I' + I'_*. \quad (5)$$

Then, a proportion $1 - R$ (with $R \in [0, 1]$) of this energy is attributed to the internal energy of the outgoing molecules, that is

$$I' + I'_* = (1 - R)\varepsilon. \quad (6)$$

This internal energy is itself distributed between the two outgoing molecules: we introduce therefore a parameter $r \in [0, 1]$ in such a way that

$$I' = r(1 - R)\varepsilon, \quad I'_* = (1 - r)(1 - R)\varepsilon. \quad (7)$$

The kinetic energy of the outgoing molecules (in the center of mass reference frame) is now

$$\frac{1}{2}\mu_{ij}|v' - v'_*|^2 = R\varepsilon. \quad (8)$$

This last equation can be parametrized by a unitary vector $\omega \in S^{N-1}$:

$$v' - v'_* = \sqrt{\frac{2R\varepsilon}{\mu_{ij}}} T_\omega \left[\frac{v - v_*}{|v - v_*|} \right], \quad (9)$$

where

$$T_\omega x = x - 2(\omega \cdot x)\omega$$

is the symmetry with respect to ω^\perp . Coming back in the laboratory reference frame, we end up with the formulas:

$$v' = \frac{m_i v + m_j v_*}{m_i + m_j} + \frac{m_j}{m_i + m_j} \sqrt{\frac{2R\varepsilon}{\mu_{ij}}} T_\omega \left[\frac{v - v_*}{|v - v_*|} \right], \quad (10)$$

$$v'_* = \frac{m_i v + m_j v_*}{m_i + m_j} - \frac{m_i}{m_i + m_j} \sqrt{\frac{2R\varepsilon}{\mu_{ij}}} T_\omega \left[\frac{v - v_*}{|v - v_*|} \right]. \quad (11)$$

Finally, we introduce (for the sake of symmetry: this will help in the computations of the Jacobian determinants) the extra parameters

$$R' = \frac{1}{2}\mu_{ij}|v - v_*|^2 \varepsilon^{-1}, \quad r' = \frac{I}{I + I_*}. \quad (12)$$

The main properties of the Borgnakke–Larsen transformations (5)–(12) are collected in the following lemma:

Lemma 1. *Let us define (for a given $\omega \in S^{N-1}$) the transformation*

$$S_\omega^{ij} : (v, v_*, I, I_*, r, R) \mapsto (v', v'_*, I', I'_*, r', R'),$$

by formulas (5)–(12).

Then S_ω^{ij} is a (one-to-one) involution of the set $E = \{(v, v_*) \in \mathbb{R}^N \times \mathbb{R}^N; I, I_* \geq 0; r, R \in [0, 1]\}$, and its Jacobian determinant J (defined here and in all this paper as the absolute value of the determinant of the Jacobian matrix of the transformation) is given by

$$J = \frac{1 - R}{1 - R'} \left(\frac{|v' - v'_*|}{|v - v_*|} \right)^{N-2} = \frac{R^{N/2-1}(1 - R)}{(R')^{N/2-1}(1 - R')}.$$

Proof. Note first that the inversion of S_ω^{ij} leads to the following formulas:

$$\varepsilon = \frac{1}{2}\mu_{ij}|v' - v'_*|^2 + I' + I'_*, \quad (13)$$

$$v = \frac{m_i v' + m_j v'_*}{m_i + m_j} + \frac{m_j}{m_i + m_j} \sqrt{\frac{2R\varepsilon}{\mu_{ij}}} T_\omega \left[\frac{v' - v'_*}{|v' - v'_*|} \right], \quad (14)$$

$$v_* = \frac{m_i v' + m_j v'_*}{m_i + m_j} - \frac{m_i}{m_i + m_j} \sqrt{\frac{2R\varepsilon}{\mu_{ij}}} T_\omega \left[\frac{v' - v'_*}{|v' - v'_*|} \right], \quad (15)$$

$$I = r'(1 - R')\varepsilon, \quad I_* = (1 - r')(1 - R')\varepsilon, \quad (16)$$

$$R = \frac{1}{2}\mu_{ij}|v' - v'_*|^2 \varepsilon^{-1}, \quad r = \frac{I'}{I' + I'_*}. \quad (17)$$

As a consequence, the transformation S_{ω}^{ij} is one to one and onto E .

In order to compute its Jacobian determinant, we shall decompose it in a chain of elementary changes of variables.

- First, we consider the passage to the center of mass reference frame. Since the transformation

$$A_1 : (v, v_*, I, I_*, r, R) \mapsto (g, G, I, I_*, r, R),$$

with $g = v - v_*$ and $G = (m_i v + m_j v_*) / (m_i + m_j)$, has a Jacobian determinant equal to 1, as well as the transformation

$$B_1 : (g', G', I', I'_*, r', R') \mapsto (v', v'_*, I', I'_*, r', R'),$$

with $g' = v' - v'_*$ and $G' = (m_i v' + m_j v'_*) / (m_i + m_j) = G$, we are led to study the transformation

$$C_1 : (g, I, I_*, r, R) \mapsto (g', I', I'_*, r', R').$$

- We now pass to spherical coordinates for the relative velocities g and g' . We perform therefore the transformations

$$A_2 : (g, I, I_*, r, R) \mapsto (|g|, g/|g|, I, I_*, r, R)$$

and

$$B_2 : (|g'|, g'/|g'|, I', I'_*, r', R') \mapsto (g', I', I'_*, r', R'),$$

and study the transformation

$$C_2 : (|g|, g/|g|, I, I_*, r, R) \mapsto (|g'|, g'/|g'|, I', I'_*, r', R'),$$

taking into account the Jacobian determinant $|g'|^{N-1}/|g|^{N-1}$ coming from A_2 and B_2 .

- In the next step, we consider the transformation

$$A_3 : (|g|, g/|g|, I, I_*, r, R) \mapsto (|g|, g/|g|, I, \varepsilon, r, R),$$

which thanks to (5) has a Jacobian determinant equal to 1. As a consequence, we only have to study the Jacobian determinant of the transformation

$$C_3 : (|g|, g/|g|, I, \varepsilon, r, R) \mapsto (|g'|, g'/|g'|, I', I'_*, r', R').$$

In the sequel, we will denote by $J[\cdot]$ the Jacobian determinant of a transformation. We use Eqs. (5), (9) and (12), in order to compute the Jacobian determinant of C_3 :

$$J \left[\left(|g|, \frac{g}{|g|}, I, \varepsilon, r, R \right) \mapsto \left(\sqrt{\frac{2R\varepsilon}{\mu_{ij}}}, T_{\omega} \left[\frac{g}{|g|} \right], r(1-R)\varepsilon, (1-r)(1-R)\varepsilon, \frac{I}{\varepsilon - \mu_{ij}|g|^2/2}, \frac{\mu_{ij}|g|^2}{2\varepsilon} \right) \right].$$

Since T_{ω} is a symmetry, the previous quantity is equal to

$$\begin{aligned} & J \left[(|g|, I, \varepsilon, r, R) \mapsto \left(\sqrt{\frac{2R\varepsilon}{\mu_{ij}}}, r(1-R)\varepsilon, (1-r)(1-R)\varepsilon, \frac{I}{\varepsilon - \mu_{ij}|g|^2/2}, \frac{\mu_{ij}|g|^2}{2\varepsilon} \right) \right] \\ &= \frac{1}{\varepsilon - \mu_{ij}|g|^2/2} J \left[(|g|, \varepsilon, r, R) \mapsto \left(\sqrt{\frac{2R\varepsilon}{\mu_{ij}}}, r(1-R)\varepsilon, (1-r)(1-R)\varepsilon, \frac{\mu_{ij}|g|^2}{2\varepsilon} \right) \right], \end{aligned}$$

and, by denoting $\rho = R\varepsilon$, it is also equal to

$$\left(\frac{\mu_{ij}|g|}{\varepsilon - \mu_{ij}|g|^2/2} \right) J \left[(\varepsilon, r, \rho) \mapsto \left(\sqrt{\frac{2\rho}{\mu_{ij}}}, r(\varepsilon - \rho), (1-r)(\varepsilon - \rho) \right) \right].$$

If we call $w = \varepsilon - \rho$, we get for the Jacobian of C_3 the formula:

$$\begin{aligned} & \left(\frac{\mu_{ij}|g|}{\varepsilon - \mu_{ij}|g|^2/2} \right) J \left[(w, r, \rho) \mapsto \left(\sqrt{\frac{2\rho}{\mu_{ij}}}, rw, (1-r)w \right) \right] \\ &= \left(\frac{\mu_{ij}|g|}{(1-R')\varepsilon} \sqrt{\frac{2}{\mu_{ij}}} \frac{1}{2\sqrt{\rho}} \right) J \left[(w, r) \mapsto (rw, (1-r)w) \right] = \sqrt{2\mu_{ij}} \frac{|g|}{(1-R')\varepsilon} \frac{w}{2\sqrt{\rho}} \\ &= \frac{1-R}{1-R'} \frac{|g|}{|g'|}. \end{aligned}$$

Taking into account the term coming from the Jacobian determinant of the spherical change of variables, we finally get

$$J[S_{\omega}^{ij}] = \frac{1-R}{1-R'} \left(\frac{|v' - v'_*|}{|v - v_*|} \right)^{N-2} = \frac{R^{N/2-1}(1-R)}{(R')^{N/2-1}(1-R')},$$

and this ends the proof of the lemma. \square

Note that when $m_i = m_j$, the Borgnakke–Larsen equations (5)–(12) reduce to

$$\begin{aligned} \varepsilon &= \frac{m_i}{4} |v - v_*|^2 + I + I_*, \\ v' &= \frac{v + v_*}{2} + \sqrt{\frac{R\varepsilon}{m_i}} T_{\omega} \left[\frac{v - v_*}{|v - v_*|} \right], \\ v'_* &= \frac{v + v_*}{2} - \sqrt{\frac{R\varepsilon}{m_i}} T_{\omega} \left[\frac{v - v_*}{|v - v_*|} \right], \\ I' &= r(1-R)\varepsilon, \quad I'_* = (1-r)(1-R)\varepsilon, \\ R' &= \frac{m_i}{4} |v - v_*| \varepsilon^{-1}, \quad r' = \frac{I}{I + I_*}, \end{aligned} \tag{18}$$

which are the equations of [6] (when $m_i = 1$).

We now introduce the Boltzmann kernels corresponding to the previous transformations. We begin with the kernel corresponding to the collisions between molecules of the same species:

Definition 1. The (nonreactive) mono-specie collision kernel for the specie i is given by

$$\begin{aligned} Q_i^m(f, f)(v, I) &= \int_{\Omega} \int_{\omega \in S^{N-1}} [f(v', I') f(v'_*, I'_*) - f(v, I) f(v_*, I_*)] \\ &\quad \times B_i(v, v_*, I, I_*, R, r, \omega) (1-R) |v - v_*|^{2-N} \frac{1}{\varphi_i(I)} dv_* dI_* dr dR d\omega, \end{aligned} \tag{19}$$

where $\Omega = \{v_* \in \mathbb{R}^N; I_* \geq 0; r, R \in [0, 1]\}$, v', I', v'_*, I'_* are defined by Eqs. (5)–(12) (or the simplified formulation (18)), and the cross sections B_i are supposed to satisfy the (microreversibility) assumptions:

$$\begin{aligned} B_i(v, v_*, I, I_*, R, r, \omega) &= B_i(v_*, v, I_*, I, R, 1-r, \omega), \\ B_i(v, v_*, I, I_*, R, r, \omega) &= B_i(v', v'_*, I', I'_*, R', r', \omega). \end{aligned} \tag{20}$$

The standard conservation properties of this kernel are consequences of the following weak formulation:

Lemma 2. Let $\psi : \mathbb{R}^N \times [0, +\infty) \rightarrow \mathbb{R}$ be a function such that the weak formulation

$$\int_{v \in \mathbb{R}^N} \int_{I \geq 0} Q_i^m(f, f)(v, I) \psi(v, I) \varphi_i(I) dI dv$$

makes sense. Then

$$\begin{aligned} &\int_{v \in \mathbb{R}^N} \int_{I \geq 0} Q_i^m(f, f)(v, I) \psi(v, I) \varphi_i(I) dI dv \\ &= \frac{1}{4} \int_{v \in \mathbb{R}^N} \int_{I \geq 0} \int_{\Omega} \int_{\omega \in S^{N-1}} [f(v', I') f(v'_*, I'_*) - f(v, I) f(v_*, I_*)] \\ &\quad \times [\psi(v', I') + \psi(v'_*, I'_*) - \psi(v, I) - \psi(v_*, I_*)] \\ &\quad \times B_i(v, v_*, I, I_*, R, r, \omega) (1-R) |v - v_*|^{2-N} dv dv_* dI dI_* dr dR d\omega. \end{aligned} \tag{21}$$

Proof. We use the changes of variables (with $\omega \in S^{N-1}$ fixed):

$$\begin{aligned}(v, v_*, I, I_*, R, r) &\mapsto (v_*, v, I_*, I, R, 1-r) \\ (v, v_*, I, I_*, R, r) &\mapsto (v', v'_*, I', I'_*, R', r'). \quad \square\end{aligned}$$

Note that this weak formulation is nothing but a rewriting (with slightly different notations and with the addition of the explicit dependence on the masses) of the main result of [7].

As a consequence, considering $\psi(v, I) = 1, m_i v_{(k)}, m_i \frac{|v|^2}{2} + I$ (for $k = 1, \dots, N, v_{(k)}$ denoting the k -th component of v), we get the conservation of the number of molecules of specie i , of momentum, and of total (kinetic + internal) energy (also for each specie i):

$$\int_{v \in \mathbb{R}^N} \int_{I \geq 0} Q_i^m(f, f)(v, I) \begin{pmatrix} 1 \\ m_i v_{(k)} \\ m_i \frac{|v|^2}{2} + I \end{pmatrix} \varphi_i(I) dI dv = 0. \quad (22)$$

We now write down the collision kernel between molecules of different species (that is, $i \neq j$), but still without chemical reactions.

Definition 2. The (nonreactive) bi-species collision kernel for the species i and j , with $i \neq j$, is given by

$$\begin{aligned}Q_{Sij}^b(f, g)(v, I) &= \int_{\Omega} \int_{\omega \in S^{N-1}} [f(v', I')g(v'_*, I'_*) - f(v, I)g(v_*, I_*)] \\ &\quad \times B_{ij}(v, v_*, I, I_*, R, r, \omega)(1-R)|v - v_*|^{2-N} \frac{1}{\varphi_i(I)} dv_* dI_* dr dR d\omega,\end{aligned} \quad (23)$$

where $\Omega = \{v_* \in \mathbb{R}^N; I_* \geq 0; r, R \in [0, 1]\}$, v', I', v'_*, I'_* are defined by Eqs. (5)–(12) (with the indices i, j corresponding to S^{ij}). In other words, when we write Q_{Sji}^b , it means that we exchange the masses m_i and m_j in Eqs. (5)–(12), and the cross sections B_{ij} are supposed to satisfy the (microreversibility) assumptions:

$$\begin{aligned}B_{ij}(v, v_*, I, I_*, R, r, \omega) &= B_{ji}(v_*, v, I_*, I, R, 1-r, \omega), \\ B_{ij}(v, v_*, I, I_*, R, r, \omega) &= B_{ij}(v', v'_*, I', I'_*, R', r', \omega).\end{aligned} \quad (24)$$

Then, the weak formulation of the kernel (23) is given by the lemma:

Lemma 3. Let $\psi_i : \mathbb{R}^N \times [0, +\infty) \rightarrow \mathbb{R}$ be functions such that the formulas

$$\int_{v \in \mathbb{R}^N} \int_{I \geq 0} Q_{Sij}^b(f, g)(v, I) \psi_i(v, I) \varphi_i(I) dI dv,$$

and

$$\int_{v \in \mathbb{R}^N} \int_{I \geq 0} Q_{Sji}^b(g, f)(v, I) \psi_j(v, I) \varphi_j(I) dI dv,$$

make sense. Then, on one hand,

$$\begin{aligned}&\int_{v \in \mathbb{R}^N} \int_{I \geq 0} Q_{Sij}^b(f, g)(v, I) \psi_i(v, I) \varphi_i(I) dI dv \\ &= -\frac{1}{2} \int_{\Omega} \int_{v \in \mathbb{R}^N} \int_{I \geq 0} \int_{\omega \in S^{N-1}} [f(v', I')g(v'_*, I'_*) - f(v, I)g(v_*, I_*)] [\psi_i(v', I') - \psi_i(v, I)] \\ &\quad \times B_{ij}(v, v_*, I, I_*, R, r, \omega)(1-R)|v - v_*|^{2-N} dv dv_* dI dI_* dr dR d\omega,\end{aligned} \quad (25)$$

and on the other hand

$$\begin{aligned}
 & \int_{v \in \mathbb{R}^N} \int_{I \geq 0} Q_{Sij}^b(f, g)(v, I) \psi_i(v, I) \varphi_i(I) dI dv + \int_{v \in \mathbb{R}^N} \int_{I \geq 0} Q_{Sji}^b(g, f)(v, I) \psi_j(v, I) \varphi_j(I) dI dv \\
 &= -\frac{1}{2} \int_{\Omega} \int_{v \in \mathbb{R}^N} \int_{I \geq 0} \int_{\omega \in S^{N-1}} [f(v', I') g(v'_*, I'_*) - f(v, I) g(v_*, I_*)] \\
 & \quad \times [\psi_i(v', I') + \psi_j(v'_*, I'_*) - \psi_i(v, I) - \psi_j(v_*, I_*)] \\
 & \quad \times B_{ij}(v, v_*, I, I_*, R, r, \omega) (1-R) |v - v_*|^{2-N} dv dv_* dI dI_* dr dR d\omega. \tag{26}
 \end{aligned}$$

Proof. In order to get formula (25), it is enough to use the change of variables

$$(v, v_*, I, I_*, R, r) \mapsto (v', v'_*, I', I'_*, R', r').$$

We now turn to formula (26). We consider the second integral in the left-hand side of Eq. (26). By expliciting the primed variables (that is, by using Eqs. (10), (11) and (7)), we obtain

$$\begin{aligned}
 & \int_{v \in \mathbb{R}^N} \int_{I \geq 0} Q_{Sji}^b(g, f)(v, I) \psi_j(v, I) \varphi_j(I) dI dv \\
 &= \int_{v \in \mathbb{R}^N} \int_{I \geq 0} \int_{\Omega} \int_{\omega \in S^{N-1}} \left[g\left(\frac{m_j v + m_i v_*}{m_i + m_j} + \frac{m_i}{m_i + m_j} \sqrt{\frac{2R\varepsilon}{\mu_{ij}}} T_\omega \left[\frac{v - v_*}{|v - v_*|}\right], r(1-R)\varepsilon\right) \right. \\
 & \quad \times f\left(\frac{m_j v + m_i v_*}{m_i + m_j} - \frac{m_j}{m_i + m_j} \sqrt{\frac{2R\varepsilon}{\mu_{ij}}} T_\omega \left[\frac{v - v_*}{|v - v_*|}\right], (1-r)(1-R)\varepsilon\right) - g(v, I) f(v_*, I_*) \left. \right] \psi_j(v, I) \\
 & \quad \times B_{ji}(v, v_*, I, I_*, R, r, \omega) (1-R) |v - v_*|^{2-N} dv dv_* dI dI_* dr dR d\omega.
 \end{aligned}$$

Then, by the change of variables (with $\omega \in S^{N-1}$ fixed)

$$(v, v_*, I, I_*, R, r) \mapsto (v_*, v, I_*, I, R, 1-r),$$

the kernel takes the form

$$\begin{aligned}
 & \int_{v \in \mathbb{R}^N} \int_{I \geq 0} Q_{Sji}^b(g, f)(v, I) \psi_j(v, I) \varphi_j(I) dI dv \\
 &= \int_{v \in \mathbb{R}^N} \int_{I \geq 0} \int_{\Omega} \int_{\omega \in S^{N-1}} \left[g\left(\frac{m_j v_* + m_i v}{m_i + m_j} - \frac{m_i}{m_i + m_j} \sqrt{\frac{2R\varepsilon}{\mu_{ij}}} T_\omega \left[\frac{v - v_*}{|v - v_*|}\right], (1-r)(1-R)\varepsilon\right) \right. \\
 & \quad \times f\left(\frac{m_j v_* + m_i v}{m_i + m_j} + \frac{m_j}{m_i + m_j} \sqrt{\frac{2R\varepsilon}{\mu_{ij}}} T_\omega \left[\frac{v - v_*}{|v - v_*|}\right], r(1-R)\varepsilon\right) - g(v_*, I_*) f(v, I) \left. \right] \psi_j(v_*, I_*) \\
 & \quad \times B_{ji}(v_*, v, I_*, I, R, 1-r, \omega) (1-R) |v - v_*|^{2-N} dv dv_* dI dI_* dr dR d\omega.
 \end{aligned}$$

The proposition is then obtained by using the change of variables

$$(v, v_*, I, I_*, R, r) \mapsto (v', v'_*, I', I'_*, R', r'). \quad \square$$

As a consequence, considering $\psi_i(v, I) = 1$ in formula (25), we get the conservation of the number of molecules of specie i :

$$\int_{v \in \mathbb{R}^N} \int_{I \geq 0} Q_{Sij}^b(g, f)(v, I) \varphi_i(I) dI dv = 0. \tag{27}$$

Considering then $\psi_i(v, I) = m_i v_{(k)}, m_i \frac{|v|^2}{2} + I$ (for $k = 1, \dots, N$) in formula (26), we get the conservation of the momentum and total (kinetic + internal) energy when all species are considered together:

$$\int_{v \in \mathbb{R}^N} \int_{I \geq 0} Q_{Sij}^b(f, g)(v, I) \begin{pmatrix} m_i v^{(k)} \\ m_i \frac{|v|^2}{2} + I \end{pmatrix} \varphi_i(I) \, dI \, dv \\ + \int_{v \in \mathbb{R}^N} \int_{I \geq 0} Q_{Sji}^b(g, f)(v, I) \begin{pmatrix} m_j v^{(k)} \\ m_j \frac{|v|^2}{2} + I \end{pmatrix} \varphi_j(I) \, dI \, dv = 0. \quad (28)$$

We conclude this section by a brief discussion relative to the assumption on the cross sections B_i and B_{ij} . We observe that the requirement that these quantities are invariant when v, v_*, I, I_*, r, R become $v', v'_*, I', I'_*, r', R'$ is automatically satisfied when they depend upon the following quantities: $\varepsilon, \frac{\mu_{ij}}{2} R |v - v_*|^2$ (because it can also be written $RR'\varepsilon$), $\frac{\mu_{ij}}{2} R |(v - v_*) \cdot \omega|^2$ (because it can still be written $RR'\varepsilon$), and $(I + I_*)(1 - R)$ (because it can also be written $(1 - R)(1 - R')\varepsilon$).

3. Scattering in presence of chemical reactions

Let us now consider the possibility for the molecules of the gas mixture to react with themselves, according to:



The mass is conserved during a collision; we denote by $M = m_1 + m_2 = m_3 + m_4$ its constant value.

Moreover, we define $r_i = m_i/M$ (so that $\mu_{ij} = (m_i m_j)/M$). We get the relation $r_1 + r_2 = r_3 + r_4 = 1$. Finally we denote by $E \geq 0$ the energy which is dissipated by (or which has to be supplied to) the system when we pass from $A_1 + A_2$ to $A_3 + A_4$.

This means that we consider the reaction (29) from the left to the right as an endothermic reaction, whereas the inverse one is an exothermic reaction.

The conservation laws of momentum and energy are:

$$m_1 v_1 + m_2 v_2 = m_3 v_3 + m_4 v_4, \\ \frac{1}{2} m_1 v_1^2 + \frac{1}{2} m_2 v_2^2 + I_1 + I_2 = \frac{1}{2} m_3 v_3^2 + \frac{1}{2} m_4 v_4^2 + I_3 + I_4 + E. \quad (30)$$

The passage to the center of mass reference frame is made thanks to the equation:

$$\frac{1}{2} M |r_i v_i + r_j v_j|^2 + \frac{1}{2} \mu_{ij} |v_i - v_j|^2 = \frac{1}{2} m_i v_i^2 + \frac{1}{2} m_j v_j^2,$$

so that equation (30) becomes

$$\frac{1}{2} \mu_{12} |v_1 - v_2|^2 + I_1 + I_2 = \frac{1}{2} \mu_{34} |v_3 - v_4|^2 + I_3 + I_4 + E.$$

We now introduce the energy

$$\varepsilon = \frac{1}{2} \mu_{12} |v_1 - v_2|^2 + I_1 + I_2 - \frac{E}{2} = \frac{1}{2} \mu_{34} |v_3 - v_4|^2 + I_3 + I_4 + \frac{E}{2}$$

and define v_3, I_3, v_4 and I_4 in function of v_1, I_1, v_2, I_2 and of the parameters r, R (in $[0, 1]$) and $\omega \in S^{N-1}$ by:

$$v_3 = r_1 v_1 + r_2 v_2 - r_4 \sqrt{\frac{2}{\mu_{34}}} \left(R\varepsilon - \frac{E}{6} \right)^{1/2} T_\omega \left[\frac{v_1 - v_2}{|v_1 - v_2|} \right], \quad (31)$$

$$v_4 = r_1 v_1 + r_2 v_2 + r_3 \sqrt{\frac{2}{\mu_{34}}} \left(R\varepsilon - \frac{E}{6} \right)^{1/2} T_\omega \left[\frac{v_1 - v_2}{|v_1 - v_2|} \right], \quad (32)$$

$$I_3 = (1 - R)r\varepsilon - \frac{E}{6}, \quad (33)$$

$$I_4 = (1 - R)(1 - r)\varepsilon - \frac{E}{6}. \quad (34)$$

Moreover, we introduce for the sake of symmetry the parameters

$$R' = \frac{1}{\varepsilon} \left(\frac{\mu_{12}}{2} |v_1 - v_2|^2 - \frac{E}{6} \right), \quad (35)$$

$$r' = \frac{I_1 - E/6}{\varepsilon(1 - R')} = \frac{I_1 - E/6}{\varepsilon - \mu_{12} |v_1 - v_2|^2 / 2 + E/6}. \quad (36)$$

The previous equations can be written backwards, and so become:

$$v_1 = r_3 v_3 + r_4 v_4 - r_2 \sqrt{\frac{2}{\mu_{12}}} \left(R' \varepsilon + \frac{E}{6} \right)^{1/2} T_\omega \left[\frac{v_3 - v_4}{|v_3 - v_4|} \right], \tag{37}$$

$$v_2 = r_3 v_3 + r_4 v_4 + r_1 \sqrt{\frac{2}{\mu_{12}}} \left(R' \varepsilon + \frac{E}{6} \right)^{1/2} T_\omega \left[\frac{v_3 - v_4}{|v_3 - v_4|} \right], \tag{38}$$

$$I_1 = (1 - R') r' \varepsilon + \frac{E}{6}, \tag{39}$$

$$I_2 = (1 - R') (1 - r') \varepsilon + \frac{E}{6}, \tag{40}$$

$$R = \frac{1}{\varepsilon} \left(\frac{\mu_{34}}{2} |v_3 - v_4|^2 + \frac{E}{6} \right), \tag{41}$$

$$r = \frac{I_3 + E/6}{\varepsilon(1 - R)}. \tag{42}$$

In the sequel, we shall denote the application corresponding to the previous change of variables (that is, to Eqs. (31)–(36)) by

$$\tilde{S}^{12} : (v_1, v_2, I_1, I_2, r, R) \mapsto (v_3, v_4, I_3, I_4, r', R').$$

In the following lemma, we prove the main properties of this transformation.

Lemma 4. *The application \tilde{S}^{12} is a one-to-one map from the set*

$$F = \left\{ (v_1, v_2) \in \mathbb{R}^N \times \mathbb{R}^N; I_1, I_2 \geq E/6; r, R \in [0, 1]; R\varepsilon \geq E/6; \right. \\ \left. \times \mu_{12} |v_1 - v_2|^2 / 2 \geq E/6; (1 - R)r\varepsilon \geq E/6; (1 - R)(1 - r)\varepsilon \geq E/6 \right\}$$

onto

$$G = \{ (v_3, v_4) \in \mathbb{R}^N \times \mathbb{R}^N; I_3, I_4 \geq 0; r', R' \in [0, 1] \},$$

and its Jacobian determinant J is given by

$$J = \left(\frac{m_1 m_2}{m_3 m_4} \right) \left(\frac{1 - R}{1 - R'} \right) \left(\frac{|v_3 - v_4|}{|v_1 - v_2|} \right)^{N-2}.$$

Proof. In order to prove the first part of the lemma, we observe that \tilde{S}^{12} is well defined on F since $R\varepsilon \geq E/6$.

Moreover, I_3 and I_4 are nonnegative since $(1 - R)r\varepsilon \geq E/6$ and $(1 - R)(1 - r)\varepsilon \geq E/6$.

Finally $0 \leq R' \leq 1$ since $\mu_{12} |v_1 - v_2|^2 / 2 \geq E/6$, $I_1, I_2 \geq E/6$, and $0 \leq r' \leq 1$ since $I_1 \geq E/6$, $\varepsilon - \mu_{12} |v_1 - v_2|^2 / 2 + E/6 = (I_1 - E/6) + (I_2 - E/6) \geq 0$.

Conversely, if $(v_3, v_4, I_3, I_4, r', R') \in G$, we deduce, by using formulas (37)–(42), that $I_1, I_2 \geq E/6$, $\mu_{12} |v_1 - v_2|^2 / 2 = R' \varepsilon + E/6 \geq E/6$, $R\varepsilon = \mu_{34} |v_3 - v_4|^2 / 2 + E/6 \geq E/6$, $r(1 - R)\varepsilon = I_3 + E/6 \geq E/6$, and finally $(1 - r)(1 - R)\varepsilon = I_4 + E/6 \geq E/6$.

The fact that \tilde{S}^{12} is one-to-one directly follows from the inversion formulas (37)–(42).

The last part of the proof is based on a series of changes of variables, and is very similar to the proof of Lemma 1.

In what follows, we shall use the following notation:

$$g = \sqrt{\frac{\mu_{12}}{2}} (v_1 - v_2), \quad g' = \sqrt{\frac{\mu_{34}}{2}} (v_3 - v_4).$$

We recall moreover that the transformations of variables which are used here refer to Eqs. (31)–(36) and (37)–(42).

The Jacobian determinant of the transformation \tilde{S}^{12} can be computed as follows:

$$J[(v_1, v_2, I_1, I_2, r, R) \mapsto (v_3, v_4, I_3, I_4, r', R')] = \left(\frac{\mu_{12}}{\mu_{34}} \right)^{N/2} J[(g, I_1, I_2, r, R) \mapsto (g', I_3, I_4, r', R')].$$

By representing g and g' in spherical coordinates, we get the Jacobian determinant of the original transformation:

$$\left(\frac{\mu_{12}}{\mu_{34}} \right)^{N/2} \left(\frac{|g'|}{|g|} \right)^{N-1} J[(|g|, I_1, I_2, r, R) \mapsto (|g'|, I_3, I_4, r', R')].$$

This means that we are led to compute the Jacobian determinant of the following transformation:

$$(|g|, I_1, I_2, r, R) \mapsto \left(\left(R\varepsilon - \frac{E}{6} \right)^{1/2}, (1-R)r\varepsilon - \frac{E}{6}, (1-R)(1-r)\varepsilon - \frac{E}{6}, \frac{I_1 - E/6}{\varepsilon - |g|^2 + E/6}, \frac{1}{\varepsilon} \left(|g|^2 - \frac{E}{6} \right) \right).$$

It is equal to

$$\frac{1}{\varepsilon - |g|^2 + E/6} J \left[(|g|, \varepsilon, r, R) \mapsto \left(\left(R\varepsilon - \frac{E}{6} \right)^{1/2}, (1-R)r\varepsilon - \frac{E}{6}, (1-R)(1-r)\varepsilon - \frac{E}{6}, \frac{1}{\varepsilon} \left(|g|^2 - \frac{E}{6} \right) \right) \right].$$

Finally, we follow the same steps as in Lemma 1. We compute

$$\begin{aligned} & J \left[(|g|, \varepsilon, r, R) \mapsto \left(\left(R\varepsilon - \frac{E}{6} \right)^{1/2}, (1-R)r\varepsilon - \frac{E}{6}, (1-R)(1-r)\varepsilon - \frac{E}{6}, \frac{1}{\varepsilon} \left(|g|^2 - \frac{E}{6} \right) \right) \right] \\ &= \varepsilon J \left[(|g|, \varepsilon, r, \rho = R\varepsilon) \mapsto \left(\left(\rho - \frac{E}{6} \right)^{1/2}, (\varepsilon - \rho)r - \frac{E}{6}, (\varepsilon - \rho)(1-r) - \frac{E}{6}, \frac{1}{\varepsilon} \left(|g|^2 - \frac{E}{6} \right) \right) \right] \\ &= 2|g| J \left[(\varepsilon, r, \rho) \mapsto \left(\left(\rho - \frac{E}{6} \right)^{1/2}, (\varepsilon - \rho)r - \frac{E}{6}, (\varepsilon - \rho)(1-r) - \frac{E}{6} \right) \right]. \end{aligned}$$

Using the change of variables (of Jacobian 1) $\varepsilon - \rho = w$ we observe that the quantity above is equal to $|g|(\rho - E/6)^{-1/2}(\varepsilon - \rho)$.

Collecting together all the computations, we finally see that

$$J[\tilde{S}^{12}] = \left(\frac{\mu_{12}}{\mu_{34}} \right)^{N/2} \left(\frac{|g'|}{|g|} \right)^{N-1} \frac{|g|}{\varepsilon - |g|^2 + E/6} \left(\rho - \frac{E}{6} \right)^{-1/2} (\varepsilon - \rho).$$

Using the original variables, this means

$$J[\tilde{S}^{12}] = \left(\frac{m_1 m_2}{m_3 m_4} \right) \left(\frac{1-R}{1-R'} \right) \left(\frac{|v_3 - v_4|}{|v_1 - v_2|} \right)^{N-2},$$

and the last part of the lemma is proven. \square

We now write down the collision kernels (one for each specie) corresponding to the chemical reaction considered here. We first define some sets:

$$F_{\text{react}}^1 = \left\{ I, I_2, R\varepsilon, \frac{\mu_{12}}{2} |v - v_2|^2, (1-R)r\varepsilon, (1-R)(1-r)\varepsilon \geq \frac{E}{6} \right\},$$

$$F_{\text{react}}^2 = \left\{ I, I_1, R\varepsilon, \frac{\mu_{12}}{2} |v - v_1|^2, (1-R)r\varepsilon, (1-R)(1-r)\varepsilon \geq \frac{E}{6} \right\},$$

$$F_{\text{react}}^3 = \left\{ I_4 \geq 0; v_4 \in \mathbb{R}^N; 0 \leq r', R' \leq 1 \right\},$$

$$F_{\text{react}}^4 = \left\{ I_3 \geq 0; v_3 \in \mathbb{R}^N; 0 \leq r', R' \leq 1 \right\},$$

and the following Heaviside functions:

$$H_i(\xi) = \begin{cases} 1 & \text{when } \xi \in F_{\text{react}}^i, \\ 0 & \text{otherwise.} \end{cases}$$

Finally, we define the following quantities:

$$\varepsilon_1 = \frac{1}{2} \mu_{12} |v - v_2|^2 + I + I_2 - \frac{E}{2},$$

$$\varepsilon_2 = \frac{1}{2} \mu_{12} |v - v_1|^2 + I + I_1 - \frac{E}{2},$$

$$\varepsilon_3 = \frac{1}{2} \mu_{34} |v - v_4|^2 + I + I_4 + \frac{E}{2},$$

$$\varepsilon_4 = \frac{1}{2} \mu_{34} |v - v_3|^2 + I + I_3 + \frac{E}{2}.$$

Definition 3. We define the reactive collision kernels by

$$\begin{aligned}
 Q_1^{\text{react}}(v, I) &= \int_{\Omega_1} \int_{\omega \in \mathcal{S}^{N-1}} H_1 \left[\left(\frac{m_1 m_2}{m_3 m_4} \right)^N f_3 \left(r_1 v + r_2 v_2 - r_4 \sqrt{\frac{2}{\mu_{34}} \left(R \varepsilon_1 - \frac{E}{6} \right)} T_\omega \left[\frac{v - v_2}{|v - v_2|} \right], (1 - R)r\varepsilon_1 - \frac{E}{6} \right) \right. \\
 &\quad \times f_4 \left(r_1 v + r_2 v_2 + r_3 \sqrt{\frac{2}{\mu_{34}} \left(R \varepsilon_1 - \frac{E}{6} \right)} T_\omega \left[\frac{v - v_2}{|v - v_2|} \right], (1 - R)(1 - r)\varepsilon_1 - \frac{E}{6} \right) \\
 &\quad \left. - f_1(v, I) f_2(v_2, I_2) \right] B_1^{\text{react}}(v, v_2, I, I_2, R, r, \omega) (m_1 m_2)^{1-N} |v - v_2|^{2-N} \frac{(1 - R)}{\varphi_1(I)} dv_2 dI_2 dr dR d\omega, \\
 Q_2^{\text{react}}(v, I) &= \int_{\Omega_2} \int_{\omega \in \mathcal{S}^{N-1}} H_2 \left[\left(\frac{m_1 m_2}{m_3 m_4} \right)^N f_3 \left(r_1 v_1 + r_2 v - r_4 \sqrt{\frac{2}{\mu_{34}} \left(R \varepsilon_2 - \frac{E}{6} \right)} T_\omega \left[\frac{v_1 - v}{|v_1 - v|} \right], (1 - R)r\varepsilon_2 - \frac{E}{6} \right) \right. \\
 &\quad \times f_4 \left(r_1 v_1 + r_2 v + r_3 \sqrt{\frac{2}{\mu_{34}} \left(R \varepsilon_2 - \frac{E}{6} \right)} T_\omega \left[\frac{v_1 - v}{|v_1 - v|} \right], (1 - R)(1 - r)\varepsilon_2 - \frac{E}{6} \right) \\
 &\quad \left. - f_1(v_1, I_1) f_2(v, I) \right] B_2^{\text{react}}(v_1, v, I_1, I, R, r, \omega) (m_1 m_2)^{1-N} |v_1 - v|^{2-N} \frac{(1 - R)}{\varphi_2(I)} dv_1 dI_1 dr dR d\omega, \\
 Q_3^{\text{react}}(v, I) &= \int_{\Omega_3} \int_{\omega \in \mathcal{S}^{N-1}} H_3 \left[\left(\frac{m_3 m_4}{m_1 m_2} \right)^N f_1 \left(r_3 v + r_4 v_4 - r_2 \sqrt{\frac{2}{\mu_{12}} \left(R' \varepsilon_3 + \frac{E}{6} \right)} T_\omega \left[\frac{v - v_4}{|v - v_4|} \right], (1 - R')r'\varepsilon_3 + \frac{E}{6} \right) \right. \\
 &\quad \times f_2 \left(r_3 v + r_4 v_4 + r_1 \sqrt{\frac{2}{\mu_{12}} \left(R' \varepsilon_3 + \frac{E}{6} \right)} T_\omega \left[\frac{v - v_4}{|v - v_4|} \right], (1 - R')(1 - r')\varepsilon_3 + \frac{E}{6} \right) \\
 &\quad \left. - f_3(v, I) f_4(v_4, I_4) \right] B_3^{\text{react}}(v, v_4, I, I_4, R', r', \omega) (m_3 m_4)^{1-N} |v - v_4|^{2-N} \frac{(1 - R')}{\varphi_3(I)} dv_4 dI_4 dr' dR' d\omega, \\
 Q_4^{\text{react}}(v, I) &= \int_{\Omega_4} \int_{\omega \in \mathcal{S}^{N-1}} H_4 \left[\left(\frac{m_3 m_4}{m_1 m_2} \right)^N f_1 \left(r_3 v_3 + r_4 v - r_2 \sqrt{\frac{2}{\mu_{12}} \left(R' \varepsilon_4 + \frac{E}{6} \right)} T_\omega \left[\frac{v_3 - v}{|v_3 - v|} \right], (1 - R')r'\varepsilon_4 + \frac{E}{6} \right) \right. \\
 &\quad \times f_2 \left(r_3 v_3 + r_4 v + r_1 \sqrt{\frac{2}{\mu_{12}} \left(R' \varepsilon_4 + \frac{E}{6} \right)} T_\omega \left[\frac{v_3 - v}{|v_3 - v|} \right], (1 - R')(1 - r')\varepsilon_4 + \frac{E}{6} \right) \\
 &\quad \left. - f_3(v_3, I_3) f_4(v, I) \right] B_4^{\text{react}}(v_3, v, I_3, I, R', r', \omega) (m_3 m_4)^{1-N} |v_3 - v|^{2-N} \frac{(1 - R')}{\varphi_4(I)} dv_3 dI_3 dr' dR' d\omega,
 \end{aligned}$$

where

$$\begin{aligned}
 \Omega_1 &= \{v_2 \in \mathbb{R}^N; I_2 \geq 0; r, R \in [0, 1]\}, \\
 \Omega_2 &= \{v_1 \in \mathbb{R}^N; I_1 \geq 0; r, R \in [0, 1]\}, \\
 \Omega_3 &= \{v_4 \in \mathbb{R}^N; I_4 \geq 0; r', R' \in [0, 1]\}, \\
 \Omega_4 &= \{v_3 \in \mathbb{R}^N; I_3 \geq 0; r', R' \in [0, 1]\}.
 \end{aligned}$$

As in the previous section, we now write down the weak form of the kernel. The following proposition holds:

Lemma 5. Let $\psi_i : \mathbb{R}^N \times [0, +\infty) \rightarrow \mathbb{R}$ be a function such that for all $i = 1, \dots, 4$, the formula

$$\int_{v \in \mathbb{R}^N} \int_{I \geq 0} Q_i^{\text{react}}(v, I) \psi_i(v, I) \varphi_i(I) dI dv$$

makes sense.

Then, if

$$\begin{aligned}
 B_1^{\text{react}}(v_1, v_2, I_1, I_2, R, r, \omega) &= B_2^{\text{react}}(v_1, v_2, I_1, I_2, R, r, \omega) = B_3^{\text{react}}(v_3, v_4, I_3, I_4, R', r', \omega) \\
 &= B_4^{\text{react}}(v_3, v_4, I_3, I_4, R', r', \omega),
 \end{aligned} \tag{43}$$

where the different variables have the same meaning as in formulas (31)–(36), then

$$\begin{aligned}
& \sum_{i=1}^4 \int_{v \in \mathbb{R}^N} \int_{I \geq 0} Q_i^{\text{react}}(v, I) \psi_i(v, I) \varphi_i(I) \, dI \, dv \\
&= - \int_F \int_{\omega \in \mathcal{S}^{N-1}} [m_3^{-N} f_3(v_3, I_3) m_4^{-N} f_4(v_4, I_4) - m_1^{-N} f_1(v_1, I_1) m_2^{-N} f_2(v_2, I_2)] \\
&\quad \times [\psi_3(v_3, I_3) + \psi_4(v_4, I_4) - \psi_1(v_1, I_1) - \psi_2(v_2, I_2)] \\
&\quad \times B_1^{\text{react}}(v_1, v_2, I_1, I_2, R, r, \omega) m_1 m_2 (1-R) |v_1 - v_2|^{2-N} \, dv_1 \, dv_2 \, dI_1 \, dI_2 \, dr \, dR \, d\omega.
\end{aligned} \tag{44}$$

Proof. Let us consider first

$$\sum_{i=1}^2 \int_{v \in \mathbb{R}^N} \int_{I \geq 0} Q_i^{\text{react}}(v, I) \psi_i(v, I) \varphi_i(I) \, dI \, dv.$$

Since $B_1^{\text{react}}(v_1, v_2, I_1, I_2, R, r, \omega) = B_2^{\text{react}}(v_1, v_2, I_1, I_2, R, r, \omega)$, this is equal to

$$\begin{aligned}
& \int_F \int_{\omega \in \mathcal{S}^{N-1}} \left[\left(\frac{m_1 m_2}{m_3 m_4} \right)^N f_3 \left(r_1 v_1 + r_2 v_2 - r_4 \sqrt{\frac{2}{\mu_{34}} \left(R\varepsilon - \frac{E}{6} \right)} T_\omega \left[\frac{v_1 - v_2}{|v_1 - v_2|} \right], (1-R)r\varepsilon - \frac{E}{6} \right) \right. \\
&\quad \times f_4 \left(r_1 v_1 + r_2 v_2 + r_3 \sqrt{\frac{2}{\mu_{34}} \left(R\varepsilon - \frac{E}{6} \right)} T_\omega \left[\frac{v_1 - v_2}{|v_1 - v_2|} \right], (1-R)(1-r)\varepsilon - \frac{E}{6} \right) - f_1(v_1, I_1) f_2(v_2, I_2) \Big] \\
&\quad \times [\psi_1(v_1, I_1) + \psi_2(v_2, I_2)] B_1^{\text{react}}(v_1, v_2, I_1, I_2, R, r, \omega) (m_1 m_2)^{1-N} (1-R) |v_1 - v_2|^{2-N} \, dv_1 \, dv_2 \, dI_1 \, dI_2 \, dr \, dR \, d\omega.
\end{aligned}$$

Since $B_3^{\text{react}}(v_3, v_4, I_3, I_4, R', r', \omega) = B_4^{\text{react}}(v_3, v_4, I_3, I_4, R', r', \omega)$, a similar formulation also holds for the two other terms in the left-hand side of Eq. (44):

$$\begin{aligned}
& \sum_{i=3}^4 \int_{v \in \mathbb{R}^N} \int_{I \geq 0} Q_i^{\text{react}}(v, I) \psi_i(v, I) \varphi_i(I) \, dI \, dv \\
&= \int_G \int_{\omega \in \mathcal{S}^{N-1}} \left[\left(\frac{m_3 m_4}{m_1 m_2} \right)^N f_1 \left(r_3 v_3 + r_4 v_4 - r_2 \sqrt{\frac{2}{\mu_{12}} \left(R'\varepsilon_4 + \frac{E}{6} \right)} T_\omega \left[\frac{v_3 - v_4}{|v_3 - v_4|} \right], (1-R')r'\varepsilon_4 + \frac{E}{6} \right) \right. \\
&\quad \times f_2 \left(r_3 v_3 + r_4 v_4 + r_1 \sqrt{\frac{2}{\mu_{12}} \left(R'\varepsilon_4 + \frac{E}{6} \right)} T_\omega \left[\frac{v_3 - v_4}{|v_3 - v_4|} \right], (1-R')(1-r')\varepsilon_4 + \frac{E}{6} \right) - f_3(v_3, I_3) f_4(v_4, I_4) \Big] \\
&\quad \times [\psi_3(v_3, I_3) + \psi_4(v_4, I_4)] B_3^{\text{react}}(v_3, v_4, I_3, I_4, R', r', \omega) (m_3 m_4)^{1-N} |v_3 - v_4|^{2-N} (1-R') \\
&\quad \times \, dv_3 \, dv_4 \, dI_3 \, dI_4 \, dr' \, dR' \, d\omega.
\end{aligned}$$

If in the last formula, we use the change of variables defined by (31)–(36) and (37)–(42), then thanks to the symmetry

$$B_1^{\text{react}}(v_1, v_2, I_1, I_2, R, r, \omega) = B_3^{\text{react}}(v_3, v_4, I_3, I_4, R', r', \omega)$$

and Lemma 4, we obtain:

$$\begin{aligned}
& \sum_{i=3}^4 \int_{v \in \mathbb{R}^N} \int_{I \geq 0} Q_i^{\text{react}}(v, I) \psi_i(v, I) \varphi_i(I) \, dI \, dv \\
&= \int_F \int_{\omega \in \mathcal{S}^{N-1}} \left[\left(\frac{m_3 m_4}{m_1 m_2} \right)^N f_1(v_1, I_1) f_2(v_2, I_2) - f_3(v_3, I_3) f_4(v_4, I_4) \right] [\psi_3(v_3, I_3) + \psi_4(v_4, I_4)] \\
&\quad \times B_1^{\text{react}}(v_1, v_2, I_1, I_2, R, r, \omega) (m_3 m_4)^{-N} (m_1 m_2) |v_1 - v_2|^{2-N} (1-R) \, dv_1 \, dv_2 \, dI_1 \, dI_2 \, dr \, dR \, d\omega.
\end{aligned}$$

This concludes the proof of the lemma. \square

If we choose the test functions $\psi_i = 1$, $\psi_i = m_i$ and $\psi_i = m_i v_{(k)}$ in the weak form of the reactive kernels, we obtain the conservation of total number of molecules, total mass and total momentum:

$$\sum_{i=1}^4 \int_{v \in \mathbb{R}^N} \int_{I \geq 0} Q_i^{\text{react}}(v, I) \begin{pmatrix} 1 \\ m_i \\ m_i v_{(k)} \end{pmatrix} \varphi_i(I) \, dI \, dv = 0. \tag{45}$$

Note that the total energy is not conserved when the reactive collisions are present.

4. The hydrodynamical limit

4.1. The mechanical and chemical equilibria

In this subsection, we write down the H-theorems corresponding to the kernels defined earlier.

We begin with the nonreactive kernels. We shall denote by q_i the Laplace transform of φ_i (as a function of $1/T$), that is

$$q_i(T) = \int_0^{+\infty} \varphi_i(I) e^{-I/T} \, dI.$$

Proposition 1. *We suppose that the cross sections B_i ($i = 1, \dots, 4$) and B_{ij} ($i \neq j$) are strictly positive a.e., as well as the functions ϕ_i ($i = 1, \dots, 4$).*

First part of the H-theorem: For all $f_i \equiv f_i(v, I) \geq 0$ ($i = 1, \dots, 4$) such that the following quantities are defined, one has

$$\begin{aligned} & \sum_{i=1}^4 \int_{v \in \mathbb{R}^N} \int_0^{+\infty} Q_i^m(f_i, f_i)(v, I) \log\left(\frac{f_i(v, I)}{m_i^N}\right) \varphi_i(I) \, dv \, dI \\ & + \sum_{i=1}^4 \sum_{j \neq i} \int_{v \in \mathbb{R}^N} \int_0^{+\infty} Q_{Sij}^b(f_i, f_j)(v, I) \log\left(\frac{f_i(v, I)}{m_i^N}\right) \varphi_i(I) \, dv \, dI \leq 0. \end{aligned}$$

Second part of the H-theorem: Moreover, the three following properties are equivalent

- For all $i = 1, \dots, 4$, $j \neq i$, $v \in \mathbb{R}^N$, $I > 0$,

$$Q_i^m(f_i, f_i)(v, I) = 0, \quad Q_{Sij}^b(f_i, f_j)(v, I) = 0;$$

$$\begin{aligned} & \sum_{i=1}^4 \int_{v \in \mathbb{R}^N} \int_0^{+\infty} Q_i^m(f_i, f_i)(v, I) \log\left(\frac{f_i(v, I)}{m_i^N}\right) \varphi_i(I) \, dv \, dI \\ & + \sum_{i=1}^4 \sum_{j \neq i} \int_{v \in \mathbb{R}^N} \int_0^{+\infty} Q_{Sij}^b(f_i, f_j)(v, I) \log\left(\frac{f_i(v, I)}{m_i^N}\right) \varphi_i(I) \, dv \, dI = 0; \end{aligned}$$

- There exists $n_i \geq 0$ ($i = 1, \dots, 4$), $u \in \mathbb{R}^N$ and $T > 0$ such that

$$f_i(v, I) = \frac{n_i}{q_i(T)} \left(\frac{m_i}{2\pi T}\right)^{N/2} e^{-\frac{1}{T}(\frac{m_i}{2}|v-u|^2 + I)}. \tag{46}$$

Proof. We begin with the first part of the H-theorem. We use Lemmas 2 and 3 for $\psi_i(v, I) = \log\left(\frac{f_i(v, I)}{m_i^N}\right)$ and observe that

$$\psi_i(v', I') + \psi_j(v'_*, I'_*) - \psi_i(v, I) - \psi_j(v_*, I_*) = \log(f_i(v', I') f_j(v'_*, I'_*)) - \log(f_i(v, I) f_j(v_*, I_*)),$$

so that

$$(f_i(v', I') f_j(v'_*, I'_*) - f_i(v, I) f_j(v_*, I_*)) (\psi_i(v', I') + \psi_j(v'_*, I'_*) - \psi_i(v, I) - \psi_j(v_*, I_*)) \geq 0.$$

We now turn to the second part of the H-theorem.

It is easy and classical to show that the first property implies the second one, and that the third one implies the first one. Suppose now that the second property holds. Since the term corresponding to the collisions between molecules of the same specie (and in fact each part of this term corresponding to a given specie) is equal to 0, we know (cf. [6]) that there exists $n_i \geq 0$, $u_i \in \mathbb{R}^N$ and $T_i > 0$ ($i = 1, \dots, 4$) such that

$$f_i(v, I) = \frac{n_i}{q_i(T_i)} \left(\frac{m_i}{2\pi T_i} \right)^{N/2} e^{-\frac{1}{T_i} \left(\frac{m_i}{2} |v - u_i|^2 + I \right)}. \quad (47)$$

Then, it remains to show that $u_i = u_j$ and $T_i = T_j$ for all $i \neq j$.

Using the terms corresponding to the collisions between the molecules of species i and j ($i \neq j$), we see that (still when $i \neq j$):

$$f_i(v', I') f_j(v'_*, I'_*) = f_i(v, I) f_j(v_*, I_*), \quad (48)$$

with v' , v'_* , I' and I'_* given by (5)–(12).

We plug (47) in formula (48). We get (for a.e. v, v_*, I, I_*, r, R)

$$\begin{aligned} & \frac{1}{T_i} \left[\frac{m_i}{2} \left| \frac{m_i v + m_j v_*}{m_i + m_j} + \frac{m_j}{m_i + m_j} \sqrt{\frac{2R\varepsilon}{\mu_{ij}}} T_\omega \left[\frac{v - v_*}{|v - v_*|} \right] - u_i \right|^2 + r(1 - R)\varepsilon \right] \\ & + \frac{1}{T_j} \left[\frac{m_j}{2} \left| \frac{m_i v + m_j v_*}{m_i + m_j} - \frac{m_i}{m_i + m_j} \sqrt{\frac{2R\varepsilon}{\mu_{ij}}} T_\omega \left[\frac{v - v_*}{|v - v_*|} \right] - u_j \right|^2 + (1 - r)(1 - R)\varepsilon \right] \\ & = \frac{1}{T_i} \left[\frac{m_i}{2} |v - u_i|^2 + I \right] + \frac{1}{T_j} \left[\frac{m_j}{2} |v_* - u_j|^2 + I_* \right]. \end{aligned} \quad (49)$$

We consider in this identity the term of degree 1 in r , and get

$$\frac{1}{T_i} - \frac{1}{T_j} = 0,$$

so that $T_i = T_j$.

Using this property and taking the term of (49) of lowest degree in \sqrt{R} , we get

$$\frac{1}{2} \frac{|m_i v + m_j v_*|^2}{m_i + m_j} - \frac{(m_i v + m_j v_*)}{m_i + m_j} \cdot (m_i u_i + m_j u_j) + \frac{\mu_{ij}}{2} |v - v_*|^2 = \frac{1}{2} m_i v^2 + \frac{1}{2} m_j v_*^2 - m_i u_i \cdot v - m_j u_j \cdot v_*.$$

Using the term in v , we get

$$-\frac{m_i u_i + m_j u_j}{m_i + m_j} m_i = -m_i u_i,$$

that is $u_i = u_j$. \square

We now turn to the question of chemical equilibrium (assuming that mechanical equilibrium is reached).

Proposition 2. We suppose that the cross sections B_i^{react} ($i = 1, \dots, 4$) are strictly positive a.e., as well as the functions ϕ_i ($i = 1, \dots, 4$).

First part of the H-theorem: For all $f_i \equiv f_i(v, I) \geq 0$ ($i = 1, \dots, 4$) such that the following quantities are defined, one has

$$\sum_{i=1}^4 \int_{v \in \mathbb{R}^N} \int_0^{+\infty} Q_i^{\text{react}}(v, I) \log \left(\frac{f_i(v, I)}{m_i^N} \right) \phi_i(I) \, dv \, dI \leq 0.$$

Second part of the H-theorem: Moreover, let f_i be defined by (46) (that is, assume that the mechanical equilibrium is reached). Then the three following properties are equivalent

- For all $i = 1, \dots, 4$, $v \in \mathbb{R}^N$, $I > 0$,

$$Q_i^{\text{react}}(v, I) = 0;$$

- $\sum_{i=1}^4 \int_{v \in \mathbb{R}^N} \int_0^{+\infty} Q_i^{\text{react}}(v, I) \log\left(\frac{f_i(v, I)}{m_i^N}\right) \varphi_i(I) \, dv \, dI = 0;$
- The following mass action law holds:

$$\frac{n_1 n_2}{n_3 n_4} = \left(\frac{m_3 m_4}{m_1 m_2}\right)^{-N/2} e^{E/T} \frac{q_1(T) q_2(T)}{q_3(T) q_4(T)}.$$

Proof. The first part of the H-theorem is a consequence of Lemma 5, when we take $\psi_i(v, I) = \log\left(\frac{f_i(v, I)}{m_i^N}\right)$. This is due to the identity:

$$\begin{aligned} & (m_3^{-N} f_3(v_3, I_3) m_4^{-N} f_4(v_4, I_4) - m_1^{-N} f_1(v_1, I_1) m_2^{-N} f_2(v_2, I_2)) \\ & \quad \times (\psi_3(v_3, I_3) + \psi_4(v_4, I_4) - \psi_1(v_1, I_1) - \psi_2(v_2, I_2)) \\ & = (m_3^{-N} f_3(v_3, I_3) m_4^{-N} f_4(v_4, I_4) - m_1^{-N} f_1(v_1, I_1) m_2^{-N} f_2(v_2, I_2)) \\ & \quad \times (\log(m_3^{-N} f_3(v_3, I_3) m_4^{-N} f_4(v_4, I_4)) - \log(m_1^{-N} f_1(v_1, I_1) m_2^{-N} f_2(v_2, I_2))) \geq 0. \end{aligned}$$

The (nonobvious implication) of the second part of the H-theorem is obtained by plugging Eq. (46) in the identity

$$m_3^{-N} f_3(v_3, I_3) m_4^{-N} f_4(v_4, I_4) = m_1^{-N} f_1(v_1, I_1) m_2^{-N} f_2(v_2, I_2). \quad \square$$

4.2. Reactive Euler equations

We introduce at this level the Hilbert expansion related to the Boltzmann system:

$$\frac{\partial f_i^\eta}{\partial t} + v \cdot \nabla_x f_i^\eta = \frac{1}{\eta} Q_i^m(f_i^\eta, f_i^\eta) + \frac{1}{\eta} \left(\sum_{j \neq i} Q_{Sij}^b(f_i^\eta, f_j^\eta) \right) + Q_i^{\text{react}}. \tag{50}$$

That is (keeping in mind that η will tend to 0), we consider a situation in which there are many nonreactive collisions (with respect to macroscopic scales) but not so many reactive collisions. As a consequence, $f_i^\eta(v, I)$ converges (at the formal level) towards the mechanical equilibrium $f_i(v, I)$ described by formula (46). That is, we have

$$f_i(v, I) = \frac{n_i}{q_i(T)} \left(\frac{m_i}{2\pi T}\right)^{N/2} e^{-\frac{1}{T}(\frac{m_i}{2}|v-u|^2 + I)}. \tag{51}$$

Note that the number of molecules of the i -th specie, their momentum and their total (kinetic + internal) energy are given by

$$\int_{\mathbb{R}^N} \int_0^{+\infty} f_i(v, I) \begin{pmatrix} 1 \\ m_i v_{(k)} \\ m_i \frac{|v|^2}{2} + I \end{pmatrix} \varphi_i(I) \, dv \, dI = \begin{pmatrix} n_i \\ m_i n_i u_{(k)} \\ m_i n_i \frac{|u|^2}{2} + \frac{N}{2} n_i T + n_i \frac{\eta_i(T)}{q_i(T)} \end{pmatrix}, \tag{52}$$

where the index (k) indicates the k -th component and

$$\eta_i(T) = \int_{I \geq 0} I \varphi_i(I) e^{-I/T} \, dI.$$

The reactive Euler equations are obtained by integrating (and partly by summing over $i = 1, \dots, 4$) the Hilbert expansion (50) against the quantities that are conserved in nonreactive collisions (number of molecules of the i -th specie, total momentum and total energy) and by letting η go to 0.

4.2.1. Conservation of the number of molecules of the i -th specie

As announced, we multiply Eq. (50) by $\varphi_i(I)$, and then we integrate with respect to v and I in $\mathbb{R}^N \times \mathbb{R}_+$. We obtain thanks to properties (22) and (27):

$$\frac{\partial}{\partial t} \int_{\mathbb{R}^N} \int_0^{+\infty} f_i^\eta \varphi_i(I) \, dv \, dI + \sum_{k=1}^N \frac{\partial}{\partial x_k} \int_{\mathbb{R}^N} \int_0^{+\infty} v_{(k)} f_i^\eta \varphi_i(I) \, dv \, dI = \int_{\mathbb{R}^N} \int_0^{+\infty} Q_i^{\text{react}} \varphi_i(I) \, dv \, dI, \tag{53}$$

where the notation $v_{(k)}$ means the k -th component of the vector v .

Letting η go to 0, we get

$$\frac{\partial}{\partial t} n_i + \sum_{k=1}^N \frac{\partial}{\partial x_k} (n_i u_{(k)}) = S_i,$$

where $S_i = (-1)^{r_i} S$, $r_1 = r_2 = 1$, $r_3 = r_4 = 0$, and

$$\begin{aligned} S = & \int_{r', R' \in [0,1]} \int_{v_3, v_4 \in \mathbb{R}^N} \int_{I_3, I_4 \in \mathbb{R}_+} \int_{\omega \in S^{N-1}} \exp\left(-\frac{1}{T} \left[\frac{m_3}{2} |v_3 - u|^2 + I_3 + \frac{m_4}{2} |v_4 - u|^2 + I_4 \right]\right) \\ & \times B_3^{\text{react}}(v_3, v_4, I_3, I_4, R', r', \omega) (m_3 m_4)^{1-N} |v_3 - v_4|^{2-N} (1 - R') \, dv_3 \, dv_4 \, dI_3 \, dI_4 \, dr' \, dR' \, d\omega \\ & \times \left[\frac{\left(\frac{m_3 m_4}{m_1 m_2}\right)^N n_1 n_2 (m_1 m_2)^{N/2} \exp(-E/T)}{(2\pi T)^N q_1(T) q_2(T)} - \frac{n_3 n_4 (m_3 m_4)^{N/2}}{(2\pi T)^N q_3(T) q_4(T)} \right]. \end{aligned}$$

4.2.2. Conservation of momentum

In order to obtain the equation of conservation for the j -th component of the momentum ($j = 1, \dots, N$), we multiply equation (50) by $m_i v_{(j)} \varphi_i(I)$, we integrate with respect to v and I in $\mathbb{R}^N \times \mathbb{R}_+$, and we sum over i ($i = 1, \dots, 4$). We get thanks to properties (22), (28) and (45):

$$\frac{\partial}{\partial t} \sum_{i=1}^4 m_i \int_{\mathbb{R}^N} \int_0^{+\infty} v_{(j)} f_i^\eta \varphi_i(I) \, dv \, dI + \sum_{k=1}^N \frac{\partial}{\partial x_k} \sum_{i=1}^4 m_i \int_{\mathbb{R}^N} \int_0^{+\infty} v_{(j)} v_{(k)} f_i^\eta \varphi_i(I) \, dv \, dI = 0. \quad (54)$$

Letting η go to 0, we obtain

$$\begin{aligned} & \frac{\partial}{\partial t} \sum_{i=1}^4 m_i \int_{\mathbb{R}^N} \int_0^{+\infty} n_i \left(\frac{m_i}{2\pi T}\right)^{N/2} \exp\left[-\left(\frac{m_i}{2} |v - u|^2 + I\right)/T\right] v_{(j)} \frac{\varphi_i(I)}{q_i(T)} \, dv \, dI \\ & + \sum_{k=1}^N \frac{\partial}{\partial x_k} \sum_{i=1}^4 m_i \int_{\mathbb{R}^N} \int_0^{+\infty} n_i \left(\frac{m_i}{2\pi T}\right)^{N/2} \exp\left[-\left(\frac{m_i}{2} |v - u|^2 + I\right)/T\right] v_{(j)} v_{(k)} \frac{\varphi_i(I)}{q_i(T)} \, dv \, dI = 0, \end{aligned}$$

which, after having computed the integral in v and I , leads to

$$\frac{\partial}{\partial t} \left[\sum_{i=1}^4 (m_i n_i) u_{(j)} \right] + \sum_{k=1}^N \frac{\partial}{\partial x_k} \left[\sum_{i=1}^4 (m_i n_i) u_{(j)} u_{(k)} + \sum_{i=1}^4 n_i T \delta_{jk} \right] = 0.$$

4.2.3. Conservation of energy

Finally, the conservation law of energy is obtained by multiplying Eq. (50) by $[m_i |v|^2/2 + I] \varphi_i(I)$, by summing over i ($i = 1, \dots, 4$) and by integrating with respect to v and I in $\mathbb{R}^N \times \mathbb{R}_+$.

We obtain in this way, thanks to properties (22) and (28):

$$\begin{aligned} & \frac{\partial}{\partial t} \sum_{i=1}^4 \int_{\mathbb{R}^N} \int_0^{+\infty} \left[\frac{m_i}{2} |v|^2 + I \right] f_i^\eta \varphi_i(I) \, dv \, dI + \sum_{k=1}^N \frac{\partial}{\partial x_k} \sum_{i=1}^4 \int_{\mathbb{R}^N} \int_0^{+\infty} \left[\frac{m_i}{2} |v|^2 + I \right] v_{(k)} f_i^\eta \varphi_i(I) \, dv \, dI \\ & = \sum_{i=1}^4 \left(\int_{\mathbb{R}^N} \int_0^{+\infty} \left[\frac{m_i}{2} |v|^2 + I \right] Q_i^{\text{react}} \right) \varphi_i(I) \, dv \, dI. \end{aligned}$$

Letting η tend to 0, we get

$$\begin{aligned} & \frac{\partial}{\partial t} \left(\frac{1}{2} \sum_{i=1}^4 (m_i n_i) |u|^2 + \frac{1}{2} \sum_{i=1}^4 n_i \left[NT + 2 \frac{\eta_i(T)}{q_i(T)} \right] \right) \\ & + \sum_{k=1}^N \frac{\partial}{\partial x_k} \left(\frac{1}{2} \sum_{i=1}^4 (m_i n_i) |u|^2 u_{(k)} + \frac{1}{2} \sum_{i=1}^4 n_i \left[(N+1)T + 2 \frac{\eta_i(T)}{q_i(T)} \right] u_{(k)} \right) = -ES. \end{aligned}$$

4.2.4. Entropy inequality

We now multiply Eq. (50) by $\log(f_i/m_i^N)\varphi_i(I)$, we sum over i ($i = 1, \dots, 4$) and we integrate with respect to v and I in $\mathbb{R}^N \times \mathbb{R}_+$.

We get thanks to the first parts of Propositions 1 and 2 the following entropy inequality:

$$\frac{\partial}{\partial t} \sum_{i=1}^4 \int_{\mathbb{R}^N} \int_0^{+\infty} f_i^\eta \left[\log\left(\frac{f_i^\eta}{m_i^N}\right) - 1 \right] \varphi_i(I) \, dv \, dI + \sum_{k=1}^N \frac{\partial}{\partial x_k} \sum_{i=1}^4 \int_{\mathbb{R}^N} \int_0^{+\infty} f_i^\eta \left[\log\left(\frac{f_i^\eta}{m_i^N}\right) - 1 \right] v_{(k)} \varphi_i(I) \, dv \, dI \leq 0.$$

Letting η tend to 0, we get the macroscopic entropy inequality:

$$\begin{aligned} & \frac{\partial}{\partial t} \left(\sum_{i=1}^4 n_i \left[\log\left(\frac{n_i}{q_i(T)} \left(\frac{1}{2\pi T m_i}\right)^{N/2}\right) - \left(1 + \frac{N}{2}\right) - \frac{1}{T} \frac{\eta_i(T)}{q_i(T)} \right] \right) \\ & + \sum_{k=1}^N \frac{\partial}{\partial x_k} \left(\sum_{i=1}^4 n_i \left[\log\left(\frac{n_i}{q_i(T)} \left(\frac{1}{2\pi T m_i}\right)^{N/2}\right) - \left(1 + \frac{N}{2}\right) - \frac{1}{T} \frac{\eta_i(T)}{q_i(T)} \right] u_{(k)} \right) \leq 0. \end{aligned} \tag{55}$$

4.3. Recapitulation and comments

The system (of $N + 5$ equations) obtained in the previous subsection is nothing else than the Euler system of polytropic, perfect and reactive gases. We rewrite it here as a whole (without repeating the entropy relation (55)):

$$\begin{aligned} & \frac{\partial}{\partial t} n_i + \sum_{k=1}^N \frac{\partial}{\partial x_k} (n_i u_{(k)}) = S_i, \\ & \frac{\partial}{\partial t} \left[\sum_{i=1}^4 (m_i n_i) u_{(j)} \right] + \sum_{k=1}^N \frac{\partial}{\partial x_k} \left[\sum_{i=1}^4 (m_i n_i) u_{(j)} u_{(k)} + \sum_{i=1}^4 n_i T \delta_{jk} \right] = 0, \\ & \frac{\partial}{\partial t} \left(\frac{1}{2} \sum_{i=1}^4 (m_i n_i) |u|^2 + \frac{1}{2} \sum_{i=1}^4 n_i \left[NT + 2 \frac{\eta_i(T)}{q_i(T)} \right] \right) \\ & + \sum_{k=1}^N \frac{\partial}{\partial x_k} \left(\frac{1}{2} \sum_{i=1}^4 (m_i n_i) |u|^2 u_{(k)} + \frac{1}{2} \sum_{i=1}^4 n_i \left[(N + 2)T + 2 \frac{\eta_i(T)}{q_i(T)} \right] u_{(k)} \right) = -ES. \end{aligned}$$

According to the equation of conservation of energy, the (internal) energy law of the mixture of gases considered here is

$$e(n_1, \dots, n_4, T) = \frac{1}{2} \sum_{i=1}^4 n_i \left[NT + 2 \frac{\eta_i(T)}{q_i(T)} \right].$$

A typical choice of the functions ϕ_i would consist in taking $\phi_i(I) = I^\alpha$ for some $\alpha > 0$. Then, the previous law becomes

$$e(n_1, \dots, n_4, T) = \frac{1}{2} \sum_{i=1}^4 n_i (N + 2(\alpha + 1))T,$$

and $\alpha = 0$ corresponds to the law of diatomic gases.

We now recall the form of the reaction terms: $S_i = (-1)^{r_i} S$, $r_1 = r_2 = 1$, $r_3 = r_4 = 0$, and

$$\begin{aligned} S = & \int_{r', R' \in [0,1]} \int_{v_3, v_4 \in \mathbb{R}^N} \int_{I_3, I_4 \in \mathbb{R}_+} \int_{\omega \in S^{N-1}} \exp\left(-\frac{1}{T} \left[\frac{m_3}{2} |v_3 - u|^2 + I_3 + \frac{m_4}{2} |v_4 - u|^2 + I_4 \right]\right) \\ & \times B_3^{\text{react}}(v_3, v_4, I_3, I_4, R', r', \omega) (m_3 m_4)^{1-N} |v_3 - v_4|^{2-N} (1 - R') \, dv_3 \, dv_4 \, dI_3 \, dI_4 \, dr' \, dR' \, d\omega \\ & \times \left[\left(\frac{m_3 m_4}{m_1 m_2}\right)^N \frac{n_1 n_2 (m_1 m_2)^{N/2} \exp(-E/T)}{(2\pi T)^N q_1(T) q_2(T)} - \frac{n_3 n_4 (m_3 m_4)^{N/2}}{(2\pi T)^N q_3(T) q_4(T)} \right]. \end{aligned}$$

This shows that the temperature dependence of the reaction rate S involves power terms (namely, $(2\pi T)^N q_1(T) q_2(T)$ and $(2\pi T)^N q_3(T) q_4(T)$ when $\phi_i(I) = I^{\alpha_i}$), which do not disappear in the mass action law as soon as $\alpha_3 + \alpha_4 - \alpha_1 - \alpha_2 \neq 0$.

Acknowledgements

This paper has been partially supported by the bilateral “Galileo” project between France and Italy. Support by the European network HYKE, funded by the EC as contract HPRN-CT-2002-00282, is also acknowledged. Finally, the authors wish to thank Giampiero Spiga for fruitful discussions in the preparation of this article.

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