An H-theorem for chemically reacting gases

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Abstract The trend to equilibrium of a quaternary mixture undergoing a reversible reaction of bimolecular type is studied in a quite rigorous mathematical picture within the framework of Boltzmann equation extended to chemically reacting gases. A characterization of the reactive summational collision invariants, equilibrium Maxwellian distributions and entropy inequality allow to prove two main results under the assumption of uniformly boundedness and equicontinuity of the distribution functions. The first establishes the tendency of the reacting mixture to evolve to an equilibrium state as time becomes large. The other states that the solution of the Boltzmann equation for the chemically reacting mixture of gases converges in strong L^1-sense to its equilibrium solution.

1 The Model Equations

In this section, we describe a model for a mixture of four species undergoing elastic and reactive (binary) collisions of type

$$A_1+A_2 \rightleftharpoons A_3+A_4.$$

For $\alpha \in \{1,2,3,4\}$, we set m_α, c_α and $f_\alpha(x, c_\alpha, t)$ the mass, velocity, and distribution function of the α species respectively.

To describe this system, we consider the Boltzmann-like equation

$$\frac{\partial f_\alpha}{\partial t} + \sum_i c_i^\alpha \frac{\partial f_\alpha}{\partial x_i} = \sum_{\beta=1}^{4} \mathscr{Q}_{\alpha\beta}^E + \mathscr{Q}_\alpha^R. \tag{1}$$

where $\mathcal{Q}^E_{\alpha\beta}$ and $\mathcal{Q}^R_\alpha$ are the production terms with respect to Elastic and Reactive collisions. These terms are given by:

$$\mathcal{Q}^E_{\alpha\beta} = \int \left(f'_\alpha f'_\beta - f_\alpha f_\beta \right) g_{\beta\alpha}\sigma_{\beta\alpha} d\Omega_{\beta\alpha} d\mathbf{c}_\beta. \tag{2}$$

where $g_{\beta\alpha} = |c_\beta - c_\alpha|$, $d\Omega_{\beta\alpha}$ is an element of solid angle and $\sigma_{\alpha\beta}$ a differential elastic cross section. The models of hard sphere and Maxwell molecules [1] are commonly adopted in literature for $\sigma_{\alpha\beta}$. Moreover,

$$\mathcal{Q}^R_{1(2)} = \int \left[f_3 f_4 \left(\frac{m_{12}}{m_{34}} \right)^3 - f_1 f_2 \right] \sigma^\star_{12} g_{21} d\Omega d\mathbf{c}_{2(1)}. \tag{3}$$

and

$$\mathcal{Q}^R_{3(4)} = \int \left[f_1 f_2 \left(\frac{m_{34}}{m_{12}} \right)^3 - f_3 f_4 \right] \sigma^\star_{34} g_{43} d\Omega' dc_{4(3)}. \tag{4}$$

Here, $m_{\alpha\beta} = \frac{m_\alpha m_\beta}{m_\alpha + m_\beta}$ and the quantities $\sigma^\star_{12}$ and $\sigma^\star_{34}$ are differential reactive cross sections for forward and backward reactions, respectively.

In the expressions (3) and (4) it was considered the micro-reversibility principle which gives a relationship between $\sigma^\star_{12}$ and $\sigma^\star_{34}$, namely,

$$\sigma^\star_{34} = \left(\frac{m_{12}}{m_{34}} \right)^2 \left(\frac{g_{21}}{g_{43}} \right)^2 \sigma^\star_{12}. \tag{5}$$

2 Collisional Invariants

For a reactive collision the conservation laws of mass, linear momentum and total energy read

$$\begin{cases} m_1 + m_2 = m_3 + m_4, \\ m_1 c_1 + m_2 c_2 = m_3 c_3 + m_4 c_4, \\ \varepsilon_1 + \frac{1}{2} m_1 c_1^2 + \varepsilon_2 + \frac{1}{2} m_2 c_2^2 = \varepsilon_3 + \frac{1}{2} m_3 c_3^2 + \varepsilon_4 + \frac{1}{2} m_4 c_4^2. \end{cases} \tag{6}$$

Above, m_α denotes the mass of molecule $\alpha = 1,\dots,4$ whereas (c_1, c_2) are the velocities of the reactants, (c_3, c_4) the velocities of the products of the forward reaction and ε_α is the formation energy of a molecule of constituent α. In a certain sense, these are the only invariants for system (1). Indeed, if we define a summational collisional invariant as a function ψ which obeys to the constraints

$$\psi_\alpha + \psi_\beta = \psi'_\alpha + \psi'_\beta, \qquad \psi_1 + \psi_2 = \psi_3 + \psi_4, \tag{7}$$

where the first constraint refers to elastic collisions whereas the second one to reactive interactions, then we have the following result:

Theorem 0.1. *Let ψ_α be a smooth function of c_i^α, of class C^2. This function is a summational collision invariant if and only if*

$$\psi_\alpha = A_\alpha + B_i m_\alpha c_i^\alpha + C \left(\frac{1}{2} m_\alpha c_\alpha^2 + \varepsilon_\alpha \right), \quad \alpha = 1,\dots,4. \tag{8}$$

where A_α and C are arbitrary scalars with $A_1 + A_2 = A_3 + A_4$, and B_i an arbitrary vector that do not depend on c_i^α.

3 Trend to Equilibrium

3.1 The Equilibrium Solution

The equilibrium solution for the present reacting mixture is characterized, at the molecular level, by the vanishing of the collision terms (3-4) on the *r.h.s.* of the reactive Boltzmann equation (1). Hence, the equilibrium distribution functions $f_\alpha^{(0)}$ are obtained when the equalities

$$\begin{cases} f_\alpha^{(0)} f_\beta^{(0)} = f_\alpha'^{(0)} f_\beta'^{(0)}, \\ \dfrac{f_1^{(0)}}{m_1^3} \dfrac{f_2^{(0)}}{m_2^3} = \dfrac{f_3^{(0)}}{m_3^3} \dfrac{f_4^{(0)}}{m_4^3}. \end{cases} \tag{9}$$

hold almost everywhere in the velocity space.

By noticing that $\ln(f_\alpha(0))$ is a summational collisional invariant , one can use Theorem 0.1 to derive an explicit expression for the equilibrium functions (see [2]). We obtain the well-known Maxwellian

$$f_\alpha^{(0)} = n_\alpha \left(\frac{m_\alpha}{2\pi kT}\right)^{3/2} e^{-\frac{m_\alpha}{2kT}\xi_\alpha^2} \tag{10}$$

with number densities n_α subjected to the mass action law

$$\frac{n_1^{eq} n_2^{eq}}{n_3^{eq} n_4^{eq}} = \left(\frac{m_1 m_2}{m_3 m_4}\right)^{3/2} \exp\left(\frac{E}{k_B T}\right). \tag{11}$$

3.2 An $\mathscr{H}$-Function for System (1)

We now define an $\mathscr{H}$-function for our system.

Definition 0.1. We put

$$\mathscr{H} = \sum_{\alpha=1}^{4} \int f_\alpha \ln\left(\frac{f_\alpha}{m_\alpha^3}\right) dc_\alpha. \tag{12}$$

The following results were proven in [2]:

Theorem 0.2. *For all $t \in [0;+\infty[$, $\frac{d\mathscr{H}}{dt}(t) \le 0$. Furthermore, let $\mathscr{H}_E$ denote the $\mathscr{H}$-function referred to equilibrium Maxwellian distributions $f_\alpha^{(0)}$. Then*

$$\forall t \in [0,+\infty[,\ \mathscr{H} - \mathscr{H}_E \ge 0. \tag{13}$$

3.3 Convergence Results

Finally, we state the following result concerning the convergence of the distribution functions to equilibrium:

Theorem 0.3. *Assuming that $\mathscr{H}$ is a continuously differentiable function, $\mathscr{H} \in \mathscr{C}^1([0;+\infty[)$, and that every f_α is uniformly bounded and equicontinuous in t, then*

$$\lim_{t \to +\infty} \mathscr{H}(t) = \mathscr{H}_E.$$

Under these conditions, f_α *converges in strong* L^1*-sense to* $f_\alpha^{(0)}$.

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