$\mathcal{H}$-Theorem and Trend to Equilibrium of Chemically Reacting Mixture of Gases

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Abstract

The trend to equilibrium of a quaternary mixture of monatomic gases 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 mixture of gases. The $\mathcal{H}$-theorem and entropy inequality allow to prove two main results under the assumption of uniformly boundedness and equicontinuity of the distribution functions. One of the results establishes the tendency of a reacting mixture to evolve to an equilibrium state as time becomes large. The other states that the solution of the Boltzmann equation for chemically reacting mixture of gases converges in strong L^1-sense to its equilibrium solution.

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1 Introduction

A large number of papers in the literature has been devoted to include chemical reaction effects in gas mixtures modeled by Boltzmann equation (BE), after the first attempts done by Prigogine and co-workers [37, 38] and afterwards by Present [36], Ross & Mazur [39], Skizgal & Karplus [42], and Xystris & Dahler [47], among others. These works are mainly directed to perturbation techniques for the solution of the chemical kinetics BE, with emphasis on the estimation of the non-equilibrium effects induced by chemical reactions and calculation of reaction rate, equilibrium constants and other transport quantities.

A different kinetic approach to chemically reactive systems has been addressed in some subsequent papers, concerning mathematical methods and related properties. In particular, existence theory for BE with inelastic collisions has been analyzed in the paper [28], where existence, uniqueness and positivity of mild solutions for initial data close to the vacuum are proven.

Multi-component reactive flows have been investigated in the work [24] and global existence and asymptotic stability results, together with decay estimates, have been obtained for the Cauchy

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problem in all space dimensions as well as for the equilibrium state, for a system of macroscopic equations derived from the kinetic theory.

Theoretical and formal developments for chemically reacting gases can also be found in the paper [40] for a mixture undergoing bimolecular reactions and in the work [27] for a more general reactive flow in which the internal structure of the molecules is also taken into account. In these last two papers, the corresponding chemical collision terms are derived in detail, the macroscopic conservation laws are explicitly deduced and properties regarding equilibrium and stability are discussed. Moreover, a strict Lyapunov functional is shown to exist, exhibiting a monotonous decreasing behavior and attaining its minimum at equilibrium.

Some relevant results have been achieved in paper [34], concerning the mathematical aspects of kinetic equations for the so called simple reacting spheres, proving global existence of renormalized solutions, for initial conditions of finite total mass, energy and entropy.

Mathematical properties related with the reaction process are discussed in paper [26], where two kinetic theories for chemical reactions are compared and existence of solutions is proven assuming that reactive collisions verify the micro-reversibility principle and elastic and reactive scattering kernels satisfy suitable boundedness conditions which are verified in the case of hard potentials with cut-off. It is worth to emphasize that the extension to reactive mixtures of the regularity theory for the nonreactive spatially homogeneous Boltzmann equation for hard potentials with cut-off developed in [1, 2, 4, 5, 31] and latter completed in [32] to prove global existence results for initial data with finite mass and energy still remains an open problem. The same happens for the theory developed for the nonreactive spatially homogeneous Boltzmann equation for soft potentials without cut-off [45] as well as with cut-off [14].

For what concerns polyatomic reactive mixtures, the modeling of transport properties, derivation of transport coefficients and investigation of non-equilibrium effects are dealt with in papers [10, 11, 18, 19] among others.

On the other hand, the so called entropy production methods, well known in literature due to their capability for the computation of bounds for the long time behavior and study of convergence to equilibrium have been used for the homogeneous version of the Boltzmann equation [3, 15, 44] but also for the inhomogeneous equation [16, 17, 46]. These methods have also been used as a fundamental tool within the framework of reacting gases, namely to obtain good a-priori estimates in the study of the long-time behavior [12, 25], develop robust numerical techniques [21, 33], and study multi-component transport properties [20, 22, 23].

However, the study of the trend to equilibrium in kinetic theory of chemically reacting gases has not yet received enough attention for what concerns, in particular, the convergence for large times of the solution of the chemical kinetics BE towards equilibrium.

The aim of the present paper is to complement the above mentioned study, extending to monatomic reactive mixtures previous results in this direction obtained by Carleman [4, 5] and Arkeryd [1, 2] for an inert one-component gas and by Cercignani & Kremer [8, 9] for a relativistic gas.

More in detail, one of the main result of the present paper states a strong L^1-convergence for the solution of the BE towards Maxwellian equilibrium as time becomes large, under the assumption of uniformly boundedness and equicontinuity of the distribution functions for the spatially homogeneous case. An entropy inequality and $\mathcal{H}$-theorem have a central role in the proposed study.

As a final remark, cartesian notation for tensors is used throughout the paper. Greek indices denote the constituents of the mixture while Latin indices denote the cartesian coordinates. The velocity vector of a molecule is denoted by $\boldsymbol{c}_\alpha$ while its components by c_i^α.

2 Reactive Boltzmann Equations

In a simple reversible bimolecular gas reaction characterized by the chemical law $A_1+A_2 \rightleftharpoons A_3+A_4$, only binary encounters between molecules are taken into account. Two types of collisions are then considered, namely the elastic and the reactive or inelastic ones.

It is well known that, for an elastic collision of two molecules, say α and β, with pre-collision velocities $(\mathbf{c}_\alpha, \mathbf{c}_\beta)$ and post-collision velocities $(\mathbf{c}'_\alpha, \mathbf{c}'_\beta)$, the mass, linear momentum and kinetic energy are preserved. On the other hand, reactive collisions assure conservation of mass and linear momentum, and conservation of total energy, which reads $\epsilon_1 + m_1 c_1^2/2 + \epsilon_2 + m_2 c_2^2/2 = \epsilon_3 + m_3 c_3^2/2 + \epsilon_4 + m_4 c_4^2/2$, where m_α $(\alpha = 1, \ldots, 4)$ denotes the mass of molecule, $(\boldsymbol{c}_1, \boldsymbol{c}_2)$ and $(\boldsymbol{c}_3, \boldsymbol{c}_4)$ the velocities of the reactants and products of the forward reaction, respectively, and ϵ_α is the formation energy of a molecule of constituent α.

A state of the gaseous mixture in the phase space spanned by the positions $\boldsymbol{x}$ and velocities $\boldsymbol{c}_\alpha$ of the molecules is characterized by the set of one-particle distribution functions $f_\alpha \equiv f(\boldsymbol{x}, \boldsymbol{c}_\alpha, t)$ with $\alpha = 1, \ldots, 4$. In the absence of external forces, the distribution function is assumed to satisfy the following Boltzmann equation

$$\frac{\partial f_\alpha}{\partial t} + c_i^\alpha \frac{\partial f_\alpha}{\partial x_i} = \sum_{\beta=1}^{4} \int \left(f'_\alpha f'_\beta - f_\alpha f_\beta \right) g_{\beta\alpha} \sigma_{\beta\alpha} d\Omega_{\beta\alpha} d\mathbf{c}_\beta + \mathcal{Q}_\alpha^R, \quad \alpha = 1, \ldots, 4, \tag{1}$$

where the first term on the right hand side refers to elastic interactions and the second one to reactive collisions. The symbols $d\Omega_{\beta\alpha}$ and $\sigma_{\alpha\beta}$ are an element of solid angle and a differential elastic cross section, respectively. The models of hard sphere and Maxwell molecules [7] are commonly adopted in literature for $\sigma_{\alpha\beta}$. The term $\mathcal{Q}_\alpha^R$ for the reactants can be expressed by

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

and the one for the products can be obtained from expression (2) by changing the indexes $1, 2$ with $3, 4$, respectively. Moreover, the quantities $\sigma_{12}^\star$ and $\sigma_{34}^\star$ are differential reactive cross sections for forward and backward reactions, respectively, which satisfy the micro-reversibility principle, namely, $m_{34}^2\, g_{43}^2\, \sigma_{34}^\star = m_{12}^2\, g_{21}^2\, \sigma_{12}^\star$. The line-of-centers model [29, 30, 35, 43] and the power-law model [41] for reactive cross sections satisfy this condition and are employed in a rather vast bibliography on reacting gases. Other main aspects regarding the chemical kinetic properties of the considered mixture, omitted here for sake of brevity, can be found in Refs. [29, 30, 43].

3 $\mathcal{H}$ - Theorem

The balance equation for the entropy density of the mixture can be obtained through the multiplication of the Boltzmann equation (1) by $\psi_\alpha = -k \ln(b f_\alpha / m_\alpha^3)$, integration over all values of $\boldsymbol{c}_\alpha$ and summation the resulting equation over all values of α. The parameter b is a suitable constant which converts the argument of the logarithm function into a dimensionless quantity. Hence, it follows

$$\frac{\partial}{\partial t}(\varrho\eta) + \frac{\partial}{\partial x_i}(\boldsymbol{\phi}_i + \varrho\eta v_i) = \Sigma_E + \Sigma_R, \tag{3}$$

where $\varrho\eta$ is the entropy density and $\boldsymbol{\phi}_i$ its flux defined by

$$\varrho\eta = -k \sum_{\alpha=1}^{4} \int f_\alpha \ln\left(\frac{b f_\alpha}{m_\alpha^3} \right) d\boldsymbol{c}_\alpha, \quad \boldsymbol{\phi}_i = -k \sum_{\alpha=1}^{4} \int f_\alpha \xi_i^\alpha \ln\left(\frac{b f_\alpha}{m_\alpha^3} \right) d\boldsymbol{c}_\alpha. \tag{4}$$

Moreover, Σ_E and Σ_R are the entropy production terms due to elastic scattering and chemical reactions, respectively. They are given by

$$\Sigma_E = -\frac{k}{4}\sum_{\alpha=1}^{4}\sum_{\beta=1}^{4}\int f'_\alpha f'_\beta \left(1-\frac{f_\alpha f_\beta}{f'_\alpha f'_\beta}\right)\ln\left(\frac{f_\alpha f_\beta}{f'_\alpha f'_\beta}\right) g_{\beta\alpha}\sigma_{\beta\alpha}d\Omega_{\beta\alpha}d\boldsymbol{c}_\beta d\boldsymbol{c}_\alpha, \tag{5}$$

$$\Sigma_R = -k\left(\frac{m_{12}}{m_{34}}\right)^3\int f_3 f_4\left[1-\left(\frac{m_{34}}{m_{12}}\right)^3\frac{f_1 f_2}{f_3 f_4}\right]\ln\left[\left(\frac{m_{34}}{m_{12}}\right)^3\frac{f_1 f_2}{f_3 f_4}\right]\sigma^\star_{12} g_{21} d\Omega d\boldsymbol{c}_1 d\boldsymbol{c}_2. \tag{6}$$

From Eqs. (5-6), one can infer that Σ_E and Σ_R are sums of nonnegative contributions, since one has $(1-x)\ln x \leq 0$, for any positive x, so that the entropy production of the whole mixture is a positive semi-definite quantity. Observe that the positivity of the entropy production of the whole mixture has been obtained as a consequence of the fact that each elastic and reactive collision yields positive entropy production, since all contributions to the sums in Eqs. (5-6) have the same sign. Accordingly, all collisions contribute to increase the entropy, and the use of this property will be important in the sequel.

Let assume that the one-particle distribution function is uniform in the space, and introduce a generalized $\mathcal{H}$-function which is proportional to the entropy of the system defined in Eq. $(4)_1$,

$$\mathcal{H} = -\frac{\varrho\eta}{k} = \sum_{\alpha=1}^{4}\int f_\alpha \ln\left(\frac{b f_\alpha}{m_\alpha^3}\right) d\boldsymbol{c}_\alpha. \tag{7}$$

From the above results about the entropy of the mixture, one obtains

$$\begin{aligned}\frac{d\mathcal{H}}{dt} \quad = \quad & \frac{1}{4}\sum_{\alpha=1}^{4}\sum_{\beta=1}^{4}\int \left(f'_\alpha f'_\beta - f_\alpha f_\beta\right)\ln\left(\frac{f_\alpha f_\beta}{f'_\alpha f'_\beta}\right) g_{\beta\alpha}\sigma_{\beta\alpha}d\Omega_{\beta\alpha}d\mathbf{c}_\beta d\mathbf{c}_\alpha \\ & + \left(\frac{m_{12}}{m_{34}}\right)^3\int\left(f_3 f_4 - \left(\frac{m_{34}}{m_{12}}\right)^3 f_1 f_2\right)\ln\left[\left(\frac{m_{34}}{m_{12}}\right)^3\frac{f_1 f_2}{f_3 f_4}\right]\sigma^\star_{12} g_{21} d\Omega d\mathbf{c}_1 d\mathbf{c}_2\,,\end{aligned} \tag{8}$$

and

$$\frac{d\mathcal{H}}{dt} = -\frac{1}{k}\frac{d}{dt}(\varrho\eta) \leq 0, \quad \forall t \in [0,+\infty[\,, \tag{9}$$

which assures that the $\mathcal{H}$-function decreases in time. This is a well known result in kinetic theory of chemically reacting gases [27, 40]. It is also well known that the equilibrium solution of the Boltzmann equations (1) defines a minimum of the $\mathcal{H}$- function.

The following result has been proven in paper [27], using different arguments.

Lemma 1. *Let $\mathcal{H}_E$ denote the $\mathcal{H}$-function referred to equilibrium Maxwellian distributions $f_\alpha^{(0)}$. Then*

$$\mathcal{H} - \mathcal{H}_E \geq 0, \quad \forall t \in [0,+\infty[\,. \tag{10}$$

Proof. Substitution of $x = f_\alpha/f_\alpha^{(0)}$ in the well-known convexity inequality $x\ln(x) \geq x-1$ yields

$$f_\alpha\left(\ln(f_\alpha) - \ln(f_\alpha^{(0)})\right) \geq f_\alpha - f_\alpha^{(0)}$$

and after some rather simple calculations one obtains

$$f_\alpha \ln\left(\frac{b f_\alpha}{m_\alpha^3}\right) - f_\alpha^{(0)}\ln\left(\frac{b f_\alpha^{(0)}}{m_\alpha^3}\right) \geq \left(f_\alpha - f_\alpha^{(0)}\right)\left(1+\ln\left(\frac{b f_\alpha^{(0)}}{m_\alpha^3}\right)\right). \tag{11}$$

Integrating inequality (11) over all velocities $\boldsymbol{c}_\alpha$ and summing for all constituents one gets

$$\mathcal{H}-\mathcal{H}_E \geq \sum_{\alpha=1}^{4}\int \left(f_\alpha - f_\alpha^{(0)}\right)\left(1+\ln\left(\frac{b f_\alpha^{(0)}}{m_\alpha^3}\right)\right) d\boldsymbol{c}_\alpha,$$

thanks to the definition (7) of the $\mathcal{H}$-function. Since $\ln\left(b f_\alpha^{(0)}/m_\alpha^3\right)$ is a collision invariant, one has (see e.g. Refs. [13, 27])

$$\mathcal{H}-\mathcal{H}_E \geq \sum_{\alpha=1}^{4}\int \left(f_\alpha - f_\alpha^{(0)}\right)\left[1+A_\alpha+m_\alpha B_i c_i^\alpha + C\left(\frac{1}{2}m_\alpha c_\alpha^2+\epsilon_\alpha\right)\right] d\boldsymbol{c}_\alpha. \tag{12}$$

The right-hand-side of inequality (12) vanishes due to the ansatz that the equilibrium Maxwellians $f_\alpha^{(0)}$ have the same local macroscopic properties as the solution f_α of Eq. (1), that is

$$\int f_\alpha d\boldsymbol{c}_\alpha = \int f_\alpha^{(0)} d\boldsymbol{c}_\alpha, \tag{13}$$

$$\sum_{\alpha=1}^{4}\int m_\alpha c_i^\alpha f_\alpha d\boldsymbol{c}_\alpha = \sum_{\alpha=1}^{4}\int m_\alpha c_i^\alpha f_\alpha^{(0)} d\boldsymbol{c}_\alpha, \tag{14}$$

$$\sum_{\alpha=1}^{4}\int \left(\frac{1}{2}m_\alpha c_\alpha^2+\epsilon_\alpha\right) f_\alpha d\boldsymbol{c}_\alpha = \sum_{\alpha=1}^{4}\int \left(\frac{1}{2}m_\alpha c_\alpha^2+\epsilon_\alpha\right) f_\alpha^{(0)} d\boldsymbol{c}_\alpha. \tag{15}$$

Finally, one gets $\mathcal{H} \geq \mathcal{H}_E$, and the proof is complete. ■

4 Trend to equilibrium

The next result, Theorem 1, shows that the Boltzmann equation (1) describes a reacting mixture which evolves towards an equilibrium state, reached for very large times. The required conditions for the distribution functions f_α expressed in the statement of Theorem 1, namely the uniform boundedness and equicontinuity in t, are rather standard hypothesis when the long-time behavior is analized (see e.g. Refs. [4, 5, 6, 8]).

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

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

Proof: Taking into account the decreasing behavior of $\mathcal{H}$, see inequality (9), and the lower bound of $\mathcal{H}$ stated in Lemma 1, the Lagrange's theorem assures the existence of $t_n \in \,]n, n+1[$, such that

$$\frac{d\mathcal{H}}{dt}(t_n) = \frac{\mathcal{H}(n+1)-\mathcal{H}(n)}{(n+1)-n}\ . \tag{16}$$

Therefore

$$\lim_{n\to\infty} t_n = +\infty \quad \text{and} \quad \lim_{n\to\infty}\frac{d}{dt}\mathcal{H}(t_n) = \ell - \ell = 0,$$

where $\ell = \lim_{t\to\infty}\mathcal{H}(t)$, whose existence results from the boundedness and decreasing behavior of $\mathcal{H}$.

Furthermore, the Ascoli-Arzelás theorem assures the existence of a convergent subsequence of

$$f_n^{(\alpha)} \stackrel{\text{def}}{=} f_\alpha(t_n),$$

which will be still denoted by $f_n^{(\alpha)}$, such that $\lim_{n\to\infty} f_n^{(\alpha)} = f_\alpha^\infty$. Moreover, the convergence is uniform in $\boldsymbol{c}_\alpha$ in any compact set $\mathcal{S} \subset \mathbb{R}^3$.

The proof proceeds by showing that the identities

$$f'^{\infty}_{\alpha}\, f'^{\infty}_{\beta} = f^{\infty}_{\alpha}\, f^{\infty}_{\beta}, \quad \text{for all} \quad \alpha, \beta \in \{1, \ldots, 4\}, \tag{17}$$

$$f^{\infty}_{3}\, f^{\infty}_{4} = \left(\frac{m_{34}}{m_{12}}\right)^3 f^{\infty}_{1}\, f^{\infty}_{2}, \tag{18}$$

hold. Otherwise, one can find a compact set of positive measure in $\mathbb{R}^3$, say $\mathcal{C}$, and constants $N \geq 0$ and $M_{\alpha\beta} \geq 0$ for some $\alpha, \beta \in \{1, \ldots, 4\}$, such that

$$\left| f'^{\infty}_{\alpha}\, f'^{\infty}_{\beta} - f^{\infty}_{\alpha}\, f^{\infty}_{\beta} \right| \geq M_{\alpha\beta}, \quad \forall \boldsymbol{c}_\alpha, \boldsymbol{c}_\beta, \boldsymbol{c}'_\alpha, \boldsymbol{c}'_\beta \in \mathcal{C}.$$

$$\left| f^{\infty}_{3}\, f^{\infty}_{4} - \left(\frac{m_{34}}{m_{12}}\right)^3 f^{\infty}_{1}\, f^{\infty}_{2} \right| \geq N, \quad \forall \boldsymbol{c}_1, \boldsymbol{c}_2, \boldsymbol{c}_3, \boldsymbol{c}_4 \in \mathcal{C},$$

where

$$N > 0 \qquad \text{or} \qquad M_{\alpha\beta} > 0. \tag{19}$$

Due to the uniform convergence of $f_n^{(\alpha)}$ to f_α^∞, for n_0 large enough and $n \geq n_0$ one has

$$\left| f'^{(\alpha)}_{n}\, f'^{(\beta)}_{n} - f^{(\alpha)}_{n}\, f^{(\beta)}_{n} \right| \geq \frac{M_{\alpha\beta}}{2}, \quad \forall \boldsymbol{c}_\alpha, \boldsymbol{c}_\beta, \boldsymbol{c}'_\alpha, \boldsymbol{c}'_\beta \in \mathcal{C}. \tag{20}$$

$$\left| f^{(3)}_{n}\, f^{(4)}_{n} - \left(\frac{m_{34}}{m_{12}}\right)^3 f^{(1)}_{n}\, f^{2)}_{n} \right| \geq \frac{N}{2}, \quad \forall \boldsymbol{c}_1, \boldsymbol{c}_2, \boldsymbol{c}_3, \boldsymbol{c}_4 \in \mathcal{C}. \tag{21}$$

Moreover, since $f^{(\alpha)}$ is bounded, say by a positive constant F_α, one obtains

$$\begin{aligned} \left| \ln\left(\frac{f^{(\alpha)}_{n} f^{(\beta)}_{n}}{f'^{(\alpha)}_{n} f'^{(\beta)}_{n}} \right) \right| &= \left| \ln\left(1 + \frac{f^{(\alpha)}_{n} f^{(\beta)}_{n} - f'^{(\alpha)}_{n} f'^{(\beta)}_{n}}{f'^{(\alpha)}_{n} f'^{(\beta)}_{n}} \right) \right| \\ &\geq \ln\left(1 + \left| \frac{f^{(\alpha)}_{n} f^{(\beta)}_{n} - f'^{(\alpha)}_{n} f'^{(\beta)}_{n}}{f'^{(\alpha)}_{n} f'^{(\beta)}_{n}} \right| \right) \geq \ln\left(1 + \frac{M_{\alpha\beta}}{2F_\alpha^2} \right), \end{aligned} \tag{22}$$

$$\left| \ln\left[\left(\frac{m_{34}}{m_{12}}\right)^3 \frac{f^{(1)}_{n} f^{(2)}_{n}}{f^{(3)}_{n} f^{(4)}_{n}} \right] \right| \geq \ln\left(1 + \frac{N}{2F_3F_4} \right). \tag{23}$$

Now from equations (20-23) it follows

$$\left| f'^{(\alpha)}_{n}\, f'^{(\beta)}_{n} - f^{(\alpha)}_{n}\, f^{(\beta)}_{n} \right| \left| \ln\left(\frac{f^{(\alpha)}_{n} f^{(\beta)}_{n}}{f'^{(\alpha)}_{n} f'^{(\beta)}_{n}} \right) \right| > \frac{M_{\alpha\beta}}{2} \ln\left(1 + \frac{M_{\alpha\beta}}{2F_\alpha^2} \right), \tag{24}$$

$$\left| f^{(3)}_{n}\, f^{(4)}_{n} - \left(\frac{m_{34}}{m_{12}}\right)^3 f^{(1)}_{n}\, f^{2)}_{n} \right| \left| \ln\left[\left(\frac{m_{34}}{m_{12}}\right)^3 \frac{f^{(1)}_{n} f^{(2)}_{n}}{f^{(3)}_{n} f^{(4)}_{n}} \right] \right| > \frac{N}{2} \ln\left(1 + \frac{N}{2F_3F_4} \right). \tag{25}$$

Therefore, for $n \geq n_0$, one obtains

$$-\frac{d}{dt}\mathcal{H}(t_n) > \frac{1}{4}\sum_{\alpha=1}^{4}\sum_{\beta=1}^{4}\frac{M_{\alpha\beta}}{2}\ln\left(1+\frac{M_{\alpha\beta}}{2F_\alpha^2}\right)\int_{\mathcal{C}\times\mathcal{C}} g_{\beta\alpha}\sigma_{\beta\alpha}d\Omega_{\beta\alpha}d\mathbf{c}_\beta d\mathbf{c}_\alpha$$
$$+\frac{N}{2}\ln\left(1+\frac{N}{2F_3F_4}\right)\int_{\mathcal{C}\times\mathcal{C}}\sigma_{12}^\star g_{21}d\Omega d\mathbf{c}_1 d\mathbf{c}_2. \tag{26}$$

In fact, it is enough to multiply inequalities (25) and (24) by $g_{\beta\alpha}\sigma_{\beta\alpha}d\Omega_{\beta\alpha}d\mathbf{c}_\beta d\mathbf{c}_\alpha$ and $\sigma_{12}^\star g_{21}d\Omega d\mathbf{c}_1 d\mathbf{c}_2$, respectively, then integrate over all velocities and, finally, take the sum of the latter resulting inequality together with the former one, previously summed over all constituents α and β.

Now, from the positivity of the measure of the compact set $\mathcal{C}$ and inequality (26), in view of (19), there exists a positive constant, say A, such that

$$-\frac{d}{dt}\mathcal{H}(t_n) > A > 0. \tag{27}$$

This last conclusion is absurd, since $\lim_{n\to\infty}\frac{d}{dt}\mathcal{H}(t_n) = 0$. Therefore Eqs. (17) and (18) hold.

Consequently, the $\mathcal{H}$-function has a critical point for $f_\alpha = f_\alpha^\infty$, as it can be seen from the expression (8) for its time derivative. Finally, the convexity of the $\mathcal{H}$-functional on the manifold defined by the conservation of moments (13-15) implies that this critical point corresponds to the minimum of $\mathcal{H}$, attained for $f_\alpha = f_\alpha^{(0)}$. Therefore $f_\alpha^\infty = f_\alpha^{(0)}$, so that

$$\lim_{n\to\infty} f_n^{(\alpha)} = f_\alpha^{(0)} \qquad \text{and} \qquad \lim_{t\to+\infty}\mathcal{H}(t) = \mathcal{H}_E. \tag{28}$$

This completes the proof of Theorem 1. ■

From the proof of the previous Theorem 1 it results, in particular, that $\lim_{t\to+\infty} f_\alpha(t) = f_\alpha^{(0)}(t)$ and the next Theorem shows that this convergence is strong in the L^1-norm.

Theorem 2. *Under the assumptions of Theorem 1, f_α converges in strong L^1-sense to $f_\alpha^{(0)}$.*

Proof: The idea is to use a rather sophisticated convexity inequality. In fact, it is not difficult to check the existence of a constant $C > 0$ such that

$$x\ln x + 1 - x \geq C|x-1|\, G\big(|x-1|\big), \quad \text{for all } x > 0, \tag{29}$$

where G is the function defined by

$$G\big(|x-1|\big) = \begin{cases} |x-1| & \text{if} \quad 0 \leq |x-1| \leq 1, \\ 1 & \text{if} \quad |x-1| > 1. \end{cases} \tag{30}$$

Now, inserting $x = f_\alpha/f_\alpha^{(0)}$ in inequality (29), one gets

$$f_\alpha\left(\ln(f_\alpha) - \ln(f_\alpha^{(0)})\right) \geq f_\alpha - f_\alpha^{(0)} + C\left|f_\alpha - f_\alpha^{(0)}\right| G\left(\left|\frac{f_\alpha}{f_\alpha^{(0)}} - 1\right|\right),$$

and after some rearrangements, it results

$$f_\alpha\ln\!\left(\frac{bf_\alpha}{m_\alpha^3}\right) - f_\alpha^{(0)}\ln\!\left(\frac{bf_\alpha^{(0)}}{m_\alpha^3}\right) \geq \left(f_\alpha - f_\alpha^{(0)}\right)\left(1+\ln\!\left(\frac{bf_\alpha^{(0)}}{m_\alpha^3}\right)\right) + C\left|f_\alpha - f_\alpha^{(0)}\right| G\left(\left|\frac{f_\alpha}{f_\alpha^{(0)}} - 1\right|\right). \tag{31}$$

From the definition (7) of the $\mathcal{H}$-function one obtains by integrating the inequality (31) over all velocities $\boldsymbol{c}_\alpha$ and summing for all constituents

$$\mathcal{H}(t)-\mathcal{H}_E \geq \sum_{\alpha=1}^{4}\int C\left|f_\alpha - f_\alpha^{(0)}\right| G\left(\left|\frac{f_\alpha}{f_\alpha^{(0)}}-1\right|\right) d\boldsymbol{c}_\alpha.$$

Above it has used the constraints (13-15) and the fact that $\ln(bf_\alpha^{(0)}/m_\alpha^3)$ defines a collisional invariant. Now, by introducing the sets

$$D_\alpha^1 = \left\{\boldsymbol{c}_\alpha \in \mathbb{R}^3 : \left|f_\alpha - f_\alpha^{(0)}\right| \leq f_\alpha^{(0)}\right\} \quad \text{and} \quad D_\alpha^2 = \left\{\boldsymbol{c}_\alpha \in \mathbb{R}^3 : \left|f_\alpha - f_\alpha^{(0)}\right| > f_\alpha^{(0)}\right\}$$

and taking into account the definition (30) of the function G, one obtains

$$\mathcal{H}(t)-\mathcal{H}_E \geq \sum_{\alpha=1}^{4}\int_{D_\alpha^1}\frac{C}{f_\alpha^{(0)}}\left|f_\alpha - f_\alpha^{(0)}\right|^2 d\mathbf{c}_\alpha + \sum_{\alpha=1}^{4}\int_{D_\alpha^2} C\left|f_\alpha - f_\alpha^{(0)}\right| d\mathbf{c}_\alpha \geq 0. \tag{32}$$

Since $\lim_{t\to+\infty}\mathcal{H}(t) = \mathcal{H}_E$, the passage to the limit for $t \to +\infty$ in the inequality (32) gives

$$\lim_{t\to+\infty}\left[\sum_{\alpha=1}^{4}\int_{D_\alpha^1}\frac{C}{f_\alpha^{(0)}}\left|f_\alpha - f_\alpha^{(0)}\right|^2 d\mathbf{c}_\alpha + \sum_{\alpha=1}^{4}\int_{D_\alpha^2} C\left|f_\alpha - f_\alpha^{(0)}\right| d\mathbf{c}_\alpha\right] = 0. \tag{33}$$

This last limit condition can be verified if and only if

$$\lim_{t\to+\infty}\int_{D_\alpha^1}\frac{1}{f_\alpha^{(0)}}\left|f_\alpha - f_\alpha^{(0)}\right|^2 d\mathbf{c}_\alpha = 0 \quad \text{and} \quad \lim_{t\to+\infty}\int_{D_\alpha^2}\left|f_\alpha - f_\alpha^{(0)}\right| d\mathbf{c}_\alpha = 0, \tag{34}$$

since all contributions to the sums in Eq. (33) have the same non-negative sign. Now, recalling the Cauchy-Schwarz inequality, one can write

$$\int_{D_\alpha^1}\left|f_\alpha - f_\alpha^{(0)}\right| d\boldsymbol{c}_\alpha = \int_{D_\alpha^1}\sqrt{f_\alpha^{(0)}}\,\frac{\left|f_\alpha - f_\alpha^{(0)}\right|}{\sqrt{f_\alpha^{(0)}}}\, d\boldsymbol{c}_\alpha \leq \left(\int_{D_\alpha^1} f_\alpha^{(0)} d\boldsymbol{c}_\alpha\right)^{\frac{1}{2}}\left(\int_{D_\alpha^1}\frac{\left|f_\alpha - f_\alpha^{(0)}\right|^2}{f_\alpha^{(0)}}\, d\boldsymbol{c}_\alpha\right)^{\frac{1}{2}}. \tag{35}$$

By combining inequality (35) with condition $(34)_1$, it follows

$$\lim_{t\to\infty}\int_{D_\alpha^1}\left|f_\alpha - f_\alpha^{(0)}\right| d\mathbf{c}_\alpha = 0. \tag{36}$$

Finally, since $\int_{D_\alpha^1}\left|f_\alpha - f_\alpha^{(0)}\right| d\boldsymbol{c}_\alpha + \int_{D_\alpha^2}\left|f_\alpha - f_\alpha^{(0)}\right| d\boldsymbol{c}_\alpha = \int\left|f_\alpha - f_\alpha^{(0)}\right| d\boldsymbol{c}_\alpha$, conditions $(34)_2$ and (36) imply that

$$\lim_{t\to\infty}\int\left|f_\alpha - f_\alpha^{(0)}\right| d\mathbf{c}_\alpha = 0,$$

which means that f_α converges strongly to $f_\alpha^{(0)}$ in the L^1-sense. The proof is then complete. ■

5 Conclusions

The problem of the trend to equilibrium in kinetic theory arises in many researches involving chemically reacting systems, as those related to numerical simulations and modeling. In fact, due to the last developments of computer technologies, more accurate descriptions are possible and very often the knowledge of the behavior of reacting systems is needed when processes for large times are analyzed. The mathematical research related to this problem may improve the understanding and the physical description of the involved phenomena. In this line, the present work can be regarded as an extension to kinetic theory of chemically reacting gases of the results for one-component inert gases due to Carleman in the works [4, 5], and which will be useful to validate numerical implementations and model approaches.

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