Kinetic theory for chemical reactions without a barrier

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Abstract A new model of the BE for binary reactive mixtures is here proposed with the aim of describing symmetric reversible reactions without a barrier, assuming appropriate reactive cross sections without activation energy and introducing suitable improvements in the elastic and reactive collision terms. The resulting model assures the correct balance equations and law of mass action, as well as good consistency properties for what concerns equilibrium and entropy inequality. Moreover the non-equilibrium effects induced by the chemical reaction on the distribution function are explicitly determined in a flow regime of slow chemical reaction.

1 Introduction

Reactions without a barrier have become an attractive subject of theoretical and experimental studies due to the central role of such reactions in combustion phenomena and many other processes with relevance in astrophysics, organic chemistry, enzymology, chemical physics and biophysics [6, 7]. The so called no-barrier theory has been used in many areas of chemistry, providing quantitative information about the reaction mechanism as well as useful guidance in chemical investigations. Mathematical and modeling approaches for reactions without barriers can help to improve the research on this subject, providing some useful informations about the kinetics of the reactions.

On the other hand, the Boltzmann equation (BE) has been extensively used in the scientific literature to treat chemically reactive systems, after the first studies conducted by Prigogine and co-workers [9] and several others, as documented for example in Refs. [5, 10] and bibliography therein cited. However, in the literature of the BE extended to chemically reacting gases, only few works consider reactive processes without a barrier and the corresponding collision terms are restricted to some particular chemical regimes for which no significant changes are needed at the model level [10].

In this paper we propose a kinetic model of the BE for a binary mixture undergoing elastic and reactive scattering, adopting an appropriate model of reactive cross section without barriers

[2, 11]. At the microscopic scale, the key idea is to modify the collision terms, introducing probability coefficients that describe the possibility of a pair of molecules to collide through an elastic mechanism or a reactive process. This improvement accounts for the fact that a great number of reactive interactions corresponds to a small number of elastic collisions, and vice-versa. In this sense, the considered model represents a new approach, since almost all existent papers introduce reactive cross sections with activation energy and control the presence of both elastic and reactive collisions assuming rather large activation energies and a steric factor which reduce the number of reactive collisions.

2 The Model Equations

We consider a binary mixture of constituents $\alpha = A, B$ with binding energies ε_A and ε_B and equal molecular masses, $m_A = m_B = m$, undergoing the reversible reaction $A + A \rightleftharpoons B + B$. Gas molecules can collide through a binary elastic process which preserves momentum and kinetic energy,

$$m\mathbf{c}_\alpha + m\mathbf{c}_\beta = m\mathbf{c}'_\alpha + m\mathbf{c}'_\beta, \quad \frac{mc_\alpha^2}{2} + \frac{mc_\beta^2}{2} = \frac{mc'^2_\alpha}{2} + \frac{mc'^2_\beta}{2}, \quad (1)$$

as well through a reactive process which preserves momentum and total energy,

$$m\mathbf{c}_A + m\mathbf{c}_{A_1} = m\mathbf{c}_B + m\mathbf{c}_{B_1}, \quad 2\varepsilon_A + \frac{m(c_A^2 + c_{A_1}^2)}{2} = 2\varepsilon_B + \frac{m(c_B^2 + c_{B_1}^2)}{2}. \quad (2)$$

In the above equations, $(\mathbf{c}_\alpha, \mathbf{c}_\beta)$ and $(\mathbf{c}'_\alpha, \mathbf{c}'_\beta)$ denote pre and post collisional velocities, whereas $(\mathbf{c}_A, \mathbf{c}_{A_1})$ and $(\mathbf{c}_B, \mathbf{c}_{B_1})$ refer to the velocities of reactants and products of the forward reaction, respectively. We use the sub-index 1 to distinguish two molecules of the same species.

Boltzmann equation

The gas mixture is characterized in the phase space by the one-particle distribution functions $f(x, \mathbf{c}_\alpha, t)$, $\alpha = A, B$, with $f_\alpha d\mathbf{x} d\mathbf{c}_\alpha$ denoting the number of α -particles in the volume element $d\mathbf{x} d\mathbf{c}_\alpha$ around position $\mathbf{x}$ and velocity $\mathbf{c}_\alpha$, at time t . We introduce $\underline{f} = \{f_\alpha, f_\beta\}$. In absence of external body forces, we propose the following system of two Boltzmann equations for the distribution functions

$$\frac{\partial f_\alpha}{\partial t} + \mathbf{c}_i^\alpha \frac{\partial f_\alpha}{\partial x_i} = \mathcal{Q}_\alpha^E(\underline{f}) + \mathcal{Q}_\alpha^R(\underline{f}), \quad \alpha = A, B,$$

where the first term on the r.h.s. refers to contributions from elastic collisions and the second one to contributions from chemical interactions. They are given by

$$\mathcal{Q}_\alpha^E(\underline{f}) = \sum_{\beta=A}^B (1 - \chi_\beta \delta_{\alpha\beta}) \int [\mathbf{f}'_\alpha \mathbf{f}'_\beta - \mathbf{f}_\alpha \mathbf{f}_\beta] \mathbf{g}_{\beta\alpha} \sigma_{\alpha\beta} d\Omega_{\alpha\beta} d\mathbf{c}_\beta \quad (3)$$

$$\mathcal{Q}_\alpha^R(\underline{f}) = \int \left[\chi_\beta f_\beta f_{\beta_1} \sigma_\beta^* \frac{g_\beta^2}{g_\alpha^2} - \chi_\alpha f_\alpha f_{\alpha_1} \sigma_\alpha^* \right] \mathbf{g}_\alpha d\Omega_\beta d\mathbf{c}_{\alpha_1}, \quad \alpha = A, B. \quad (4)$$

In the reactive term, it is implicit that the index $\beta = A, B$ is always different from the index α , since the chemical reaction predicts that the reactants and products are of different species. Moreover, $\mathbf{g}_{\alpha\beta}$ stands for relative velocity of an elastic collision and $\mathbf{g}_A, \mathbf{g}_B$ for those of the reactants and products involved in chemical interactions. The symbols $d\Omega_{\alpha\beta}$ and $d\Omega_\beta$ represent elements of

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solid angles which characterize the scattering processes $\sigma_{\alpha\beta}$ is the differential elastic cross section, σ_{α}^* and σ_{β}^* are differential reactive cross sections for forward and backward reactions.

We have introduced probability coefficients χ_A and χ_B relative to the AA and BB encounters, in order to account for the possibility of a pair of molecules of the same species interact through an elastic collision or a reactive process. This represents an improvement in the kinetic theory of chemically reacting gases, suitable to treat chemical reactions without activation energy.

Differential cross sections

For what concerns the differential cross sections of elastic encounters, we adopt the simple model of rigid spheres, namely $\sigma_{\alpha\beta} = d^2/4$, where d is the molecular diameter.

On the other hand, for reactive cross sections we have to adopt a suitable model to describe chemical reactions without a barrier, so that such a model should not consider an activation energy. In particular, if we consider an attractive potential energy of the form $V(r) = -K/r^n$, we can choose the following reactive model (see Refs. [2, 11]),

$$\sigma_{\alpha}^* = \frac{d_r^2}{4} \left(\frac{mg_{\alpha}^2}{4kT_0} \right)^{n-1/2}, \quad (5)$$

where T_0 is a characteristic temperature, d_r a reactive collision diameter and the exponent n may range from $-3/2$ to $1/2$. The values $n = 1/2$, $n = 0$ and $n = 1/6$ stand for hard-spheres reactions, ion-molecule reactions and reactions of neutral species, respectively.

3 The Macroscopic Equations

It is well known that the Boltzmann equations (3) give a detailed microscopic picture which is not necessary in general for applied studies involving the model. Instead of these equations, one has to consider the corresponding macroscopic ones, which are time-space evolution equations for mean quantities, as density, momentum and energy.

Transfer equations

These equations result from Eq. (3), when one multiplies the equation by an arbitrary function, say $\psi_{\alpha} \equiv \psi(x, \mathbf{c}_{\alpha}, t)$, and then integrate the resulting equation over all velocities $\mathbf{c}_{\alpha}$. It results the so called transport equation for constituent α

$$\begin{aligned} & \frac{\partial}{\partial t} \int \psi_{\alpha} f_{\alpha} d\mathbf{c}_{\alpha} + \frac{\partial}{\partial x_i} \int \psi_{\alpha} c_i^{\alpha} f_{\alpha} d\mathbf{c}_{\alpha} - \int \left(\frac{\partial \psi_{\alpha}}{\partial t} + c_i^{\alpha} \frac{\partial \psi_{\alpha}}{\partial x_i} \right) f_{\alpha} d\mathbf{c}_{\alpha} \\ &= \sum_{\beta=A}^B (1 - \chi_{\beta} \delta_{\alpha\beta}) \int (\psi'_{\alpha} - \psi_{\alpha}) f_{\alpha} f_{\beta} g_{\beta\alpha} \sigma_{\alpha\beta} d\Omega_{\alpha\beta} d\mathbf{c}_{\beta} d\mathbf{c}_{\alpha} \\ & - \frac{v_{\alpha}}{2} \int (\psi_{\alpha} + \psi_{\alpha_1}) \chi_A \left[\frac{\chi_B}{\chi_A} f_B f_{B_1} - f_A f_{A_1} \right] \sigma_A^* g_A d\Omega d\mathbf{c}_{A_1} d\mathbf{c}_A. \end{aligned} \quad (6)$$

The corresponding transport equation for the mixture is obtained by summing Eqs. (6) over all constituents, yielding

$$\frac{\partial}{\partial t} \sum_{\alpha=A}^B \int \psi_{\alpha} f_{\alpha} d\mathbf{c}_{\alpha} + \frac{\partial}{\partial x_i} \sum_{\alpha=A}^B \int \psi_{\alpha} c_i^{\alpha} f_{\alpha} d\mathbf{c}_{\alpha} - \sum_{\alpha=A}^B \int \left(\frac{\partial \psi_{\alpha}}{\partial t} + c_i^{\alpha} \frac{\partial \psi_{\alpha}}{\partial x_i} \right) f_{\alpha} d\mathbf{c}_{\alpha}$$

$$\begin{aligned}
&= \frac{1}{4} \sum_{\alpha, \beta=A}^B (1 - \chi_{\beta} \delta_{\alpha\beta}) \int (\psi_{\alpha} + \psi_{\beta} - \psi'_{\alpha} - \psi'_{\beta}) \left[f'_{\alpha} f'_{\beta} - f_{\alpha} f_{\beta} \right] g_{\beta\alpha} \sigma_{\beta\alpha} d\Omega_{\beta\alpha} d\mathbf{c}_{\beta} d\mathbf{c}_{\alpha} \\
&\quad + \frac{1}{2} \int (\psi_A + \psi_{A_1} - \psi_B - \psi_{B_1}) \chi_A \left[\frac{\chi_B}{\chi_A} f_B f_{B_1} - f_A f_{A_1} \right] \sigma_A^* g_A d\Omega d\mathbf{c}_{A_1} d\mathbf{c}_A. \quad (7)
\end{aligned}$$

Macroscopic fields

For the considered gas mixture, the macroscopic picture is described by seven scalar fields namely the partial particle number densities n_{α} , the partial internal energies density $\rho_{\alpha} \epsilon_{\alpha}$ (with $\alpha = A, B$) and the velocity of the mixture v_i . In terms of the one-particle distribution function f_{α} these fields are defined by

$$n_{\alpha} = \int f_{\alpha} d\mathbf{c}_{\alpha} = \frac{\rho_{\alpha}}{m} \quad \text{with} \quad n = \sum_{\alpha=A}^B n_{\alpha} \quad \text{and} \quad \rho = \sum_{\alpha=A}^B \rho_{\alpha}. \quad (8)$$

$$v_i = \frac{1}{\rho} \sum_{\alpha=A}^B \int m c_i^{\alpha} f_{\alpha} d\mathbf{c}_{\alpha}, \quad (9)$$

$$\rho_{\alpha} \epsilon_{\alpha} = \int \frac{m}{2} \xi_{\alpha}^2 f_{\alpha} d\mathbf{c}_{\alpha}. \quad (10)$$

where $\xi_{\alpha}^{\alpha} = c_i^{\alpha} - v_i$ is the molecular peculiar velocity of constituent α . We assume that both constituents have the same temperature T , which is the temperature of the mixture, so that its internal energy density of constituent α is in fact given by $\rho_{\alpha} \epsilon_{\alpha} = 3n_{\alpha} kT/2$.

Field equations

The balance equations for the fields (8-10) are obtained from the transfer equations (6) and (7) with pertinent choices of ψ_{α} . More in detail Eq. (6) with $\psi_{\alpha} = 1$ or $\psi_{\alpha} = m\xi_{\alpha}^2/2$, and Eq. (7) with $\psi_{\alpha} = m c_i^{\alpha}$ lead to the equations for particle number densities, momentum and internal energies in the form

$$\frac{\partial n_{\alpha}}{\partial t} + \frac{\partial}{\partial x_i} (n_{\alpha} u_i^{\alpha} + n_{\alpha} v_i) = \tau_{\alpha} \quad (11)$$

$$\frac{\partial \rho v_i}{\partial t} + \frac{\partial}{\partial x_j} (\rho v_i v_j + p_{ij}) = 0. \quad (12)$$

$$\frac{3}{2} \frac{\partial n_{\alpha} kT}{\partial t} + \frac{\partial}{\partial x_i} \left(q_i^{\alpha} + \frac{3}{2} n_{\alpha} kT v_i \right) - \frac{\rho_{\alpha}}{\rho} u_i^{\alpha} \frac{\partial p_{ij}}{\partial x_j} + p_{ij}^{\alpha} \frac{\partial v_j}{\partial x_i} = \zeta_{\alpha}. \quad (13)$$

In the above equations, τ_{α} is the rate of reaction and ζ_{α} the production term of internal energy density of constituent α , given by

$$\tau_{\alpha} = \int \left[\chi_{\beta} f_{\beta} f_{\beta_1} \sigma_{\beta}^* \frac{g_{\beta}^2}{g_{\alpha}^2} - \chi_{\alpha} f_{\alpha} f_{\alpha_1} \sigma_{\alpha}^* \right] g_{\alpha} d\Omega_{\beta\alpha} d\mathbf{c}_{\alpha_1} d\mathbf{c}_{\alpha}. \quad \text{with} \quad \tau_B = -\tau_A. \quad (14)$$

$$\begin{aligned}
\zeta_{\alpha} &= \sum_{\beta=A}^B (1 - \chi_{\beta} \delta_{\alpha\beta}) \int \frac{1}{2} m (\xi_{\alpha}^{\prime 2} - \xi_{\alpha}^2) f_{\alpha} f_{\beta} g_{\beta\alpha} \sigma_{\beta\alpha} d\Omega_{\beta\alpha} d\mathbf{c}_{\beta} d\mathbf{c}_{\alpha} \\
&\quad + \int \frac{m}{4} (\xi_{\alpha}^2 + \xi_{\alpha_1}^2) \left[\chi_{\beta} f_{\beta} f_{\beta_1} \sigma_{\beta}^* \frac{g_{\beta}^2}{g_{\alpha}^2} - \chi_{\alpha} f_{\alpha} f_{\alpha_1} \sigma_{\alpha}^* \right] g_{\alpha} d\Omega_{\beta\alpha} d\mathbf{c}_{\alpha_1} d\mathbf{c}_{\alpha}. \quad (15)
\end{aligned}$$

Moreover, u_i^{α} , q_i^{α} and p_{ij}^{α} are the diffusion velocity, heat flux and pressure tensor of each constituent, defined by

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$$u_i^\alpha = \frac{1}{n_\alpha} \int \xi_i^\alpha f_\alpha d\mathbf{c}_\alpha, \quad q_i^\alpha = \int \frac{1}{2} m \xi_\alpha^2 \xi_i^\alpha f_\alpha d\mathbf{c}_\alpha, \quad p_{ij}^\alpha = \int m \xi_i^\alpha \xi_j^\alpha f_\alpha d\mathbf{c}_\alpha,$$

with

$$\sum_{\alpha=A}^B \rho_\alpha u_i^\alpha = 0, \quad q_i = \sum_{\alpha=A}^B q_i^\alpha, \quad p_{ij} = \sum_{\alpha=A}^B p_{ij}^\alpha.$$

4 Consistency of the Model

The model here proposed has good consistency properties for what concerns conservation laws, chemical exchange rates, trend to equilibrium and entropy production. These features are confirmed through the following results whose detailed proofs are here omitted for sake of brevity.

Theorem 0.1. *The elastic collision terms (3) are such that*

$$\int_{\mathbb{R}^3} \mathcal{Q}_\alpha^E(f) d\mathbf{c}_\alpha = 0, \quad \alpha = A, B. \quad (16)$$

Proof. The proof follows from the definition of the elastic collision terms resorting to the usual symmetry properties of the gain and loss contributions. $\square$

The result of Theorem 0.1 is well known in the literature of the Boltzmann equation for inert mixtures (see, for example Ref. [3]). It means that elastic collisions do not modify the concentration of each constituent, as expected.

Theorem 0.2. *The elastic and reactive collision terms (3) and (4) are such that*

$$\sum_{\alpha=A}^B \int_{\mathbb{R}^3} \psi_\alpha(c_\alpha) \left(\mathcal{Q}_\alpha^E(f) + \mathcal{Q}_\alpha^R(f) \right) d\mathbf{c}_\alpha = 0. \quad (17)$$

for $\psi_\alpha = m$, $\psi_\alpha = mc_\alpha$, $\psi_\alpha = \varepsilon_\alpha + \frac{1}{2} mc_\alpha^2$, $\alpha = A, B$.

Proof. The proof follows from the definition of the elastic and reactive collision terms and uses similar symmetry techniques to those referred in the proof of the previous result. $\square$

The result of Theorem 0.2 states that elastic and reactive collision terms are consistent with the physical conservation laws for mass, momentum and total energy of the whole mixture.

Theorem 0.3. *The reactive collision terms (4) are such that*

$$\int_{\mathbb{R}^3} \mathcal{Q}_A^R(f) d\mathbf{c}_A = - \int_{\mathbb{R}^3} \mathcal{Q}_B^R(f) d\mathbf{c}_B. \quad (18)$$

Proof. The proof follows the same line of arguments. In particular one changes the reactant variables with the corresponding ones of the products. $\square$

Theorem 0.3 states that reactive collision terms assure the correct chemical exchange rates for the considered chemical process.

Theorem 0.4. *The following statements are equivalent:*

(a) *The distribution functions are Maxwellian, that is*

$$f_\alpha^M = n_\alpha \left(\frac{m}{2\pi kT} \right)^{3/2} \exp \left(-\frac{m(c_\alpha - u)^2}{2kT} \right), \quad \alpha = A, B. \quad (19)$$

with the particle number densities n_α restricted to de mass action law

$$\frac{2(\epsilon_A - \epsilon_B)}{kT} = \ln \left(\frac{\chi_A n_A^2}{\chi_B n_B^2} \right); \quad (20)$$

$$(b) \quad \mathcal{Q}_A^E(\underline{f}) = 0 \quad \text{and} \quad \mathcal{Q}_A^R(\underline{f}) = 0;$$

$$(c) \quad \mathcal{Q}_A^E(\underline{f}) + \mathcal{Q}_A^R(\underline{f}) = 0.$$

Proof. The proof proceeds showing that (a) $\Rightarrow$ (b) $\Rightarrow$ (c) $\Rightarrow$ (a). The first implication comes straightforward from the substitution of expressions (19) and (20) into the definitions (3) and (4) of the elastic and reactive collision terms. The second implication is trivially satisfied. For the last implication one has to use again the symmetry properties and the well known inequality $(1-x)\ln x \leq 0$ for all $x > 0$. $\square$

Theorem 0.4 defines the equilibrium solutions to the reactive system (3) of Boltzmann equations. More in detail, expressions (19), alone, define a mechanical equilibrium solution, whereas expressions (19) and (20), together, define a mechanical, thermal and chemical equilibrium solution.

Theorem 0.5. *The elastic and reactive collision terms (3) and (4) are such that*

$$\sum_{\alpha=A}^B \int \left(\mathcal{Q}_\alpha^E(\underline{f}) + \mathcal{Q}_\alpha^R(\underline{f}) \right) \ln(\sqrt{\chi_\alpha} f_\alpha) d\mathbf{c}_\alpha \leq 0. \quad (21)$$

Proof. If we multiply each equation of system (3) by $\ln(\sqrt{\chi_\alpha} f_\alpha)$, then integrate over the velocity $\mathbf{c}_\alpha$ and take the sum over all constituents, we obtain

$$\sum_{\alpha=A}^B \int \left(\mathcal{Q}_\alpha^E(\underline{f}) + \mathcal{Q}_\alpha^R(\underline{f}) \right) \ln(\sqrt{\chi_\alpha} f_\alpha) d\mathbf{c}_\alpha = \Sigma_E + \Sigma_R. \quad (22)$$

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

$$\begin{aligned} \Sigma_E = \frac{k}{4} \sum_{\alpha=A}^B \sum_{\beta=A}^B (1 - \chi_\beta \delta_{\alpha\beta}) \int f'_\alpha f'_\beta \\ \times \left(1 - \frac{f_\alpha f_\beta}{f'_\alpha f'_\beta} \right) \ln \left(\frac{f_\alpha f_\beta}{f'_\alpha f'_\beta} \right) g_{\beta\alpha} \sigma_{\beta\alpha} d\Omega_{\beta\alpha} d\mathbf{c}_\beta d\mathbf{c}_\alpha. \end{aligned} \quad (23)$$

$$\Sigma_R = \frac{k}{2} \int \chi_B f_B f_{B_1} \left(1 - \frac{\chi_A f_A f_{A_1}}{f_B f_{B_1}} \right) \ln \left(\frac{\chi_A f_A f_{A_1}}{f_B f_{B_1}} \right) \sigma_A^* g_A d\Omega d\mathbf{c}_{A_1} d\mathbf{c}_A. \quad (24)$$

The expressions on the r.h.s of Eqs. (23) and (24) define negative semi-definite quantities, thanks again to the inequality $(1-x)\ln x \leq 0$. $\square$

The result expressed in Theorem 0.5 means that elastic and reactive collision terms assure a positive entropy production, since it is equivalent to the inequality

$$\frac{\partial}{\partial t} (\rho \eta) + \frac{\partial}{\partial x_i} (\phi_i + \rho \eta v_i) \geq 0. \quad (25)$$

where

$$\rho\eta = -k \sum_{\alpha=A}^B \int f_{\alpha} \ln(\sqrt{\chi_{\alpha}} f_{\alpha}) d\mathbf{c}_{\alpha}, \quad \phi_i = -k \sum_{\alpha=A}^B \int f_{\alpha} \xi_i^{\alpha} \ln(\sqrt{\chi_{\alpha}} f_{\alpha}) d\mathbf{c}_{\alpha}, \quad (26)$$

are the entropy density and its flux, respectively.

5 The Non-Equilibrium Distribution Function

In the literature of the Boltzmann equation extended to chemically reacting gases, the determination of the non-equilibrium distribution function containing the effects induced by the chemical reaction constitutes a fundamental topic. See, for example, paper [10] and references cited therein. In fact, the chemical reaction induces a perturbation of the local equilibrium, disturbing the molecular velocity distribution function from its Maxwellian form. As a consequence, important qualitative changes of the system properties occur.

The deviations induced by the chemical reaction on the distribution functions have been explicitly computed in the paper [8], using the Chapman-Enskog method [4] combined with Sonine polynomial representation of the distribution functions. A chemical regime of slow processes has been considered, meaning that the reaction is close to its initial stage. In this case, reactive collisions are less frequent than elastic encounters and the chemical relaxation time is larger than the elastic one. This means that reactive collision terms and material time derivatives, $\mathcal{D} = (\partial/\partial t) + v_i \partial/\partial x_i$, are of the same order whereas the gradients of the fields are of successive order. The Boltzmann equation (3) can then be re-written as

$$\begin{aligned} \mathcal{D} f_{\alpha} + \lambda \xi_i^{\alpha} \frac{\partial f_{\alpha}}{\partial x_i} - \int \left[\chi_{\beta} f_{\beta} f_{\beta_1} \sigma_{\beta}^* \frac{g_{\beta}^2}{g_{\alpha}^2} - \chi_{\alpha} f_{\alpha} f_{\alpha_1} \sigma_{\alpha}^* \right] g_{\alpha} d\Omega_{\beta} d\mathbf{c}_{\alpha_1} \\ = \frac{1}{\lambda} \sum_{\beta=A}^B (1 - \chi_{\beta} \delta_{\alpha\beta}) \int [f'_{\alpha} f'_{\beta} - f_{\alpha} f_{\beta}] g_{\beta\alpha} \sigma_{\alpha\beta} d\Omega_{\alpha\beta} d\mathbf{c}_{\beta}, \end{aligned} \quad (27)$$

where λ is a formal parameter of the order of the Knudsen number [4]. We then insert the expansions

$$f_{\alpha} = f_{\alpha}^M + \lambda f_{\alpha}^{(1)} + \lambda^2 f_{\alpha}^{(2)} + \dots \quad \text{and} \quad \mathcal{D} = \mathcal{D}^{(0)} + \lambda \mathcal{D}^{(1)} + \lambda^2 \mathcal{D}^{(2)} + \dots \quad (28)$$

into the Boltzmann Eqs. (27) and equate equal powers of λ . We then obtain the integral equations for f_{α}^M and $f_{\alpha}^{(1)}$ in the form [8],

$$\sum_{\beta=A}^B (1 - \chi_{\beta} \delta_{\alpha\beta}) \int [f_{\alpha}^{M'} f_{\beta}^{M'} - f_{\alpha}^M f_{\beta}^M] g_{\beta\alpha} \sigma_{\alpha\beta} d\Omega_{\alpha\beta} d\mathbf{c}_{\beta} = 0, \quad (29)$$

$$\mathcal{D}^{(0)} f_{\alpha}^M - \int \left[\chi_{\beta} f_{\beta}^M f_{\beta_1}^M \sigma_{\beta}^* \frac{g_{\beta}^2}{g_{\alpha}^2} - \chi_{\alpha} f_{\alpha}^M f_{\alpha_1}^M \sigma_{\alpha}^* \right] g_{\alpha} d\Omega_{\beta} d\mathbf{c}_{\alpha_1} \quad (30)$$

$$= \sum_{\beta=A}^B (1 - \chi_{\beta} \delta_{\alpha\beta}) \int [f_{\alpha}^{(1)'} f_{\beta}^{M'} + f_{\alpha}^{M'} f_{\beta}^{(1)'} - f_{\alpha}^{(1)} f_{\beta}^M - f_{\alpha}^M f_{\beta}^{(1)}] g_{\beta\alpha} \sigma_{\alpha\beta} d\Omega_{\alpha\beta} d\mathbf{c}_{\beta}.$$

The solution of the integral equation (29) is the Maxwellian distribution function given by expression (19), with partial number densities n_{α} completely uncorrelated, since no chemical equilibrium condition is involved. Concerning Eq. (30), since the field gradients are absent, one admits that its solution is a small deviation from the Maxwellian distribution, expressed in terms of Sonine polynomials as

$$f_{\alpha}^{(1)} = f_{\alpha}^M \left[a_1^{\alpha} \left(\frac{3}{2} - \frac{m \xi_{\alpha}^2}{2kT} \right) + a_2^{\alpha} \left(\frac{15}{8} - \frac{5m \xi_{\alpha}^2}{4kT} + \frac{m^2 \xi_{\alpha}^4}{8k^2 T^2} \right) \right]. \quad (31)$$

where $\xi_i^\alpha = c_i^\alpha - v_i$ is the peculiar velocity of constituent α , and a_1^α and a_2^α are scalar coefficients to be determined using the Chapman-Enskog method. See the details reported in paper [8]. We have obtained $a_1^A = a_1^B = 0$ and a_2^A, a_2^B given by

$$a_2^A = \frac{2\chi_A x_A}{15x_A^2\chi_A + 16x_A\chi_A - 31} \left(\frac{T}{T_0}\right)^{n-\frac{1}{2}} \Gamma\left(n + \frac{3}{2}\right) n(n-1) \left(\frac{d_t}{d}\right)^2, \quad (32)$$

$$a_2^B = \frac{x_A(x_A\chi_A - 1)}{1 - x_A} a_2^A. \quad (33)$$

where $x_A = n_A/n$ and $x_B = 1 - x_A$ represent the molar fraction of the constituents. Expressions (31) with coefficients $a_1^\alpha = 0$ and coefficients a_2 given by Eqs. (32) and (33) completely determine the non-equilibrium distribution function $f_\alpha^{(1)}$, in the considered slow chemical regime. The consequent non-equilibrium effects induced on the macroscopic properties of the reacting mixture can then be evaluated as well. This study is reported in paper [8], where some numerical simulations have been implemented, showing satisfactory results that are in agreement with experimental predictions.

Furthermore, other different chemical regimes are investigated in a paper in preparation in view of studying transport properties, see Ref. [1]. Some details about the approximating procedure employed to determine the non-equilibrium distribution function are reported in that paper.

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