Travelling waves in a mixture of gases with bimolecular reversible reactions

A. Rossani\(^1\), A.M. Scarfone\(^2\)

\(^a\)Istituto Nazionale di Fisica della Materia and Dipartimento di Fisica Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Torino, Italy

\(^b\)Istituto Nazionale di Fisica Nucleare, Università di Cagliari, Cittadella Universitaria, 09042 Monserrato Cagliari, Italy

Abstract

Starting from the kinetic approach for a mixture of reacting gases whose particles interact through elastic scattering and a bimolecular reversible chemical reaction, the equations that govern the dynamics of the system are obtained by means of the relevant Boltzmann-like equation. Conservation laws are considered. Fluid dynamic approximations are used at the Euler level to obtain a close set of PDEs for six unknown macroscopic fields. The dispersion relation of the mixture of reacting gases is explicitly derived in the homogeneous equilibrium state. A set of ODE that governs the propagation of a plane travelling wave is obtained using the Galilei invariance. After numerical integration some solutions, including the well-known Maxwellian and the hard spheres cases, are found for various meaningful interaction laws. The main macroscopic observables for the gas mixture such as the drift velocity, temperature, total density, pressure and its chemical composition are shown.

Key words: Kinetic and transport theory, Chemical reactions, Travelling waves, Boltzmann equations.

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1 Introduction

The study of chemically reacting gases has been dealt with using the kinetic theory since the 1940s \cite{1}, and a large amount of literature has been developed about chemically reacting rarefied flows. This research field led to applications in the study of combustion \cite{2}, detonation (see \cite{3} and references therein) and

\(^1\) alberto.rossani@polito.it; corresponding author.

\(^2\) antonio.scarfone@polito.it

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atmospheric chemistry [4], fields in which a precise knowledge of the dynamics of the reacting gases mixture is required. Due to the increasing complexity that arises from a detailed microscopic description, there are not many results in literature and they mainly concern numerical simulations and applications. Starting from the kinetic approach, fluid dynamic approximations have been constructed as simplified tools for a description, at a macroscopic level, of the mixture we are dealing with [5,6]. In order to recall some of the main contributions in this field, we can quote Ref.s [7,8] where the Chapman-Enskong approximation method was used in the homogeneous space case for an accurate evaluation of the chemical reaction rate and, more recently, the Grad method which was applied in both the homogeneous and non-homogeneous space cases, in order to calculate the reaction rate and transport coefficients [5,9].

In a recent paper [10], Rossani and Spiga obtained a more explicit derivation of kinetic equations with a chemical reaction, and succeeded in completely characterizing the equilibrium distributions and in proving an H-theorem for them. A generalization to many level molecules was performed in [11].

In the present work, the authors deal with a gas that undergoes to the following reversible bimolecular reaction

\[ A + B \rightleftharpoons C + D. \] (1.1)

It should be mentioned that the kinetic theory governing reaction (1.1) has been the subject of investigation in recent years. For instance, in [12] the kinetic model of a diatomic gas with both dissociation and recombination reactions through a transition state was proposed, whereas in [13] the extended Boltzmann equation governing reaction (1.1) was investigated in the Lorentzian gas limit.

In the first part of this paper, starting from the nonlinear system of kinetic equations for a mixture of particles \( A, B, C, \) and \( D \), we derive the balance equations for the different chemical species as well as the conservation equations for the macroscopic quantities such as mass, momentum and total energy. By adopting the Euler approximation, in the case of a homogeneous equilibrium state, we analytically derive the dispersion relation for the mixture of the reacting gases, where we found a relationship like \( k^2 P(i \omega) + \omega^2 Q(i \omega) = 0 \), where \( P \) and \( Q \) are polynomials of the first order in \( i \omega \), with real coefficients. In the second part, we deal with the study of the propagation of a plane travelling wave. It can be remarked that, although many results can be found in literature about this important fluid dynamic problem for a dissociating gas (see [14,15] and references therein), the explicit treatment of a travelling wave with bimolecular reversible reactions is very recent [3].

In the dynamics of non-reacting gases, viscosity and heat conduction are responsible for the structure of a travelling wave [15]. However, here we make the
assumption that relaxation due to elastic scattering is much quicker than the one due to chemical interactions. In this way we can neglect viscosity and heat conduction, so that only the chemical reaction is responsible for the structure of the travelling wave. Under the previous hypothesis on relaxation times, we construct a close set of nonlinear PDEs that govern the propagation of a plane steady travelling wave through the reacting gas.

By taking advantage of the Galilei invariance of the Euler equations, we can adopt the reference frame in which the travelling wave is at rest. The resulting ODE system is reduced to a single nonlinear ODE which is solved numerically for several meaningful interaction laws, including the case of Maxwell and hard sphere molecules. Results on the whole gas (drift velocity, temperature, total density and pressure) as well as its chemical composition (molar fractions of the four components) are plotted. The effects of the different choices for the interaction laws on the structure of the travelling wave are discussed.

2 Kinetic equations

Let us consider a mixture of four gases $A$, $B$, $C$ and $D$, which can interact, apart from all the elastic collisions, according to the reversible bimolecular reaction given in (1.1). In the sequel, we denote the particles $A$, $B$, $C$ and $D$ with the index $i = 1$, $2$, $3$, $4$. The distribution functions $f_i(x, \mathbf{v}, t)$ for particles $i$, endowed with masses $m_i$ and internal energy $E_i$ (available in the case of reactive interactions), obey the following system of nonlinear integro-differential Boltzmann equations (see [10] for details):

$$
\frac{\partial f_i}{\partial t} + \mathbf{v} \cdot \nabla f_i = J_i[f] + Q_i[f],
$$

(2.1)

where the vector $f \equiv (f_1, f_2, f_3, f_4)$. In Eq. (2.1), $Q_i$ are the well known elastic collision integrals [15] while $J_i$ are the chemical collision terms given by:

$$
J_1[f](\mathbf{v}) = \int \int \left[ \frac{\mu_{12} V_{12}^2}{\mu_{34} V_{12}} I_{12}^{12} f_3(v') f_4(w') - V_{34} I_{34}^{34} f_1(v) f_2(w) \right] \, dw \, d\Omega',
$$

(2.2)

where $V_{12} = |\mathbf{v} - \mathbf{w}|$, $V_{34} = |\mathbf{v}' - \mathbf{w}'|$, $\zeta = \Omega \cdot \Omega'$, with $\Omega = (\mathbf{v} - \mathbf{w})/V_{12}$, $\Omega' = (\mathbf{v}' - \mathbf{w}')/V_{34}$ and

$$
J_3[f](\mathbf{v}) = \int \int \left[ \frac{\mu_{12} V_{12}^2}{\mu_{34} V_{34}} I_{34}^{34} f_1(v') f_2(w') - V_{12} I_{12}^{12} f_3(v) f_4(w) \right] \, dw \, d\Omega',
$$

(2.2)
where, now, \( V_34 = |\mathbf{v} - \mathbf{w}|, \ V_{12} = |\mathbf{v}' - \mathbf{w}'|, \ \Omega = (\mathbf{v} - \mathbf{w})/V_{34} \) and \( \Omega' = (\mathbf{v}' - \mathbf{w}')/V_{12} \). The explicit expressions of the post-collision velocities \( \mathbf{v}' \) and \( \mathbf{w}' \), (which can be found in Ref. [10]), are omitted here for the sake of brevity.

The integrals \( J_2[f] \) and \( J_4[f] \) are obtained from \( J_1[f] \) and \( J_3[f] \) by introducing the following index exchange: \( 1 \rightleftharpoons 2, \ 3 \rightleftharpoons 4 \). In Eqs (2.2) and (2.3), \( I_{12}^{12} \equiv I_{34}^{12}(V_{34}, \zeta) \) and \( I_{12}^{34} \equiv I_{12}^{34}(V_{12}, \zeta) \) are the differential cross-sections of the forward and backward reaction, respectively, that are related by means of the following microreversibility relationship: \( \mu_{12}^2 V_{12}^2 I_{12}^{12}(V_{12}, \zeta) = \mu_{34}^2 V_{34}^2 I_{12}^{34}(V_{34}, \zeta) \), where \( \mu_{ij} = m_i m_j/M \) are the reduced masses, and \( M = m_1 + m_2 = m_3 + m_4 \) (mass conservation) is the total mass of the reactants/products. The chemical collision terms satisfy the following important properties [10]: \( \int J_i[f] \, d\mathbf{v} = \int J_2[f] \, d\mathbf{v} = -\int J_3[f] \, d\mathbf{v} = -\int J_4[f] \, d\mathbf{v} = G_{34} - G_{12} \), where

\[
G_{34} = \int \int V_{34} I_{12}^{12} f_3(v) f_4(v') \, d\mathbf{v} \, d\mathbf{v}' \, d\Omega', \quad (2.4)
\]

\[
G_{12} = \int \int V_{12} I_{12}^{34} f_1(v) f_2(v') \, d\mathbf{v} \, d\mathbf{v}' \, d\Omega'. \quad (2.5)
\]

In the following we derive macroscopic balance laws starting from the kinetic equation (2.1).

By integrating Eq. (2.1) over \( d\mathbf{v} \) and using the relation \( \int Q_i[f] \, d\mathbf{v} = 0 \) [15], we obtain the balance equations for particles \( i \):

\[
\frac{\partial n_i}{\partial t} + \nabla \cdot (n_i \mathbf{u}_i) = S_i, \quad (2.6)
\]

where the density \( n_i \), the drift velocity \( \mathbf{u}_i \) of the species \( i \), and the source term \( S_i \) due to the chemical interactions, are given by: \( n_i = \int f_i(v) \, d\mathbf{v} \), \( \mathbf{u}_i = (1/n_i) \int \mathbf{v} f_i(v) \, d\mathbf{v} \) and \( S_i = \lambda_i (G_{34} - G_{12}) \) with \( \lambda_i = 1 \) for \( i = 1, 2 \) and \( \lambda_i = -1 \) for \( i = 3, 4 \).

By multiplying Eq. (2.1) by \( m_i, \ m_i \mathbf{v} \) and \( E_i + m_i \mathbf{v}^2/2 \), by summing over \( i \) and by integrating over \( d\mathbf{v} \), we obtain the conservation equations for the mass, momentum and total energy:

\[
\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = 0, \quad (2.7)
\]

\[
\frac{\partial \rho}{\partial t} (\rho \mathbf{u}) + \nabla \cdot (\rho \mathbf{u} \otimes \mathbf{u} + \mathbf{P}) = 0, \quad (2.8)
\]

\[
\frac{\partial e}{\partial t} + \nabla \cdot [(e I + \mathbf{P}) \cdot \mathbf{u} + \mathbf{q}_{th} + \mathbf{q}_{ext}] = 0, \quad (2.9)
\]

where \( I \) is the unit tensor. Equations (2.7), (2.8), and (2.9) were derived by making use of the property [10] \( \sum_{i=1}^4 \int \psi_i(v) (J_i[f] + Q_i[f]) \, d\mathbf{v} = 0 \) which is
valid for $\psi_i = m_i, \psi_i = m_i v$ (three components), and $\psi_i = E_i + m_i v^2/2$ (mass, momentum, and total energy conservation). In Eq.s (2.7)-(2.9) $\rho = \sum_i m_i n_i$ is the total density and $u = (1/\rho) \sum_i m_i n_i u_i$ is the drift velocity of the mixture. We also posed $\Pi = \sum_i m_i \int (v - u) \otimes (v - u) f_i(v) dv, q_{\text{th}} = \frac{1}{2} \sum_i m_i f_i(v) dv$ and $q_{\text{int}} = \sum_i E_i \int (v - u) f_i(v) dv = \sum_i E_i n_i (u_i - u)$ which represent the stress tensor, the thermal energy flux and the internal energy flux, respectively. Finally, $\epsilon = \frac{1}{2} \rho u^2 + e_{\text{th}} + e_{\text{int}}$ is the total energy density where $e_{\text{th}} = \frac{3}{2} n \chi T$ and $e_{\text{int}} = \sum_i E_i n_i$ are the thermal energy density ($n = \sum_i n_i$ is the total density, $\chi$ is the Boltzmann constant and $T$ is the absolute temperature) and the internal energy density, respectively. Equations (2.6), (2.8) and (2.9) are exact but do not constitute a closed system. After suitable assumptions, this system can be made close in order to obtain a simplified tool for the macroscopic description of the mixture, in terms of $n_i, u$ and $T$.

3 Euler approximation

If the characteristic time of relaxation due to elastic interactions is much shorter than the one due to the reactions, we can set $Q_i[f] = 0$, whose solutions are the Maxwell distribution functions [15]:

$$f_i(v) = n_i \left(\frac{m_i}{2 \pi \chi T}\right)^{3/2} \exp \left[-\frac{m_i}{2 \chi T} (v - u)^2\right].$$  \hspace{1cm} (3.1)

At this point, $u_i, \Pi, q_{\text{th}}$ and $q_{\text{int}}$, as well as the source terms $S_i$, can be calculated as follows:

$$u_i = u, \quad \Pi = p \mathbb{I}, \quad q_{\text{th}} = q_{\text{int}} = 0,$$ \hspace{1cm} (3.2)

where $p = n \chi T$ is the pressure and

$$S_i = \lambda_i \left[\nu_{34}(T) n_3 n_4 - \nu_{12}(T) n_1 n_2\right],$$ \hspace{1cm} (3.3)

where the effective collision frequencies $\nu_{ij}$ are given by

$$\nu_{12}(T) = \left(\frac{\sqrt{m_1 m_2}}{2 \pi \chi T}\right)^3 \times$$

$$\int \int \int V_{12} I_{34}^{34}(V_{12}, \zeta) \exp \left(-\frac{m_1 v^2 + m_2 w^2}{2 \chi T}\right) dv dw d\Omega',$$ \hspace{1cm} (3.4)
\begin{align*}
\nu_{34}(T) &= \left(\frac{\sqrt{m_3 m_4}}{2 \pi \chi T}\right)^3 \times \\
&\int \int \int V_{34} I_{34}(V_{34}, \zeta) \exp \left(\frac{-m_3 \mathbf{v}^2 + m_4 \mathbf{w}^2}{2 \chi T}\right) \ d\mathbf{v} \ d\mathbf{w} \ d\Omega', \tag{3.5}
\end{align*}
and satisfy the following relationship [16]:

\begin{align*}
\frac{\nu_{34}(T)}{\nu_{12}(T)} &= \mathcal{R} \exp \left(\frac{\Delta E}{\chi T}\right), \tag{3.6}
\end{align*}

(the Arrhenius law), where \(\mathcal{R} = (\mu_{12}/\mu_{34})^{3/2}\) and \(\Delta E = E_3 + E_4 - (E_1 + E_2)\)
(without any loss of generality, we can take \(\Delta E > 0\)). At chemical equilibrium, 
\(G_{12} = G_{34}\), that is, \(S_i = 0\).

In this work we will consider the following class of microscopic collision frequencies:

\[ V_{34} I_{34}(V_{34}, \zeta) = C_{34}(\zeta) V_{34}^\delta \]

where \(C_{34}\) is a certain function of the \(\cos(\zeta)\) and \(\delta \leq 1\) describes the interaction law. The cases \(\delta = 0\) and \(\delta = 1\)
are well known as Maxwell and hard sphere models, respectively. After some calculations, from Eq. (3.5), we explicitly obtain

\begin{align*}
\nu_{34}(T) &= 4 \sqrt{\pi} \left(\frac{2 \chi T}{\mu_{34}}\right)^{\delta/2} \Gamma \left(\frac{\delta + 3}{2}\right) \int_{-1}^{1} C_{34}(\zeta) \ d\zeta \\
&= A_{34} (\chi T)^{\delta/2}, \tag{3.7}
\end{align*}

where \(\Gamma\) is the gamma function [17], with \(\delta > -3\).

Due to the Arrhenius law, we soon obtain

\begin{align*}
\nu_{12}(T) &= \frac{A_{34}}{\mathcal{R}} (\chi T)^{\delta/2} \exp \left(\frac{-\Delta E}{\chi T}\right), \tag{3.8}
\end{align*}

where \(A_{34}\) is a constant.

### 4 Dispersion relation

Let us introduce the following notations to indicate a homogeneous equilibrium state \(n_i \equiv n_i^e, T \equiv T^e\) with \(S_i \equiv S_i^e = 0\) and we assume, without any loss of generality, \(\mathbf{u} = 0\).

We consider the propagation of a harmonic plane wave:

\begin{align*}
n_i &= n_i^e + N_i \exp[i \ (\chi x - \omega t)], \tag{4.1}
\end{align*}
\[ u = \mathcal{U} \exp[i(kx - \omega t)] , \]
\[ T = T^e + \mathcal{T} \exp[i(kx - \omega t)] , \]

where \( u = \mathbf{u} \cdot \mathbf{i} \), where \( \mathbf{i} \) is the unit vector along the wave propagation.

By inserting Eqs. (4.1)-(4.3) into Eqs. (2.6), (2.8) and (2.9), after the linearization with respect to \( N_i, \mathcal{U} \) and \( \mathcal{T} \), we obtain:

\[ -i \omega N_1 + i \kappa n^e_1 \mathcal{U} = S^*_1 , \]
\[ -i \omega (N_1 - N_2) + i \kappa (n^e_1 - n^e_2) \mathcal{U} = 0 , \]
\[ -i \omega (N_1 + N_3) + i \kappa (n^e_1 + n^e_3) \mathcal{U} = 0 , \]
\[ -i \omega (N_1 + N_4) + i \kappa (n^e_1 + n^e_4) \mathcal{U} = 0 , \]
\[ -i \omega \rho' \mathcal{U} + i k \chi \left( n^e \mathcal{T} + T^e \sum_i N_i \right) = 0 , \]
\[ -i \omega \left( n^e \mathcal{T} + T^e \sum_i N_i \right) - i \omega \sum_i E_i N_i + i \kappa \left( \frac{5}{2} \chi n^e + \sum_i E_i n^e_i \right) \mathcal{U} = 0 , \]

where

\[ S^*_1 = \nu_{34}(T^e) (n^e_3 N_4 + n^e_4 N_3) - \nu_{12}(T^e) (n^e_1 N_2 + n^e_2 N_1) \]
\[ + \mathcal{T} \left[ \nu'_{34}(T^e) n^e_3 n^e_4 - \nu'_{12}(T^e) n^e_1 n^e_2 \right] . \]

Since at equilibrium \( \nu_{34}(T^e) n^e_3 n^e_4 = \nu_{12}(T^e) n^e_1 n^e_2 = R \), from Eq. (3.6) it follows that \( \nu'_{34}(T^e) n^e_3 n^e_4 - \nu'_{12}(T^e) n^e_1 n^e_2 = -R \Delta E/\chi T^2 \).

Non trivial solutions of the system of Eq.s (4.4)-(4.9) for \( N_i, \mathcal{U} \) and \( \mathcal{T} \), are obtained if, and only if, the determinant of the coefficients vanishes. This condition gives the dispersion relationship, which links \( k \) and \( \omega \) [16]:

\[ - \frac{\omega^2}{a^2_e} + k^2 - i \omega \tau \left( -\frac{\omega^2}{a^2_f} + k^2 \right) = 0 , \]

where the coefficients \( a_e \) and \( a_f \) are the equilibrium flow and frozen flow speed of sound, respectively, while \( \tau \) is a characteristic time of the reaction. Explicitly, we have

\[ a^2_f = \frac{5}{3} \chi \frac{n^e T^e}{\rho^e} , \]
\[ a^2_e = a^2_f \left[ \sum_i \frac{1}{n^e_i} + \frac{2}{5} n^e \left( \frac{\Delta E}{\chi T^e} \right)^2 \right] \left[ \sum_i \frac{1}{n^e_i} + \frac{2}{3} n^e \left( \frac{\Delta E}{\chi T^e} \right)^2 \right]^{-1} . \]
\[
\frac{1}{\tau} = R \left[ \sum_i \frac{1}{n_i^e} + \frac{2}{5} n_e^e \left( \frac{\Delta E}{\chi^e} \right)^2 \right].
\] (4.14)

It is easy to verify that \( a_f > a_e \), according to non-equilibrium thermodynamics [18]. We can observe that the dispersion relation can be written as \( k^2 P(i \omega) + \omega^2 Q(i \omega) = 0 \) where \( P \) and \( Q \) are first order polynomials of \( i \omega \).

5 Travelling wave solutions

When the macroscopic fields \( n_i, u_i \) and \( T \) only depend on one spatial coordinate \( x \) and on the time \( t \) the macroscopic balance laws in the Euler approximation become:

\[
\partial_t n_i + \partial_x (n_i u) = S_i,
\] (5.1)
\[
\partial_t (\rho u) + \partial_x (\rho u^2 + n \theta) = 0,
\] (5.2)
\[
\partial_t e + \partial_x [(e + n \theta) u] = 0,
\] (5.3)

where \( \theta = \chi T \).

In the following we consider the travelling wave solutions of the system described by Eq.s (5.1)-(5.3), that is, we look for solutions that only depend on the independent variable \( \xi = x - vt \) where, due to the Galilei invariance of the system, we can set the velocity \( v \) of the travelling wave equal to zero. Eq.s (5.1)-(5.3) become:

\[
\frac{d}{d\xi} (n_i u) = S_i,
\] (5.4)
\[
\frac{d}{d\xi} (\rho u^2 + n \theta) = 0,
\] (5.5)
\[
\frac{d}{d\xi} [(e + n \theta) u] = 0,
\] (5.6)

which is a system of six nonlinear ODEs that have to be solved with the appropriate initial conditions. In the following we use a plus/minus superscript to indicate the asymptotic values at \( \xi = \pm \infty \). We anticipate that the soliton solution will connect two asymptotic equilibrium states. This means

\[
S_i^\pm = 0.
\] (5.7)
We fix the values of the density $n_i^-$ and the drift velocity $u^-$ as initial data, at $\xi \to -\infty$. Then, from Eq. (5.7), using Eqs (3.3) and (3.6), it follows that

$$\theta^- = \Delta E \left\{ \log \left[ R^{-1} \left( \frac{n_i^- n_j^-}{n_i n_j} \right) \right] \right\}^{-1} .$$

(5.8)

Taking into account the definition of $S_i$, Eqs (5.4) can be rewritten as follows:

$$\frac{d}{d\xi} (n_i u) = S_i ,$$

(5.9)

$$\frac{d}{d\xi} \left[ (n_i - \lambda_j n_j) u \right] = 0 , \quad j = 2, 3, 4 .$$

(5.10)

Eqs (5.5), (5.6) and (5.10) are of immediate integration and give the constants of motion of the system. Eq. (5.9) is the only dynamical equation and allows us to obtain the structure of the wave after integration.

From Eqs (5.10) we obtain:

$$[n_i (\xi) - \lambda_j n_j (\xi)] u(\xi) = (n_i^- - \lambda_j n_j^-) u^- ,$$

(5.11)

and taking into account the definitions of the quantities $n, \rho, e_{\text{int}}$, given in section 2, we obtain the following relations:

$$n(\xi) = \frac{\mu}{u(\xi)} ,$$

(5.12)

$$\rho(\xi) = \frac{\varphi}{u(\xi)} ,$$

(5.13)

$$e_{\text{int}}(\xi) = \frac{\epsilon}{u(\xi)} - \Delta E n_i (\xi) ,$$

(5.14)

where $\mu = n^- u^-, \varphi = \rho^- u^-$ and $\epsilon = e^- u^- + \Delta E u^- n_i^-$. By using Eq. (5.5) we obtain

$$\theta(\xi) = \frac{u(\xi)}{\mu} [\tau - \varphi u(\xi)] ,$$

(5.15)

with $\tau = \rho^- (u^-)^2 + n^- \theta^-$, which gives the temperature $\theta(\xi)$ as a function of velocity $u(\xi)$.

If we now introduce Eq. (5.15) into Eq. (5.6), and use Eqs (5.12)-(5.14) we obtain, after integration,

$$n_i (\xi) = \frac{\alpha_i}{u(\xi)} + \lambda_i \left[ \beta u(\xi) + \gamma \right] , \quad i = 1, \cdots, 4$$

(5.16)
it should be observed that \( n_i \) is singular for \( u = 0 \), with \( \alpha_i = \lambda_i \left( (\epsilon - \varepsilon)/\Delta E - (n_i^+ - \lambda_i n_i^-) u^- \right) \), \( \beta = -2 \varphi/\Delta E \), \( \gamma = 5 \tau/2 \Delta E \) where \( \varepsilon = \left[ \rho^- (u^-)^2/2 + 5 n^- \theta^-/2 + e_{\text{int}}^- \right] u^- \). Eq. (5.16) gives the concentrations \( n_i(\xi) \) as functions of only the velocity \( u(\xi) \).

Finally, by using Eq. (5.16) in Eq. (5.9) follows the nonlinear ODE:

\[
\frac{du}{d\xi} = R[u],
\]

(5.17)

with

\[
R[u] = \frac{S_i[u]}{2\beta u + \gamma}.
\]

(5.18)

Eq. (5.17), after numerical integration, gives us \( u(\xi) \) and, if Eqs (5.15)-(5.16) are used, we can find \( \theta(\xi) \) and \( n_i(\xi) \).

Some conditions are now discussed that have to be satisfied to obtain physically meaningful results. It is well known that solitons of Eq. (5.17) reach finite asymptotic values which are two consecutive zeros of \( R[u] \) [19]. This implies, as we anticipated, \( S_i^\pm = 0 \), so that the solitary wave connects two asymptotic states where the system is at chemical equilibrium. By choosing the initial data \( n_i^- > 0 \) and \( u^- \), we obtain \( \theta^- \) from Eq. (5.8), which must be positive. This implies the following constraint on \( n_i^- \) (the first condition):

\[
\frac{n_i^- n_i^-}{n_i^- n_i^-} > R.
\]

(5.19)

Subsequently, we solve the transcendental equation \( S_i[u] = 0 \). Its roots are the asymptotic values \( u^\pm \) of \( u(\xi) \). Regular solutions of Eq. (5.17) require that there are no singularities of \( R[u] \) in the interval \([u_{\text{min}}, u_{\text{max}}]\), where \( u_{\text{min}} = \min(u^-, u^+) \) and \( u_{\text{max}} = \max(u^-, u^+) \). Singularities in \( R[u] \) arise both for \( u = 0 \) and \( 2 \beta u + \gamma = 0 \). The condition \( u \neq 0 \) implies \( u^- u^+ > 0 \) (the second condition), while \( 2 \beta u + \gamma \neq 0 \) for \( u \in [u_{\text{min}}, u_{\text{max}}] \) is the third condition that has to be satisfied. Finally, by using Eqs (5.15) and (5.16), from \( u^+ \) we obtain the asymptotic values \( n_i^+ \) and \( \theta^+ \), which must be positive (the fourth condition). When all these conditions are satisfied, by choosing an arbitrary initial value \( u_0 \in [u_{\text{min}}, u_{\text{max}}] \), we can finally forward and backward integrate Eq. (5.17) in order to obtain the structure of the travelling wave which connects the two chemical equilibrium states at \( \pm \infty \).

In the following we present and discuss some numerical solutions which connect the same asymptotic equilibrium, for various choices of \( \delta \). The behaviour of the gas is depicted in figure 1 as a whole, by plotting: the drift velocity \( u \), temperature \( \theta \), total density \( n \) and pressure \( p \). It should be observed that, as
Fig. 1. Plot, in arbitrary units, of the drift velocity $u$, temperature $\theta$, total density $n$ and pressure $p$, for different values of the parameter $\delta$: $\delta = 1$ (dash-dot line), $\delta = 0$ (dash-dot-dot line), $\delta = -1$ (dot line), $\delta = -2$ (dash line) and $\delta \to -3$ (solid line).

$\theta < 1$ in our example, for lower $\delta$ is the higher are $\nu_{12}$ and $\nu_{34}$, and the steeper the curves. On the other hand, in the case $\theta > 1$, we would get smoother and smoother curves for increasingly lower values of $\delta$.

The molar fractions $\chi_i$ are plotted in figure 2 for the four species, which are defined by $\chi_i = n_i / n$. This quantity has another interesting meaning. It is easy to realize that $\chi_i$ is proportional to the current density $j_i = n_i u$. The slopes $\chi_i' = d \chi_i / d \xi$ are simply related by $\chi_1' = \chi_2' = -\chi_3' = -\chi_4'$, for each value of $\delta$.

Finally, it is possible to observe that, as the temperature decreases, $\nu_{12}$ decreases with respects to $\nu_{34}$. This means that the backward reaction prevails over the forward one, that is, the number of particles 1 and 2 increases while the number of particles 3 and 4 decreases, as can be seen in the plots.

6 Conclusions

We have studied a kinetic model for a mixture of gases with bimolecular reversible reactions, in the extended kinetic theory. The kinetic equations have been obtained starting from the Boltzmann equation and taking into account both the elastic collision integrals and the chemical collision terms between
Fig. 2. Plot, in arbitrary units, of the molar fractions $\chi_i$, for different values of the parameter $\delta$: $\delta = 1$ (dash-dot line), $\delta = 0$ (dash-dot-dot line), $\delta = -1$ (dot line), $\delta = -2$ (dash line) and $\delta \rightarrow -3$ (solid line).

the particles. A closed set of equations is obtained in the Euler approximation, under the assumption that the relaxation due to the elastic scattering is much quicker than the one due to the chemical interaction. Six partial differential equations are derived which govern the evolution of the corresponding unknown macroscopic fields (the densities $n_i$, momentum and total energy). Some numerical results have also been presented for the simple case of a plane steady travelling wave solution, for various meaningful interaction laws. Finally, the shape of the soliton that represent the main macroscopic observables for the gas mixture (the drift velocity, temperature, total density, pressure and chemical composition) are discussed.

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