Steady detonation problem for slow and fast chemical reactions

F. Conforto, M. Groppi, R. Monaco, and G. Spiga

1 Dipartimento di Matematica, Università di Messina, Contrada Papardo, Salita Sperone 31, 98166 Messina, Italy fiamma@dipmat.unime.it
2 Dipartimento di Matematica, Università di Parma, Via D’Azeglio 85, 43100 Parma, Italy maria.groppi@unipr.it, giampiero.spiga@unipr.it
3 Dipartimento di Matematica, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Torino, Italy roberto.monaco@polito.it

Summary. Two sets of hydrodynamic equations for a mixture of four gases undergoing a bimolecular chemical reaction are discussed. The former consists in a system of balance laws for the case of a chemical relaxation time of the same order of the macroscopic processes (slow reaction). Conversely, the latter is a system of conservation laws for the case of short chemical relaxation time (fast reaction). After the analysis of the hyperbolic nature of the hydrodynamic equations, we formulate and solve the problem of the stationary propagation of a detonation wave. The differences of the shock structure in the two cases are shown by the presented numerical results.

1 Introduction and kinetic preliminaries

A rigorous mathematical modelling of chemically reacting gas mixtures in view of practical applications is a fundamental problem in the scientific literature [Cer00, Gio99]. On the other hand, kinetic approaches to chemical reactions in a gas have steadily gained interest and importance in the last decades. Indeed, consideration of the kinetic level is a necessary though difficult step in order to go deeper into the physical understanding of the process; moreover, kinetic equations represent also the starting point for a consistent derivation, via suitable expansion algorithms and closure strategies, of adequate hydrodynamic equations for reacting flows at a macroscopic level [Gio99]. The task is quite formidable even in absence of chemical reactions, and it is typically accomplished by an asymptotic procedure of Hilbert or Chapman-Enskog type with respect to the small parameter constituted by the Knudsen number, labelling the importance of collision terms in collision dominated regimes [CC70, FK72].

In the present work, however, we confine ourselves only to the reactive Euler equations following as zero order asymptotics from the kinetic scheme
proposed in [RS99, GS99] for a simple bimolecular chemical reaction. We shall assume that the typical relaxation time for mechanical encounters (elastic scattering) and/or the characteristic time relevant to chemical interactions are much shorter than the typical macroscopic times. Hydrodynamic variables are determined by the dominant operator driving the process, and quite different scenarios occur in different physical situations. In particular, we shall examine here those which appear as most significant, namely the case of dominant elastic scattering only (slow chemical reaction), and the one in which the dominant role is played by the whole, mechanical plus chemical, collision term (fast chemical reaction). The two physical situations imply different hydrodynamics, and the relevant equations will be applied and compared to each other in the solution of a typical problem like propagation of steady detonation waves.

We consider a mixture of four gases \( A_s, s = 1, \ldots, 4 \) which, besides all elastic collisions, can interact according to the bimolecular chemical reaction

\[
A_1 + A_2 \rightleftharpoons A_3 + A_4,
\]

under the simplifying assumption of translational degrees of freedom only.

In what follows, \( f_s \) denotes the \( s \)-th one-particle distribution function, with \( \boldsymbol{f} \) for the vector \( (f_1, f_2, f_3, f_4) \), symbols \( m_s \) and \( E_s \) stand for particle mass and internal energy of chemical link, with \( m_1 + m_2 = m_3 + m_4 = M \) (mass conservation). Index ordering may always be chosen in such a way that \( \Delta E = E_3 + E_4 - E_1 - E_2 \geq 0 \) (endothermic direct reaction in (1)).

After suitable scaling, the set of dimensionless extended Boltzmann equations reads as

\[
\frac{\partial f_s}{\partial t} + \mathbf{v} \cdot \frac{\partial f_s}{\partial \mathbf{x}} = \frac{1}{\epsilon^p I_s[\boldsymbol{f}]} + \frac{1}{\epsilon^q J_s[\boldsymbol{f}]} \quad s = 1, 2, 3, 4
\]

where \( I_s \) and \( J_s \) denote the elastic and the chemical collision terms, respectively. The former include scattering contributions to the species \( s \) due to encounters with molecules of any other species \( r \), different or not, whereas the latter is made up by a single collision integral, since there is a unique chemical reaction in which species \( s \) is gained or lost. Explicit expressions for all collision terms may be found in the quoted literature, to which we refer the interested reader, in terms of suitable differential cross sections and pre–collisional velocities. The direct reaction in (1) can occur only if the kinetic energy of the relative motion overcomes the endothermic threshold \( \Delta E \).

The crucial point for what follows is that the scaling singles out spontaneously the mechanical and chemical Knudsen numbers, labelled respectively by \( \epsilon^p \) and \( \epsilon^q \), where \( p \) and \( q \) are integers, and \( \epsilon \) denotes the small parameter. Slow chemical reaction corresponds to the option \( p = 1 \), \( q = 0 \), in which the process is driven by elastic scattering and chemical relaxation times are of the order of macroscopic times. The choice \( p = 1 \), \( q = 1 \) describes instead the case of fast chemical reaction, in which mechanical and chemical
encounters together are dominant in the evolution. For both physical situations we are interested in the slow macroscopic regime in the limit when \( \epsilon \to 0 \), after the fast transient taking place in the \( O(\epsilon) \) initial layer. The difference is in that the transient corresponds to a sudden approach to an equilibrium which is only mechanical, in the former case, and both mechanical and chemical, in the latter. We shall not enter into the detailed structures and properties of the various collision operators, which may be found elsewhere [RS99, GS99, BS04, BGS05]. Here we consider only two different set of hydrodynamic equations, obtained by two suitable closures at the Euler level.

2 Hydrodynamic equations

The mechanical operator \( \mathbf{I} \) has a 8–dimensional linear space of collision invariants (number of molecules in each species, total momentum, total kinetic energy), and the relevant hydrodynamic quantities, moments of the distribution function, may be identified as the four number densities \( n_s \), the three components of the mass velocity \( \mathbf{u} \), and the gas temperature \( T \). Of course, other choices might be devised, and they could involve mass densities \( \rho_s \), global number (or mass) density \( n \) (or \( \rho \)), thermal energy \( \frac{3}{2}nKT \), but we shall stick here to the previous ones.

On using, for the slow reaction case, such collision invariants as test functions, macroscopic, \( \epsilon \)-independent, conservation equations are obtained as weak forms of the kinetic equations (2). Clearly, conservation is meant with respect to the dominant operator \( \mathbf{I} \) only, which does not appear in the final output. These equations are exact but not closed, because of the appearance of other independent moments contributed by the streaming operator (drift velocity of each species, viscous stress tensor, heat flux), and also of complicated integrals of the distribution functions themselves, contributed by the chemical collision term. The Euler closure is achieved upon resorting, in computing all additional moments and integrals, to the equilibrium distribution functions relevant to the dominant operator. Such functions are indeed in a one–to–one relationship with the eight conserved quantities above, and, more precisely, the \( s \)-th equilibrium distribution is provided by a Maxwellian with density \( n_s \), drift velocity \( \mathbf{u} \), and temperature \( T \). Reactive Euler equations constitute a set of 8 partial differential equations, and read as [RS99]

\[
\begin{align*}
\frac{\partial n_s}{\partial t} + \frac{\partial}{\partial x} \cdot (n_s \mathbf{u}) &= \sigma_s Q_s \\
\frac{\partial (\rho \mathbf{u})}{\partial t} + \frac{\partial}{\partial x} \cdot \left( \rho \mathbf{u} \otimes \mathbf{u} + nKT \mathbf{I} \right) &= 0 \\
\frac{\partial}{\partial t} \left( \frac{1}{2} \rho \mathbf{u}^2 + \frac{3}{2} nKT \right) + \frac{\partial}{\partial x} \left[ \left( \frac{1}{2} \rho \mathbf{u}^2 + \frac{5}{2} nKT \right) \mathbf{u} \right] &= Q \Delta E
\end{align*}
\]

with \( \sigma_1 = \sigma_2 = -\sigma_3 = -\sigma_4 = 1 \) and \( n = \sum_{s=1}^{4} n_s \), \( \rho = \sum_{s=1}^{4} m_s n_s \) global number and mass density, respectively. The source term \( Q \), coming from the chemical collision integral, is given by

\[
Q = \left[ n_3 n_4 \left( \frac{m_1 m_2}{m_3 m_4} \right)^{\frac{3}{2}} \exp \left( \frac{\Delta E}{K T} \right) - n_1 n_2 \right] \gamma_{12}^{34}(T),
\]

where \( \gamma_{12}^{34}(T) \) is a suitable Gaussian–weighted collision frequency for the chemical reaction [GS01].

A different scenario is in order for \( p = q = 1 \), namely when the whole collision operator \( I + J \) plays the dominant role. Now the space of collision invariants is only 7–dimensional. In fact, the number of molecules in each species does not remain constant under the action of \( J \), and there are only three independent combinations of species in which the number of particles is conserved, which may be chosen as the pairs \((1, 3), (1, 4), (2, 4)\). The total number of molecules and the total mass are of course still conserved, as well as the total momentum. Moreover, energy is conserved only if each particle is endowed with its chemical energy \( E_s \), in addition to its kinetic energy \( \frac{1}{2} m_s v^2 \).

The relevant hydrodynamic variables may be chosen as three combinations of number densities, like \( n_1 + n_3, n_1 + n_4, n_2 + n_4 \), mass velocity \( u \), and total (thermal plus chemical) internal energy \( \frac{3}{2} n_k T + \sum_{s=1}^{4} E_s n_s \). Again, other options could be adopted, like, as we shall see, \( n_1 - n_2, n_1 + n_3, n_1 + n_4, u, \frac{3}{2} n_k T - n_1 \Delta E \). For any choice of independent collision invariants, the corresponding weak forms of the kinetic equations are appropriate, \( \epsilon \)-independent, macroscopic conservation equations, describing conservation laws with respect to the whole collision operator. Once more, the resulting equations are exact but not closed, and their Euler closure is achieved by substituting collision equilibria for the actual distribution functions, whenever they appear in form not amenable to hydrodynamic variables. Such equilibria constitute now a 7–parameter family, and they are provided by Gaussian shapes, sharing again common drift velocity \( u \) and temperature \( T \), but with number densities \( n_s \) which are not independent, since they must obey the well known mass action law of chemistry

\[
\frac{n_1 n_2}{n_3 n_4} = \left( \frac{m_1 m_2}{m_3 m_4} \right)^{\frac{3}{2}} \exp \left( \frac{\Delta E}{K T} \right).
\]

According to the several possible options mentioned before for the hydrodynamic variables, there are several ways of writing down the fast reactive Euler equations. Choosing to play with the same classical 8 unknown fields of the slow case, they can be cast as a set of 7 partial differential equations [BGS05, BS04]
Slow and fast reactions

\[ \frac{\partial}{\partial t} (n_s + n_r) + \frac{\partial}{\partial x} \left[ (n_s + n_r) \mathbf{u} \right] = 0 \quad (s, r) = (1, 3), (1, 4), (2, 4) \]

\[ \frac{\partial}{\partial t} (\rho \mathbf{u}) + \frac{\partial}{\partial x} \cdot (\rho \mathbf{u} \otimes \mathbf{u} + nKT \mathbf{I}) = 0 \]

\[ \frac{\partial}{\partial t} \left( \frac{1}{2} \rho u^2 + \frac{3}{2} nKT + \sum_{s=1}^{4} E_s n_s \right) + \frac{\partial}{\partial x} \cdot \left[ \left( \frac{1}{2} \rho u^2 + \frac{5}{2} nKT + \sum_{s=1}^{4} E_s n_s \right) \mathbf{u} \right] = 0, \]

which, coupled to the transcendental equation (5), makes up the pertinent self-consistent system governing the evolution.

Notice that, as clear on physical grounds, chemical reactions are accounted for in different manner in the two different situations. In the slow reaction case, they proceed at the same pace as streaming, and they act on the evolution through the source term \( Q \). In the fast reaction case, due to the much shorter chemical relaxation time, chemical equilibrium is reached instantaneously; the mass action law provides the closure of the macroscopic differential equations, where otherwise there would be no trace of chemical reactions.

### 3 Hyperbolic balance equations in the different regimes

Equations (3), (6) in one dimension can be written in the following conservative form

\[ \frac{\partial}{\partial t} \mathbf{F}(\mathbf{U}) + \frac{\partial}{\partial x} \mathbf{G}(\mathbf{U}) = \mathbf{H}(\mathbf{U}) \]  

where in the slow reaction case

\[ \mathbf{F}(\mathbf{U}) = \left( n_1, n_2, n_3, n_4, \rho u, \frac{1}{2} \rho u^2 + \frac{3}{2} nKT \right)^T \]

\[ \mathbf{G}(\mathbf{U}) = \left( n_1 u, n_2 u, n_3 u, n_4 u, \rho u^2 + nKT, \left( \frac{1}{2} \rho u^2 + \frac{5}{2} nKT \right) u \right)^T \]

with the field vector \( \mathbf{U} \) given by

\[ \mathbf{U} = (n_1, n_2, n_3, n_4, u, T)^T, \]

whereas in the fast one we preferred to re-write the system (6) in a slightly different form:

\[ \mathbf{F}(\mathbf{U}) = \left( y_1, y_2, y_3, \rho u, \frac{1}{2} \rho u^2 + \mathcal{U} \right)^T \]

\[ \mathbf{G}(\mathbf{U}) = \left( y_1 u, y_2 u, y_3 u, \rho u^2 + nKT, \left( \frac{1}{2} \rho u^2 + \mathcal{U} + nKT \right) u \right)^T \]
where we chose as field variables the vector

\[ \mathbf{U} = (y_1, y_2, y_3, u, \mathbf{U})^T, \]

being

\[ y_1 = n_1 - n_2, \quad y_2 = n_1 + n_3, \quad y_3 = n_1 + n_4, \quad \mathbf{U} = \frac{3}{2} nKT - n_1 \Delta E. \quad (9) \]

Moreover in the former case the vector function \( \mathbf{H}(\mathbf{U}) \) is given by

\[ (Q, Q, -Q, -Q, 0, Q \Delta E); \]

conversely, in the latter, \( \mathbf{H}(\mathbf{U}) \) is the null vector. Thus, equations (3) turn out to be a set of balance laws, whereas equations (6) are conservation laws.

In equations (9) \( T \) has to be understood as a known function of the densities as imposed by (5), which determines also the scalar pressure \( p = nKT \).

Total number and mass densities, in terms of the field variables, are

\[ n = y_2 + y_3 - y_1, \quad \rho = m_3 y_2 + m_4 y_3 - m_2 y_1. \quad (10) \]

The same equations (9) establish a one–to–one relationship between the set of variables \((n_1, n_2, n_3, n_4)\) and \((y_1, y_2, y_3, \mathbf{U})\). In fact they can be inverted yielding

\[ n_2 = n_1 - y_1, \quad n_3 = y_2 - n_1, \quad n_4 = y_3 - n_1, \quad (11) \]

with \( n_1 \) given implicitly by the following transcendental equation

\[ \mathcal{F}(n_1; y_1, y_2, y_3, \mathbf{U}) = \frac{3(y_2 + y_3 - y_1) \Delta E}{2 \log \left[ \left( \frac{m_3 m_4}{m_1 m_2} \right)^{3/2} \frac{n_1(n_1 - y_1)}{(y_2 - n_1)(y_3 - n_1)} \right]} - n_1 \Delta E - \mathbf{U} = 0, \quad (12) \]

where the left hand side is a monotonically decreasing function of \( n_1 \), ranging from \(+\infty\) to \(-\min\{y_2, y_3\} \Delta E - \mathbf{U} < 0\). Therefore there exists a unique root

\[ n_1 = n_1(y_1, y_2, y_3, \mathbf{U}), \quad (13) \]

and it is easy to check that (13) is a homogeneous function of order one in its variables.

Now, the hyperbolic nature of equations (3),(6) can be easily proven. In fact the characteristic velocities of the set (7), namely the eigenvalues of the matrix

\[ [\nabla \mathbf{U} \mathbf{F}(\mathbf{U})]^{-1} \nabla \mathbf{U} \mathbf{G}(\mathbf{U}), \quad (14) \]

are real functions of the field variables \( \mathbf{U} \). In particular, for the slow reaction case, we have

\[ \lambda_1 = u - \sqrt{\frac{5}{3} \frac{nKT}{\rho}}, \quad \lambda_{2,3,4,5} = u, \quad \lambda_6 = u + \sqrt{\frac{5}{3} \frac{nKT}{\rho}}. \quad (15) \]
Calculation of the eigenvalues for the fast reaction case is a bit more complicated so that it is convenient to re-write the set (6) in the following way

\[
\frac{\partial y_i}{\partial t} + u \frac{\partial y_i}{\partial x} + y_i \frac{\partial u}{\partial x} = 0 \quad i = 1, 2, 3
\]

\[
\frac{\partial u}{\partial t} + u \frac{\partial u}{\partial x} + \frac{2}{3\rho} \frac{\partial}{\partial x} (U + n_1 \Delta E) = 0
\]

\[
\frac{\partial U}{\partial t} + u \frac{\partial U}{\partial x} + \left( \frac{5}{3} U + 2 \frac{n_1}{3} \Delta E \right) \frac{\partial u}{\partial x} = 0.
\]

With this equivalent choice of the vectors \( F \) and \( G \) the matrix (14) becomes

\[
\begin{pmatrix}
  u & 0 & 0 & y_1 & 0 \\
  0 & u & 0 & y_2 & 0 \\
  0 & 0 & u & y_3 & 0 \\
  \frac{2\Delta E}{3\rho} \frac{\partial n_1}{\partial y_1} & \frac{2\Delta E}{3\rho} \frac{\partial n_1}{\partial y_2} & \frac{2\Delta E}{3\rho} \frac{\partial n_1}{\partial y_3} & u & 2 \frac{1}{3\rho} \left( 1 + \Delta E \frac{\partial n_1}{\partial U} \right) \\
  \frac{5}{3} U + 2 \frac{n_1}{3} \Delta E & u
\end{pmatrix}
\]

and standard algebra provides the following expression for the five eigenvalues

\[
\lambda_1 = u - c, \quad \lambda_{2,3,4} = u, \quad \lambda_5 = u + c,
\]

where

\[
c^2 = \frac{2U + 2}{3} \rho \Delta E \frac{\partial n_1}{\partial U} + \frac{2\Delta E}{3\rho} \left( y_1 \frac{\partial n_1}{\partial y_1} + y_2 \frac{\partial n_1}{\partial y_2} + y_3 \frac{\partial n_1}{\partial y_3} + U \frac{\partial n_1}{\partial U} \right).
\]

Now, resorting to Euler’s theorem on homogeneous functions and expressing \( \frac{\partial n_1}{\partial U} \) in terms of the implicit function theorem, yields the more manageable form

\[
c^2 = \frac{5}{3} \frac{nKT}{\rho} \left[ 1 + 2 \Delta E \left( \frac{\partial F}{\partial n_1} \right)^{-1} \right],
\]

where

\[
\frac{\partial F}{\partial n_1} = -\Delta E \left\{ 1 + \frac{3n \left( \frac{1}{n_1} + \frac{1}{n_2} + \frac{1}{n_3} + \frac{1}{n_4} \right)}{2\log^2 \left( \frac{m_3 m_4}{m_1 m_2 n_1 n_2 n_3 n_4} \right)} \right\}.
\]

Knowledge of \( y_1, y_2, y_3, U \) allows to calculate all densities, and consequently \( \frac{\partial F}{\partial n_1} \), in terms of the field variables. Observe that the last quantity is smaller than \(-\Delta E\), so that it results
Thus, comparison of (15) with (18), shows that in the fast reaction case the slowest and fastest characteristic velocities are closer to $u$ than in the slow reaction case.

The numerical calculation of $c$ goes through the solution of the transcendental equation (12) for $n_1$ as function of the given $y_i$ and $U$, and through the use of (10) and (11), to be inserted into (21) and finally into (20), after determining $T$ by means of (5).

4 Steady detonation problem

A steady detonation wave is a shock wave that propagates with constant velocity $D$ in one direction, say $x$, and is driven by a chemical process [FD79, Kuo86]. This process can be described as follows
(a) Ahead of the shock wave, $\forall x > x_0$ the gas mixture is in thermal and chemical equilibrium, and no chemical reaction takes place.
(b) At the point $x_0$ there is a jump discontinuity moving with velocity $D$.
(c) If the chemical reaction is very fast (infinite reaction rate) then the combustion process is exhausted within the shock front and behind the shock the mixture is again in chemical equilibrium. This kind of detonation is referred in literature (see, for instance, [FD79]) as the simplest model of detonation.
(d) If the chemical processes are relatively slow (finite reaction rate) then the shock front is followed by a finite region characterized by chemical disequilibrium until a point $x_F < x_0$, where the mixture reaches again equilibrium. This kind of detonation is well described in literature and accounted as the ZND–model [FD79, Kuo86].

In paper [CGMS04] the detonation process has been quantitatively determined, for the slow reaction case, by using the following procedure
(i) Apply the Rankine-Hugoniot conditions [Kuo86] to (7), across the jump. By this first step one relates the field variables in the unperturbed region ahead the shock, say $U_0$, to those in the edge of the shock, say $U_N$, at given $D$. In formulae

$$U_N = U_N(U_0; D), \quad U_N = \lim_{x \to x_G^-} U, \quad U_0 = \lim_{x \to x_G^+} U.$$

(ii) Introduce the transformation $z = x - Dt$ in order to re-write equation (7) in the form

$$\frac{d}{dz} [G(U) - DF(U)] = H(U).$$

(iii) Re-arrange the last equation so that it can be re-written as a normal system of ODE’s in the field variables, namely
where $K$ vanishes with $H$.

(iv) Solve, at least numerically, equation (23) with the boundary conditions

$$
\lim_{z \to z_{i_{F}}} U(z) = U_{N}, \quad \left. \frac{dU}{dz} \right|_{z = z_{F}} = 0.
$$

In order to assure stability to the solution of the steady detonation problem, some constraints must be fulfilled. By ordering in an increasing way the eigenvalues of the system and by calling with $\lambda_{k}$ the greatest one, the following well-known Lax evolutionary conditions [Lax57] must be satisfied

$$
D > \lambda_{k}(U_{0}), \quad \lambda_{k-1}(U) < D < \lambda_{k}(U) \quad \forall z \in [x_{F}, x_{0}].
$$

In paper [CGMS04] the above procedure has been applied to equation (3). We resume here the results, without going into details that will be explained deeper in the case of equation (6).

From the Rankine-Hugoniot conditions applied to (3) we have obtained

$$
n_{iN} = \frac{D - u_{0}}{D - u_{N}} n_{i0}, \quad i = 1, \ldots, 4
$$

$$
T_{N} = \frac{1}{K} \left[ \frac{\rho_{0}(u_{N} - u_{0})}{n_{0}} + \frac{KT_{0}}{D - u_{0}} \right] (D - u_{N})
$$

$$
u_{N} = \frac{3}{4} D + \frac{1}{4} u_{0} - \frac{5}{4} \frac{n_{0}KT_{0}}{\rho_{0}(D - u_{0})}.
$$

After applying steps (ii) and (iii) of the above procedure, the last expressions have been used as initial data for integrating numerically the ODE’s (23), which in this case turn out to be

$$
\frac{dn_{i}}{dz} = \frac{Q}{D - u} \left[ \frac{2\Delta E_{n_{i}}}{5nKT - 3\rho(D - u)^{2}} - \sigma_{i} \right], \quad i = 1, \ldots, 4
$$

$$
\frac{du}{dz} = \frac{2Q\Delta E}{5nKT - 3\rho(D - u)^{2}}
$$

$$
\frac{dT}{dz} = \frac{2Q\Delta E[\rho(D - u)^{2} - nKT]}{nK(D - u)[5nKT - 3\rho(D - u)^{2}]}.
$$

Observe that such an integration, as shown in the next section, must be performed until the second boundary condition of step (iv) is satisfied.

Conversely, in the case of equation (6) the procedure, though going through the same steps, is in some respect a bit more complicated. Application of the Rankine-Hugoniot conditions to the form (7), (8) yields, after some algebra
\[ n_1N = \frac{D - u_0}{D - u_N} n_{10} - B(u_N, U_0; D) \]
\[ n_2N = \frac{D - u_0}{D - u_N} n_{20} - B(u_N, U_0; D) \]
\[ n_3N = \frac{D - u_0}{D - u_N} n_{30} + B(u_N, U_0; D) \]
\[ n_4N = \frac{D - u_0}{D - u_N} n_{40} + B(u_N, U_0; D) \]
\[ T_N = \frac{1}{K} \left[ \frac{u_N - D}{u_0 - D} KT_0 + \frac{\rho_0}{n_0} (u_N - D)(u_0 - u_N) \right], \]

where

\[ B(u_N, U_0; D) = \frac{5n_0 KT_0 (u_N - u_0)}{2\Delta E (D - u_N)} + \frac{\rho_0 (D - u_0)(u_N - u_0)}{2\Delta E (D - u_N)} (4u - 3D - u_0). \]

So, by using the Rankine-Hugoniot conditions we are able to express the variables \( n_1N, n_2N, n_3N, n_4N, T_N \) in terms of \( u_N \). Of course, following this strategy, we did not use yet the mass action law. This is just what is needed in order to determine the unknown field variable \( u_N \), and then all other variables at the von Neumann point. In fact, by casting expressions (27) into (5) we obtain the following transcendental equation for \( u_N \):

\[ \frac{n_{1N}(u_N)}{n_{3N}(u_N)} \frac{n_{2N}(u_N)}{n_{4N}(u_N)} - \left( \frac{m_1 m_2}{m_3 m_4} \right)^2 \exp \left( \frac{\Delta E}{KT_N(u_N)} \right) = 0. \]  

By solving (28) numerically, one expresses the perturbed field as function of the unperturbed state and the parameter \( D \).

Instead, application of the steps (ii), (iii), (iv) of the solution procedure is trivial now, since for the fast reaction case the vector function \( K(U) \) in equation (23) is zero. Therefore the solution of the detonation problem behind the shock remains constant and equal to the equilibrium found by (27) and (28).

In conclusion, the solution to the steady detonation problems joined to the hydrodynamic equations (3) and (6), corresponds, respectively, to the behavior of the \textit{ZND-model} and of the \textit{simplest model}, as described in the points (c) and (d) at the beginning of this section.

5 Numerical results

It is reasonable to expect that the final equilibrium behind the shock associated to a given physical state in the unperturbed region is the same for
the two models. It corresponds indeed to a collision equilibrium and does not depend on the relative importance of the two contributions making up the collision operator. The difference arises in the jump discontinuities (and then in the Von Neumann points) and in the existence or not of a reaction region following the shock. Such expectation is confirmed by our numerical results, where, for fixed $U_0$, the final state $U_F$, asymptotically reached in the case of slow chemical reaction, coincides with the Von Neumann state $U_N$ relevant to fast chemical reaction.

In all calculations the transcendental equation (28) was numerically solved by Newton’s method, and for the set (26) of ODE’s we resorted to an adaptive Runge-Kutta scheme of high order. In the numerical procedure it was checked that at each step the Lax stability conditions (24) are satisfied.

As an illustrative example of our computations we report here the density and the temperature profiles for a steady detonation in which the physical parameters characterizing the gas have been chosen as

$$m_1 = 0.018, \quad m_2 = 0.001, \quad m_3 = 0.017, \quad m_4 = 0.002, \quad \Delta E = 63311.$$ (29)

Chemical cross sections have been taken such that the microscopic collision frequency of the exothermic reaction is independent of the impact speed (chemical “Maxwell model”), which, accounting for the microreversibility, amounts to the option [GS01]

$$\gamma_{34}^{12} = 4\pi\beta = \text{constant}, \quad \gamma_{34}^{12}(T) = \left(\frac{m_3m_4}{m_1m_2}\right)^2 \exp\left(\frac{-\Delta E}{KT}\right) \gamma_{34}^{12}. \quad (30)$$

For the slow case, in which the chemical relaxation time is much longer than the mechanical one and comparable to the macroscopic time, the factor $\beta$ characterizing the strength of the chemical reaction takes the value $\beta = 10^5$. The fast case, in which chemical and mechanical relaxation times are comparable and much shorter than the macroscopic time, does not require any chemical cross section, as global equilibrium is reached instantaneously and no chemical collision term appears in the Euler equations. In a sense this latter model corresponds to the limiting case of the former one for $\beta \rightarrow \infty$.

Moreover, the unperturbed state is given by

$$n_{10} = 0.8, \quad n_{20} = 0.9, \quad n_{30} = 0.05, \quad n_{40} = 0.1, \quad u_0 = 0, \quad (31)$$

with $T_0 = 1285.41$, as follows from mass action law.

Fig. 1 shows the trend of the single densities $n_i$ versus $z$ in the different regions, and the relevant step discontinuities, for both cases of slow and fast reaction (left and right plots, respectively). They are constant on the regularity regions in the fast case, whereas a reaction zone with a width of about $2 \times 10^{-3}$ units appears in the slow case. Final equilibrium states are of course coincident. This is clear in Fig. 2, where we plot two quantities relevant to the mixtures as a whole, namely total density $n$ (left), and temperature $T$ (right),
**Fig. 1.** Trends of densities $n_i$ for fixed $D = 3100$: slow reaction (left), fast reaction (right)

**Fig. 2.** Comparison of total density $n$ (left) and temperature $T$ (right) for fixed $D = 3100$
Comparing the two cases, as anticipated, the asymptotic approach of the slow profile to the same equilibrium predicted by the fast model is evident. Notice that temperature increases across the shock, and that energy is released in the process. This is in agreement with mass action law (5), since the ratio \( \frac{n_1n_2}{n_3n_4} \) is smaller behind the shock than ahead of it, which requires a higher temperature in the final state with respect to the unperturbed state.

Finally, we would like to comment on the effects of the parameter \( \beta \), determining the intensity of the chemical source term for the slow reaction case. If it is increased, we observe that, with the states \( \mathbf{U}_F \) and \( \mathbf{U}_N \) remaining of course unchanged, the transition becomes steeper and steeper, and correspondingly the reaction zone becomes thinner and thinner. In the limit \( \beta \to \infty \) the trends of all physical quantities reproduce then, as expected, the scenario which is in order for the fast reaction case.

**Acknowledgements**

This paper has been partially supported by the INdAM Intergroup Project 2004 “Equazioni cinetiche con dissipazione e corrispondenti equazioni fluidodinamiche: modellizzazione e metodi numerici”.

**References**

