

Computations of Unsteady Dissociating Nitrogen Flows

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Abstract:

A time-accurate computer program has been developed to solve flows involving nonequilibrium chemical reactions and vibrational relaxation. The program is based on a multidomain approach and an explicit MacCormack scheme. Results are presented for three simple test cases, involving nitrogen dissociation in a closed box.

Introduction:

The growing interest in the field of hypersonic flow computations stimulated the development of a code able to treat nonequilibrium chemically reacting flows. Several approaches [1], [2] are already giving good results for chemical equilibrium, but very few codes that can treat a non equilibrium flow are available [3], and most of them are not time accurate.

A program has been developed to treat unsteady hypersonic flows with non equilibrium chemistry and vibrational nonequilibrium. Even though this program is able to handle any number of chemical species, the results presented here correspond only to the case of dissociating nitrogen. The time accuracy is preserved by the scheme.

Governing equations:

the governing equations are of the general form:

$$\frac{\delta f}{\delta t} + \nabla \cdot F(f) - u' \cdot \nabla f = S$$

with:

$$f = \begin{bmatrix} X_1 \\ \vdots \\ X_n \\ \rho u_1 \\ \rho u_2 \\ \rho e_t \\ \\ E_{vib_1} \\ \vdots \\ E_{vib_m} \end{bmatrix} \quad S = \begin{bmatrix} \dot{X}_{1_{react}} \\ \vdots \\ \dot{X}_{n_{react}} \\ 0 \\ 0 \\ \Delta H_{react} \\ \frac{E_{vib_1}^{(eq)} - E_{vib_1}}{\tau_{v1}} \\ \\ \frac{E_{vib_m}^{(eq)} - E_{vib_m}}{\tau_{vm}} \end{bmatrix}$$

and :

$$\underset{\sim}{F}(f) = \underset{\sim}{\left[ \begin{array}{c} u \underset{\sim}{X}_1 - \underset{\sim}{\rho} \underset{\sim}{D}_1 \underset{\sim}{\nabla} (\underset{\sim}{X}_1 / \underset{\sim}{\rho}) \\ \vdots \\ u \underset{\sim}{X}_n - \underset{\sim}{\rho} \underset{\sim}{D}_n \underset{\sim}{\nabla} (\underset{\sim}{X}_n / \underset{\sim}{\rho}) \\ \underset{\sim}{\rho} \underset{\sim}{u} \otimes \underset{\sim}{u} + \underset{\sim}{P} \underset{\sim}{I}_2 - \underset{\sim}{\tau} \\ (\underset{\sim}{\rho} e_t + \underset{\sim}{P} - \underset{\sim}{\tau}) \underset{\sim}{u} + \underset{\sim}{q} - \sum_{i=1}^{i=n} \underset{\sim}{\rho} h_i \frac{\underset{\sim}{\rho} \underset{\sim}{D}_i}{\underset{\sim}{X}_i} \underset{\sim}{\nabla} (\underset{\sim}{X}_i / \underset{\sim}{\rho}) \\ \\ E_{vib_1} \underset{\sim}{u} \\ \vdots \\ E_{vib_m} \underset{\sim}{u} \end{array} \right]}$$

This system is completed by the thermodynamic relations:

$$P = \sum_{i=1}^{i=n} \underset{\sim}{X}_i R T ; \quad \underset{\sim}{\rho} = \sum_{i=1}^{i=n} \underset{\sim}{m}_i \underset{\sim}{X}_i$$

By associating the diatomic species to the first m indices, and the monoatomic species to indices m+1 to n:

$$\underset{\sim}{\rho} e_t = \underset{\sim}{\rho} u^2 / 2 + \left( \sum_{i=1}^{i=m} \frac{5}{2} \underset{\sim}{X}_i + \sum_{i=m+1}^{i=n} \frac{3}{2} \underset{\sim}{X}_i \right) R T + \sum_{i=1}^{i=m} \underset{\sim}{X}_i E_{vib_i}$$

The heat of reaction is obtained from the chemical source term:

$$\Delta H_{react} = \sum_{i=1}^{i=n} \dot{\underset{\sim}{X}}_{react_i} \Delta H_{f_i}$$

The details on the computation of thermodynamic and transport properties can be found in reference [4].

As the code uses a multidomain approach, two kinds of boundary conditions have been used for the test case: adiabatic wall and connection between two consecutive domains.

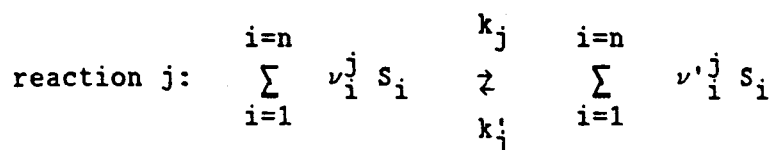
For an adiabatic wall, the velocity  $\underset{\sim}{u}$  is imposed equal to the velocity of the wall. The walls are assumed to be impermeable and non ablative. Thus, the boundary conditions can be summarized for a motionless wall as:

$$\underset{\sim}{u} = \underset{\sim}{0}, \quad \underset{\sim}{\frac{\partial X_i}{\partial n}} = \underset{\sim}{0}, \quad \underset{\sim}{\frac{\partial T}{\partial n}} = \underset{\sim}{0}.$$

For the boundary between two overlapping domains, the values are simply reported from one domain to another.

### Chemical source term

Let us assume we have  $n$  species,  $S_1, \dots, S_n$  undergoing  $p$  reactions:



Where the  $k_j$  represent the forward rates, and  $k_j'$  the backward rates of reaction. These rates are functions of temperature:

$$k_j'(T) = A T^B \exp (E/T)$$

$k_j$  is obtained from  $k_j'$  and the constant of equilibrium  $K_e$ :

$$k_j(T) = K_e(T) k_j'(T)$$

with

$$K_e(T) = (\alpha + \beta T + \gamma T^2) \exp (-\varepsilon/T)$$

The rate of production of specie  $S_i$  is related to the concentrations  $X_j$  of the different species present in the solution by:

$$\frac{dX_i}{dt} = f_i(X_1, \dots, X_n, T)$$

with:

$$f_i(X_1, \dots, X_n) = \sum_{j=1}^{j=p} (\nu_i^j - \nu_i^j) \cdot (k_i \prod_{l=1}^{l=n} X_l^{\nu_l^j} - k'_i \prod_{l=1}^{l=n} X_l^{\nu'_l{}^j})$$

Let us consider a point M in the field at a certain instant t. The chemical composition at M is:

$$X_1(M, t), X_2(M, t), \dots, X_n(M, t)$$

If the point M follows the movements of the fluid, at time t+Δt its new position will be M'.

$$\underset{\sim}{MM'} = \underset{\sim}{u} \cdot \underset{\sim}{\Delta t}$$

The new composition :  $X_1(M', t+\Delta t), \dots, X_n(M', t+\Delta t)$ , is reached through three different processes: convection, diffusion and chemical reactions.

This last contribution is modeled by a source term  $\Delta t \cdot \dot{X}_i$  reaction. This term is the difference of the concentrations  $X_i$  of specie i between time t and time t+Δt, for a reaction taking place at a given temperature T(M, t), with an initial concentration  $X_i(M, t)$ . Thus, introducing f, define above:

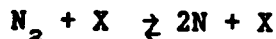
$$\dot{X}_i \text{ reaction} = \int_t^{t+\Delta t} f(X_1(M, \tau), \dots, X_n(M, \tau), T(t)) d\tau$$

and the initial composition of the mixture is:

$$X_i(M, t) = X_i(M', t) + \underset{\sim}{M'M} \cdot \underset{\sim}{\nabla} X_i(M', t).$$

Application to the case of N<sub>2</sub>.

For the dissociation of N<sub>2</sub>, the chemical reactions are:



where X is a catalyser (N, or N<sub>2</sub>). In this case, calling x<sub>1</sub> the concentration of N, and x<sub>2</sub> the concentration of N<sub>2</sub>, the following relations apply:

$$\frac{dx_1}{dt} = 2 (k'_1 x_1 + k'_2 x_2) (K_e x_2 - x_1^2)$$

$$x_1 + 2 x_2 = x_1^0 + 2 x_2^0 = C \quad (\text{conservation of atoms N})$$

In this system, k'<sub>1</sub> is the reverse reaction rate for the reaction of dissociation catalysed by N, k'<sub>2</sub> for the one catalysed by N<sub>2</sub>, and K<sub>e</sub> the equilibrium constant. The values of the necessary constants allowing the computation of k'<sub>1</sub>, k'<sub>2</sub> and K<sub>e</sub> are taken from reference [5]. This system admits an analytical solution:

$$g(x_1) = g(x_1^0) \exp(-(t-t_0)(2k_1 - k_2))$$

with:

$$g(x_1) = |x_1+a|^{(a-b)(a-d)} |x_1+b|^{(b-a)(b-d)} |x_1+d|^{(d-a)(d-b)}$$

where:

$$a = \frac{k_1}{2k_1 - k_2}; \quad b = \frac{K_e/2 + \sqrt{\Delta}}{2}; \quad d = \frac{K_e/2 - \sqrt{\Delta}}{2} = -x_1 \text{ equilib.}$$

$$\text{and: } \Delta = K_e^2/4 + 2K_e.C$$

Details of the numerical resolution can be found in reference [4]. This technique can easily be extended to the case of a mixture of dissociating nitrogen and oxygen, whenever the two dissociations are uncoupled.

## Results:

The code has been applied to three different test cases. In all of them, the geometry is a rectangular box (fig.1), closed, filled with a mixture of molecular nitrogen,  $N_2$ , and of atomic nitrogen,  $N$ .

For the first test case, the box is at a given uniform temperature  $T$  and pressure  $P$ . The initial concentrations of  $N_2$  and  $N$  do not correspond to equilibrium composition for the initial pressure and temperature. A very small time step is chosen, adapted to the chemical reactions ( $10^{-18}$  s). The mixture temperature and pressure increase and in turn the equilibrium composition is modified. An equilibrium is finally reached as shown by the plot of pressure versus time at a point near the walls (fig.2). The recombination of  $N$  yield a final pressure and temperature higher than the initial one.

In the second test case, the box is initially partitioned by a membrane. The pressures and temperatures on the two sides of the box are the same and the compositions are different. For this test case, we freeze the chemical reactions, i.e. we impose a species production term always equal to zero. In this situation, the possible physical phenomena are limited to diffusion and convection. These processes are considerably slower than the chemical reactions as the flow is nearly motionless and a much larger time interval is needed to reach the equilibrium. As expected, the concentrations of  $N_2$  and  $N$  tend to become uniform in the box (fig.3).

The third test case differs from the second case by taking into account the equilibrium chemistry. The diffusion of mass, momentum and energy is a relatively slow process. The convective terms also appear. But the main effect is due to the chemical reactions. The initial conditions correspond to a mixture with a concentration of  $N$  over the equilibrium value for the local pressure and temperature. Thus the atoms of  $N$  will tend to recombine, as in the first case. On both sides of the membrane, at  $t=0$ , we have same pressure and same temperature. But the density and the molar masses are different, and thus correspond to different equilibrium compositions. In turn, the heat released by the chemical reactions on the two sides of the box will be different. Therefore, strong gradients of pressure and temperature appear. An acoustic wave develops and propagates into the box [6], as shown in fig. 4. The frequency of this wave corresponds clearly to the first longitudinal mode of excitation of the box. A strong damping of the wave can also be observed in the fig. 4. This wave is correctly taken into account by the scheme which is time accurate. The last part of the curve corresponds to convection and diffusion processes, tending to produce an uniform temperature and composition. This computation is performed with a quite large time step ( $2 \cdot 10^{-7}$  s). One thousand iterations, for 110 points of grid, took 8 minutes on a VAX 8550. Even though this test case corresponds to equilibrium chemistry, the program is computing the source terms as the limit (for a long time step) of nonequilibrium chemistry source terms.

### Aknowledgement:

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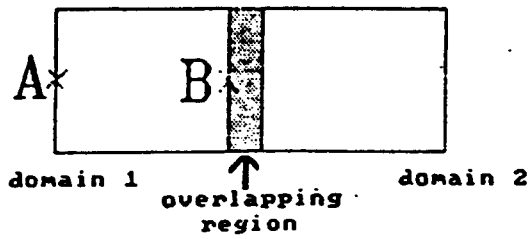


fig. 1: TEST CASE GEOMETRY

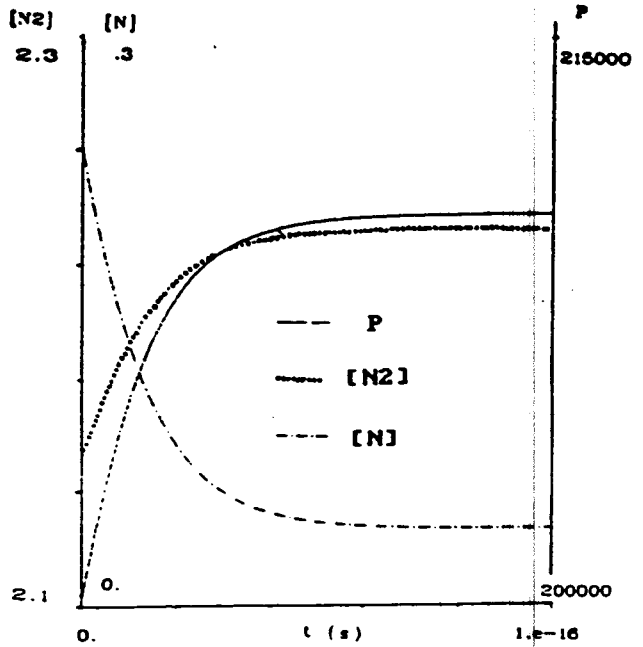


fig. 2: VARIATION OF PRESSURE AND CONCENTRATION OF N VERSUS TIME (REACTING MIXTURE, UNIFORM INITIAL COMPOSITION)

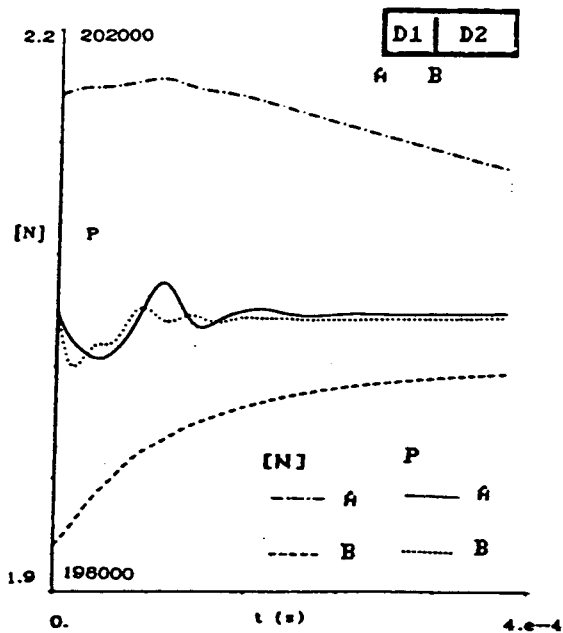


fig. 3: VARIATION OF PRESSURE AND CONCENTRATION OF N VERSUS TIME (FROZEN CHEMISTRY, NONUNIFORM INITIAL COMPOSITION)

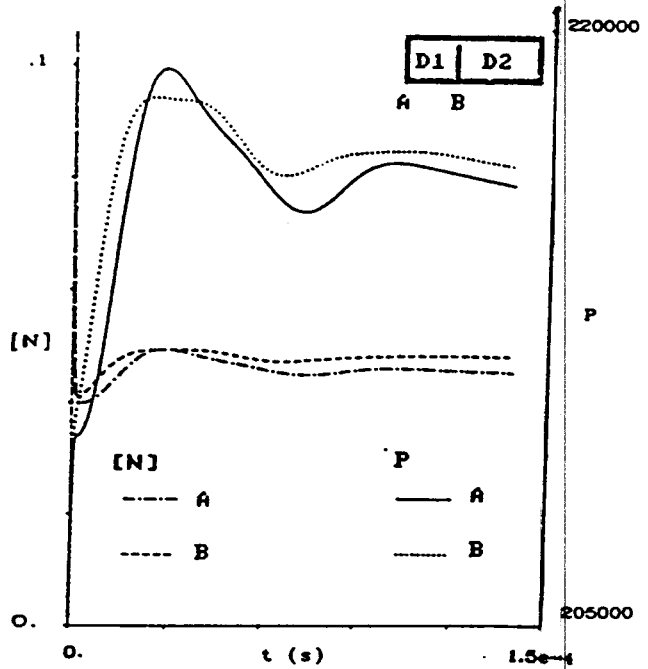


fig. 4: VARIATION OF PRESSURE AND CONCENTRATION OF N VERSUS TIME (REACTING MIXTURE, NONUNIFORM INITIAL COMPOSITION)