Physico-Chemistry of Planetary Atmospheric Entry Plasmas

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Abstract. This contribution deals with the description of the physico-chemistry in the reactive flow produced near the surface of a body entering a planetary atmosphere in hypersonic regime. A shock layer is formed in which a boundary layer is developed where energy is released to the body surface. $\text{N}_2$ is chosen as a test-case of Earth atmospheric reentry to illustrate the main characteristics of the flow. The vibrational and electronic specific Collisional-Radiative model CoRaM-$\text{N}_2$ is described and implemented in a one-dimensional Euler flow solver. The well-known FIRE II flight experiment conditions are used to illustrate the behaviour of the different ground and excited states of atomic and molecular species. The results show that the three successive phases occur: vibrational excitation, dissociation and ionisation. Radiation plays a minor role. According to the upstream thermodynamic conditions, the boundary layer edge can be in local thermodynamic equilibrium or not. The different strategies using thermal protection systems are discussed to reduce the damaging of the entering body.

1. Introduction

Three weeks before the SPIG 2012 conference in Zrenjanin, the news reported an example of perfect control of a planetary atmospheric entry phase. Indeed, NASA succeeded in landing the rover Curiosity on the ground of Mars. After a long journey of 8 months and more than 550 millions of kilometres, the rover entered the atmosphere mainly composed by $\text{CO}_2$ and $\text{N}_2$ molecules at a speed close to 6 km s$^{-1}$. The ground pressure level on Mars is of 650 Pa which is 160 times lower than on Earth. Density of the atmosphere is close to $10^{-2}$ kg m$^{-3}$ on the ground level and decreases according to a law of exponential type with altitude. At $z = 100$ km, density is $10^{-7}$ kg m$^{-3}$. These values correspond to weak order of magnitude with respect to those observed on Earth. Nevertheless, Martian atmosphere is dense enough to be strongly slowed down near the probe which leads to a strong compression. The resulting increase of the pressure induces a force exerted on the probe the intensity of which is strong enough to slow down the probe in turn during its free fall. Afterward, using supersonic parachutes and a sky crane, the probe landed with a very small velocity close to 1 m s$^{-1}$.

In terms of energy, the probe lost all its kinetic energy over the phase of entry. This lost energy is converted into thermal energy during the compression process at the probe surface. The characteristic time scales of this compression are smaller than the ones needed to reach equilibrium. The flow near the probe surface therefore departs from equilibrium.

The main characteristics of the flow near the entering body will be described in the present contribution. The discussion will be focused on thermal and chemical non equilibrium. In
Figure 1. Schematic structure of the flow around a probe entering a planetary atmosphere. Focus on the stagnation streamline corresponding to the strongest gradients zone. A Shock Layer (SL) is formed by the sudden decrease of the flow velocity near the surface. A typical fluid particle undergoes a strong compression crossing the shock front limiting the SL, and a strong heating. Flowing close to the probe surface, this fluid particle releases part of its energy to the wall which is protected by a Thermal Protection System (TPS) forming a heatshield.

particular, state-to-state simulations based on the elaboration of Collisional-Radiative (CR) models will be detailed.

2. Post-shock front relaxation

The strong decrease of the flow velocity \( u_1 \) near the wall induces the formation of a Shock Layer (SL) where density is largely higher than in the upstream flow. This SL is limited by the probe surface and a detached shock front. Its typical thickness \( \Delta \) is of several centimetres. Figure 1 displays a schematic view of the flow structure around the entering body. Incident fluid particles cross the detached shock front and undergo the strong compression. Despite a rough decrease, their velocity \( u_2 \) is then high enough to prevent Local Thermodynamic Equilibrium (LTE). Let us consider the first Damköhler number

\[
Da_1 = \frac{\Delta}{u_2 \tau_{CR}}
\]

where \( \tau_{CR} \) is the characteristic time scale to reach equilibrium through collisional and radiative elementary processes. Indeed, its order of magnitude is of unity which means that the flow is in local chemical non equilibrium. The kinetic energy converted into thermal energy leads to ionisation phenomena. A gas \( \rightarrow \) plasma transition is therefore observed. The characteristic time scale required to obtain Maxwell-Boltzmann equilibrium for each type of particles (heavy particles and electrons) is short enough to have second Damköhler number \( Da_2 = \Delta/(u_2 \tau_{MB}) \) much higher than unity. The concept of temperature can then be used to characterize the translation mode of each type of particle (\( T_A \) for the heavy particles and \( T_e \) for electrons). Unfortunately, the characteristic time \( \tau_{e-A} \) to obtain thermal equilibrium between \( T_A \) and \( T_e \) is significant. The third Damköhler number \( Da_3 = \Delta/(u_2 \tau_{e-A}) \) is lower than unity. The flow then departs from thermal equilibrium.
Table 1. Species and states involved in the nitrogen Collisional-Radiative model CoRaM-N2 described in section 2. Elementary processes between these states and species are listed in table 2.

| Species | States |
|---------|--------|
| N₂      | X¹Σ⁺ (v = 0 → vmax = 67), A³Σ⁺, B³Πg, W³Δw, B³Σ⁻, a¹Σ⁻, a¹Πg, w¹Δu, G³Σ⁺, C³Πu, E³Σ⁺ |
| N⁺      | X²Σ⁺, A²Πu, B²Σ⁺, a⁴Σ⁺, D²Πg, c²Σ⁺ |
| N        | 4S³/2, 2D⁰ = (2D⁰/2 + 2 D³/2), 2P⁰ = (2P⁰/2 + 2 P³/2), 4P¹/2, ... (63 states) |
| N⁺      | 3P₀, 3P₁, 3P₂, 1D₁, 1S₀, 3S₂, 3D⁰, 3D₂, 3D⁰ |
| e⁻      | - |

The plasma flow is therefore in thermal and chemical non equilibrium. Owing to the specific energy of the flow around several 10⁷ J kg⁻¹, the excited states population density is strong which leads to significant radiative losses. In order to simulate with relevance the SL dynamics, a state-to-state approach is mandatory. This approach consists in considering each species on its excited states as an independent species. Denoting x the normal coordinate to the wall and yX, the mass fraction of this species X on its excited state i, the balance equation can be written as

$$\frac{dy_X}{dx} = \frac{m_X}{\rho u} \left( [\dot{X}_i]_C + [\dot{X}_i]_R \right)$$

where mX, is the mass of the species, ρ the density of the flow, u its velocity and [X_i]_C + [X_i]_R the collisional and radiative source terms.

Earth and Mars atmospheres have a common compound. Indeed, N₂ molecules are found in both atmospheres in different abundance. The mole fraction of these molecules is 0.78 for the Earth’s atmosphere and 0.025 for the Martian atmosphere. Titan, the largest satellite of Saturn, has an atmosphere the nitrogen molecules mole fraction of which is 0.98. N₂ is therefore particularly interesting for entry situations. This explains why N₂ is considered as a benchmark and is often chosen for simulations or experiments in ground test facilities. In typical entry situations, N₂ molecules can lead to the formation on ground and excited states of N₂, N₂⁺, N and N⁺. Table 1 summarizes these species and states. We have developed a Collisional-Radiative model for them. This CR model is named CoRaM-N₂. The involved elementary processes are listed in table 2.

This CR model accounts for vibrational processes, electronic excitation, excitation transfer, dissociation, and ionisation either by electron impact or heavy particle impact. Charge exchange and dissociative recombination are also taken into account. Each backward rate coefficient is derived from the forward rate coefficient using the detailed balance principle. Radiative transitions are also involved in the Collisional-Radiative model. Escape factors are implemented in order to simulate the possible self-absorption of the plasma.

In 1965, NASA launched the FIRE (Flight Investigation of Reentry Environment) II probe in the framework of the Apollo program. This probe experienced a reentry at hypersonic velocity (mach number M₁ > 30) in order to provide information on heat flux on the probe surface [19]. The results of this experiment are still intensively studied and the related conditions are retained here to illustrate the behaviour of the species inside the shock layer (elapsed time from the launch t = 1640 ~ 1641 s, altitude z ~ 58 km).

Assuming a discontinuity at the shock front (located in x = 0) treated with the classical
Table 2. Elementary processes of the nitrogen Collisional-Radiative model CoRaM-N\(_2\) involving the species and states listed in table 1.

| Type                      | Elementary processes                                                                 | References |
|---------------------------|--------------------------------------------------------------------------------------|------------|
| **Vibrational processes**  | \(N_2(X,v) + e^- \rightarrow N_2(X,w) + e^-\)                                       | [3]        |
|                           | \(N_2(X,v) + e^- \rightarrow 2 N(\frac{1}{2}S_{3/2}^0) + e^-\)                     | [3]        |
|                           | \(N_2(X,v) + (N_2 \text{ or } N) \rightarrow N_2(X,w) + (N_2 \text{ or } N)\)       | [4, 5]     |
|                           | \(N_2(X,v) + N(\frac{1}{2}S_{3/2}^0) \rightarrow 3 N(\frac{1}{2}S_{3/2}^0)\)      | [4, 5]     |
|                           | \(N_2(X,v_{\text{max}}) + N_2 \rightarrow 2 N(\frac{1}{2}S_{3/2}^0) + N_2\)        | [4, 5]     |
|                           | \(N_2(X,v_1) + N_2(X,v_2) \rightarrow N_2(X,w_1) + N_2(X,w_2)\)                   | [4]        |
| **Electronic excitation** | \(N_2(i) + e^- \rightarrow N_2(j) + e^-\)                                          | [6]        |
|                           | \(N_2(i) + (N_2 \text{ or } N) \rightarrow N_2(j) + (N_2 \text{ or } N)\)         | [6, 7, 8]  |
|                           | \(N_2^+(i) + e^- \rightarrow N_2^+(j) + e^-\)                                     | [9]        |
|                           | \(N(i) + e^- \rightarrow N(j) + e^-\)                                              | [1, 10]    |
|                           | \(N(i) + (N_2 \text{ or } N) \rightarrow N(j) + (N_2 \text{ or } N)\)             | [6, 7, 8, 11] |
|                           | \(N^+(i) + e^- \rightarrow N^+(j) + e^-\)                                         | [1]        |
|                           | \(N^+(i) + (N_2 \text{ or } N) \rightarrow N^+(j) + (N_2 \text{ or } N)\)        | [6, 7, 8]  |
| **Excitation transfer**   | \(N_2(A) + N_2(A) \rightarrow N_2(X) + N_2(B)\)                                   | [6]        |
|                           | \(N_2(A) + N_2(A) \rightarrow N_2(X) + N_2(C)\)                                  | [12]       |
|                           | \(N_2(A) + N_2(B) \rightarrow N_2(X) + N_2(C)\)                                  | [11]       |
|                           | \(N_2(A) + N(\frac{1}{2}S_{3/2}^0) \rightarrow N_2(X) + N(2P_o)\)                | [6]        |
|                           | \(N_2(B) + N(\frac{1}{2}S_{3/2}^0) \rightarrow N_2(X) + N(2P_o)\)                | [11]       |
|                           | \(N_2(C) + N(\frac{1}{2}S_{3/2}^0) \rightarrow N_2(X) + N(2P_o)\)                | [11]       |
| **Dissociation**          | \(N_2(i \neq X) + e^- \rightarrow N(j) + N(k) + e^-\)                             | [9]        |
|                           | \(N_2^+(i) + e^- \rightarrow N(j) + N^+(k) + e^-\)                               | [9]        |
| **Ionisation**            | \(N_2(i) + e^- \rightarrow N_2^+(j) + 2 e^-\)                                     | [9]        |
|                           | \(N_2(i) + (N_2 \text{ or } N) \rightarrow N_2^+(j) + e^- + (N_2 \text{ or } N)\) | [7, 8]     |
|                           | \(N(i) + e^- \rightarrow N^+(j) + 2 e^-\)                                         | [1, 10, 13]|
|                           | \(N(i) + (N_2 \text{ or } N) \rightarrow N^+(j) + e^- + (N_2 \text{ or } N)\)    | [7, 8]     |
| **Charge exchange**       | \(N_2(X) + N^+(\frac{3}{2}P_0) \rightarrow N_2^+(X) + N(\frac{1}{2}S_{3/2}^0 \text{ or } 2P_o)\) | [12]       |
|                           | \(N_2(X) + N^+(\frac{3}{2}P_0) \rightarrow N_2^+(X) + N(\frac{3}{2}S_{3/2}^0 \text{ or } 4S_o)\) | [12]       |
| **Dissociative recombination** | \(N_2^+(X) + e^- \rightarrow N(\frac{3}{2}S_{3/2}^0) + N(2D_o \text{ or } 2P_o)\) | [14]       |
|                           | \(N_2^+(X) + e^- \rightarrow N(2D_o) + N(2D_o)\)                                | [14]       |
| **Radiation**             | \(N_2(B^3\Pi_u) \rightarrow N_2(A^3\Sigma^+_u) + h\nu \text{ (1st positive)}\)   | [10, 15]   |
|                           | \(N_2(C^3\Pi_u) \rightarrow N_2(B^3\Pi_g) + h\nu \text{ (2nd positive)}\)       | [10, 15]   |
|                           | \(N_2^+(B^3\Sigma^+_u) \rightarrow N_2^+(X^2\Sigma^+_g) + h\nu \text{ (1st negative)}\) | [10, 15]   |
|                           | \(N(i) \rightarrow N(j < i) + h\nu\)                                            | [2]        |
|                           | \(N^+(i) \rightarrow N^+(j < i) + h\nu\)                                         | [2]        |
Species number density profiles along the stagnation streamline in the FIRE II flight conditions [19]. Rankine-Hugoniot equations are used crossing the shock front (all inner modes of energy storage frozen, except the translation increased from 250 K to 50,000 K approximately by energy conservation). We can note that the plasma goes successively through the following phases. First, the molecules dissociates. Then, the atoms are ionised. After \( x \approx 10^{-2} \) m, the relaxation of the plasma is observed. The dissociation and ionisation degrees reach 0.98 and 0.1, respectively.

Rankine-Hugoniot equations, figure 2 displays the spatial profiles of the species densities along the \( x \)-axis on the stagnation streamline for the upstream flow conditions \( M_1 = 33, p_1 = 33 \) Pa, and \( T_1 = 250 \) K. Equation (2) is solved in coupling with the momentum and energy balance equations according to a one-dimensional (1D) Euler flow solver. A 2T (two temperatures) approach is considered for which translation of electrons and heavy particles are separately treated owing to the \( Da_2 \) and \( Da_3 \) Damköhler numbers order of magnitude discussed previously.

Just behind the shock front, a rapid vibrational excitation is observed. The concomitant excitation of the electronic excited states of \( N_2 \) takes place. The vibrational excitation allows the dissociation of \( N_2 \) either under \( N_2 \) molecules impact at the beginning or under \( N \) impact when the dissociation degree reached high enough values. Ionisation of the gas closely follows dissociation. The ionisation degree becomes quickly of the order of 0.1. At \( x = 10^{-4} \) m from the shock front, the dissociation and ionisation phases are achieved. The remaining relaxation is much more quiet. To better understand these different phases, a thorough examination of the
Figure 3. $T_A$, $T_e$ and $T_v$ profiles in the conditions of figure 2. Electron temperature is plot starting from $\simeq 10^{-5}$ m for which electron density is high enough and the concept of temperature relevant. For $x > 10^{-3}$ m, thermal equilibrium is observed.

temperatures of the flow is performed.

We define the vibrational temperature $T_v$ as the excitation temperature of the first five vibrational levels of $N_2(X)$ calculated with

$$T_v = -\frac{1}{k_B \left[ \frac{d}{dE_{X,v}} \left( \ln[N_2(X,v)] \right) \right]_{ls}}$$

where $ls$ means that the derivative is the slope of the least square line and $E_{X,v}$ is the vibrational energy. Figure 3 displays the profile of $T_v$ compared with that of $T_e$ and $T_A$. Just behind the shock front, $T_A$ has strongly increased owing to the Rankine-Hugoniot assumptions while the shock does not affect electrons owing to their weak mass. Indeed, the regime is subsonic for electrons and their temperature after the shock front remains at the same level as that in upstream flow. Nevertheless, the electron density is negligibly small so that the concept of electron temperature is questionable. Therefore, figure 3 reports $T_e$ for $x \gtrsim 10^{-5}$ m for which electron density has sufficiently increased.

Since the vibration is frozen at the shock front, $T_v$ equals $T_1$. The vibrational levels are quickly excited thanks to the vibration-translation elementary processes. $T_A$ decreases while $T_v$ increases. Energy is taken from translation and given to excitation, ionisation and mainly to
Figure 4. Boltzmann plot of N atoms at different $x$-values from the shock front. A rapid relaxation is observed toward an excitation temperature close to $T_A = T_e$ at thermal equilibrium.

dissociation. When $T_v$ reaches a maximum ($x \approx 10^{-4}$ m), the $T_A$ decrease rate is maximum. Afterward, the relaxation goes on until the coupling between all temperatures ($x \approx 10^{-3}$ m) which means that thermal equilibrium is then reached.

The plasma relaxation can be further examined using Boltzmann plots displayed on Figure 4 relative to the N atoms excited states. The distribution is first far from equilibrium with strong underpopulation with respect to $T_A$. Indeed, at $x = 3 \times 10^{-5}$ m, the main collision partners of N atoms are N$_2$ and N. If equilibrium were fulfilled, the excited states should be more populated according to a ratio close to 40. When approaching $x \approx 10^{-3}$ m, the coupling takes place by collision with all types of particles and stabilizes with an excitation temperature close to $T_e = T_A = 8 \, 000$ K. Although many transitions are optically thin, the departure from the Boltzmann equilibrium is negligibly small for $x > 10^{-3}$ m.

Such a study can also be performed for the molecular excited states. Their relaxation is slower than for atoms. Between $10^{-3}$ m and $10^{-2}$ m, the excitation equilibrium is not reached. The complete relaxation of the plasma in LTE is in fact achieved for $x \approx 10^{-2}$ m. The influence of radiation is negligibly small. Nevertheless, we can observe the influence of these radiative losses. Indeed, they cause the slow decrease of the temperature of the plasma.

Of course, Earth or Mars atmospheres are not composed by N$_2$ molecules only. The case of post-shock flows in N$_2$-O$_2$ mixtures related to entry into the Earth’s atmosphere has been
treated recently in a simplified way [20, 21]. Conversely to the model of the present section, the state-to-state approach has been developed for electronic excited states of molecules and atoms only. The N$_2$ and O$_2$ vibrational states have not been considered as independent species. They have been lumped together and the concept of global dissociation or recombination similar to the global ionisation thoroughly described in [22] has been used. The more complete model CoRaM-Air accounting for the vibrational states of N$_2$, O$_2$, NO (obtained by Zeldovich neutral exchange processes) and electronic excited states of Ar has been elaborated [23]. The equivalent model CoRaM-Mars has been elaborated for Martian atmosphere entries. At the moment, only relaxation calculations at constant pressure and temperature can be performed. Their coupling with energy and momentum balances for post-shock calculations is in progress.

3. Plasma-wall interaction

The previous study focused on the post-shock relaxation put forward the high levels of temperature and the thermodynamic equilibrium of the plasma near the entering body surface. The pressure equals 4 × 10$^4$ Pa at $x \approx \delta$ from the shock front. The collision frequency is then high enough and the velocity sufficiently small to ensure LTE. Of course, these conditions are particular. If the calculations are performed for higher altitude where the Mach number $M_1$ is higher and temperature $T_1$ and pressure $p_1$ lower, the non equilibrium zone is thicker and the boundary layer edge is not in LTE. But the levels of temperatures are higher. In any case, the entering body therefore interacts with a high temperature plasma and can be strongly heated.

The heating process has different contributions. The first contribution results from the conduction of all energy storage modes (translation, rotation, vibration and electronic excitation). These conduction phenomena take place owing to the difference between the plasma temperature and the surface temperature which is necessarily limited by its melting or sublimation point. This conductive part induces the formation of boundary layers characterized by gradients of translation temperatures and ground and excited states number densities. The second contribution results from radiation emitted everywhere in the plasma. Indeed, a part of this emission can reach and partially be absorbed by the entering body surface. The third contribution is due to dissociated species which can be adsorbed on the surface and recombine by catalysis. The dissociation energy then released to the surface enhances the heat flux observed at the wall.

The previous contributions generally are of the same order of magnitude. No one can then be ignored in the energy balance at the wall. They lead to significant values of the parietal heat flux, typically between 1 and 10 MW m$^{-2}$. Such heat fluxes induce a strong heating therefore a damaging of the entering body. To reduce the damage as much as possible, two strategies have been developed. First, refractory materials treated against oxidation can be used as TPS. They reduce the part of the heat flux resulting from the recombination of oxygen in O$_2$ molecules catalyzed by the surface. These materials are in fact used as heatshield in the case the heat flux corresponds to weak values. They are reusable and were in the past developed for the American Space Shuttle and the Russian Bor and Buran vehicles [24]. The second strategy consists in using the damage resulting from the heat flux for the protection of the surface. Ablative materials are used. During heating, the pyrolysis of the material is obtained which leads to the endothermic formation of hydrocarbons gases. Their mixing with other species and heat transfer inside the boundary layer then reduce the net heat flux. Since the material ablates, its behaviour in known conditions has therefore to be particularly well characterized in order to optimize the heatshield sizing. The material used for the entry of the Curiosity rover in the Martian atmosphere (Phenolic Impregnated Carbon Ablator, PICA) belongs to this second type of TPS [25].
4. Conclusion
In this contribution, the physico-chemistry of flows produced by bodies entering into a planetary atmosphere has been thoroughly examined. A shock layer is produced in the vicinity of the entering body’s surface owing to the compression of the incident hypersonic flow. This compression leads to the dissociation and the ionisation of the incident gas molecules. Then, the plasma thus produced releases part of its energy to the surface with significant heat fluxes. The entering body is protected using either reusable or ablative material heatshield.

The description of the behaviour of the nitrogen shock layer flow resulted from the implementation of our electronic and vibrational specific Collisional-Radiative model CoRaM-N$_2$ in a 1D Euler flow solver accounting for the momentum and energy balance equations. The shock front is treated as a discontinuity in the framework of the Rankine-Hugoniot assumptions. Results put forward the successive phases allowing the conversion of the initially cold gas into plasma. N$_2$ is vibrationally excited, dissociate and the atoms are then ionised.

Based on CoRaM-N$_2$, two other vibrational and electronic specific CR models (CoRaM-Air and CoRaM-Mars) are in elaboration in the purpose of their implementation in 1D Euler flow solvers. They will be used to simulate the physico-chemistry inside shock layers formed during atmospheric entries into Earth and Mars atmospheres. Although many entries were successful, a lot of work remains to be performed to improve the sizing of heatshield. In the future, missions to Mars (ExoMars in 2016-2018 by ESA and Russia), to Titan (Titan-Saturn-System-Mission in 2020 by NASA and ESA) as well as round-trip using the Soyous vehicle for astronauts coming back from the International Space Station, will require an ever deeper understanding of this type of physical situation.

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