

École polytechnique de Louvain

Gas-surface interaction modelling during atmospheric entry

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Abstract

Developing ablative Thermal Protection Systems (TPS) is the next stage for understanding the universe. These TPS are designed to endure extreme conditions, enabling spacecraft to enter planetary atmospheres, collect samples from other planets, and will be used for human missions. As no ground test can reproduce the exact flight conditions, simulation tools are used to design and size the TPS. Four categories of solvers can be found: flow, material, loosely coupled and unified solvers. This thesis is aimed at enhancing the flow solver implemented in Argo. This improvement builds upon the previous developments of the code in which a material solver and a unified solver have been implemented. Even though flow solvers are less accurate than unified solvers when focusing on the gas-surface interactions, they remain powerful tools in the early stages of the development of a TPS. Indeed, their computational costs remain lower for the results they can get. To achieve this, a mass and energy balance accounting for the gas-surface interactions is implemented. The material response is modeled using simplifying assumptions. The models used in this thesis allow to consider the catalytic reactions and the re-radiation of the energy due to the surface. Those models were first tested against test codes and then, the physical solutions were observed for different wall conditions and mixture properties.

Chapter 1

Introduction

1.1 Context

Planetary exploration is important for the progress of mankind. The scientific discoveries can lead to the enhancement of life or to the innovation of technologies. From the first satellite launched from Earth to the first humans on the moon, a big leap was made. Continuing with the spirit of always pushing further, some missions are now focused on collecting samples from other planets and the ultimate goal is to send humans to other planets and return them unharmed.

For those kind of mission, numerous aspect must be taken into account. The main focus in this thesis is the planetary atmospheric entry. Indeed, severe conditions are encountered and the vehicle must withstand them. Consequently Thermal Protection Systems (TPS) were developed to protect the integrity of the vehicle.

TPS can be reusable or ablative. The choice is driven by the predicted heat loads the vehicle must endure. Examples of heat loads for different entry missions are given in Table 1.1 where high energy values come mainly from the high speeds conditions. Note that the amount of energy that must be dissipated by the TPS is actually a small portion of the total kinetic energy. This fraction depends on the shape of the vehicle and the flow regime.

In Fig. 1.1, the Earth re-entry trajectories are shown for different missions and the crossing line for the choice between reusable or ablative TPS is drawn. Reusable TPS are chosen when the heat load is relatively low. They are made from insulating materials and re-radiation plays an important role in dissipating the energy. As an example, we can show the tiles on the bottom of the Space Shuttle Discovery in Fig. 1.2.

Entry	$V [km/s]$	$E/m [MJ/kg]$
MER	5.6	16
Apollo	11.4	66
Mars return	14	98
Galileo	47.4	1130

Table 1.1: Entry velocity and energy that must be dissipated by the TPS for several missions. Data from [1]

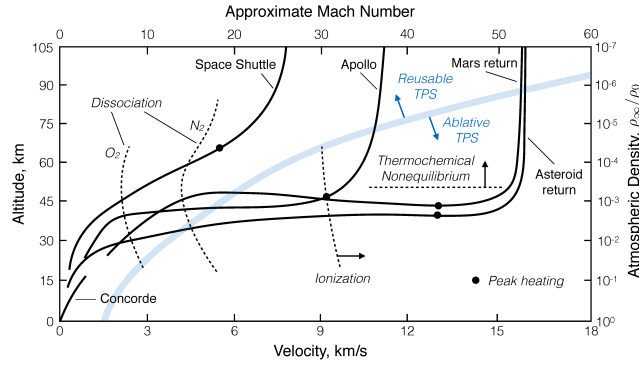


Figure 1.1: Trajectories of several Earth atmospheric entry missions. Blue line shows the crossing line between reusable and ablative TPS. Figure from [2]

The ablative TPS can still dissipate a part of the energy through radiation, still a big part of the energy is dissipated through the degradation of the heat shield. The Galileo probe designed to study Jupiter was equipped with an ablative TPS. In Fig. 1.3, we can depict the dimensioning of the TPS before the atmospheric entry and what was left after. In this representations, three main points can be seen : (1) the initial mass of the TPS ($152 [kg]$) is very consequent compared to the total mass of the vehicle ($335 [kg]$), (2) less than 50% of the ablative material was consumed and (3) the margins taken at the extremities were barely sufficient while at the center they were over predicted.

Safety margins must be taken in order to ensure the successful execution of the mission. Nevertheless, those margins are taken at the expense of sacrificing the utility mass and hence the costs for the same mission are higher. As seen in Fig. 1.4, the mass of the TPS constitute a big proportion of the total mass.

The three observations made previously also stress our lack of understanding as the predicted and the actual results were very different. Hence the physical

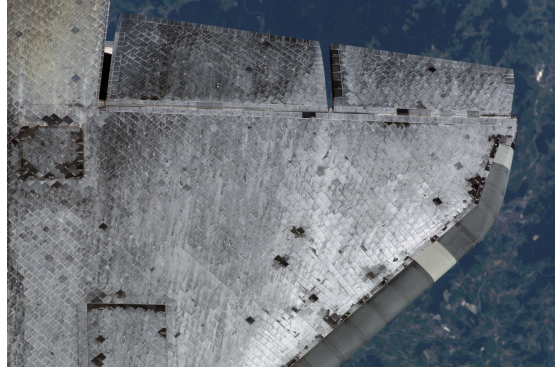


Figure 1.2: Insulated tiles on the wing of the Space Shuttle Discovery. Credit: NASA

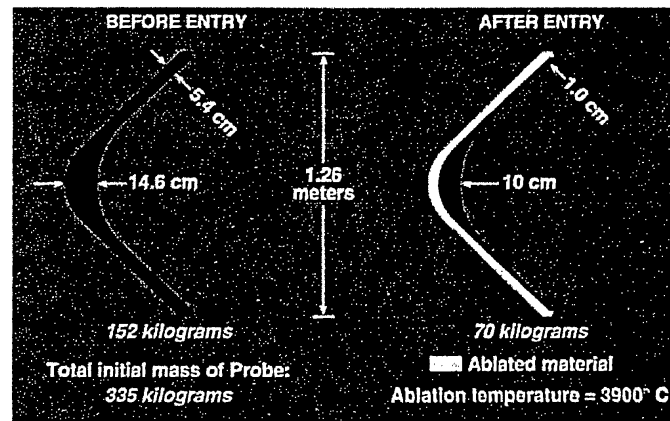


Figure 1.3: TPS of the Galileo probe before and after Jupiter entry. Figure from [3]

overview of atmospheric entry will be discussed.

1.2 Physical overview

During atmospheric entry, the vehicle decelerates from hypersonic ($Ma > 5$) to subsonic velocities. As long as the vehicle does not decelerate to subsonic velocities, “a detached reactive shock layer appears in front of the vehicle” [5]. Besides, a thermal boundary layer is found inside the shock layer close to the vehicle. The different phenomena that can occur inside each layer are shown in Fig. 1.5.

Before the shock layer, the gas has a low density and temperature but the velocity is high. After the compression shock, the gas is denser and the velocity

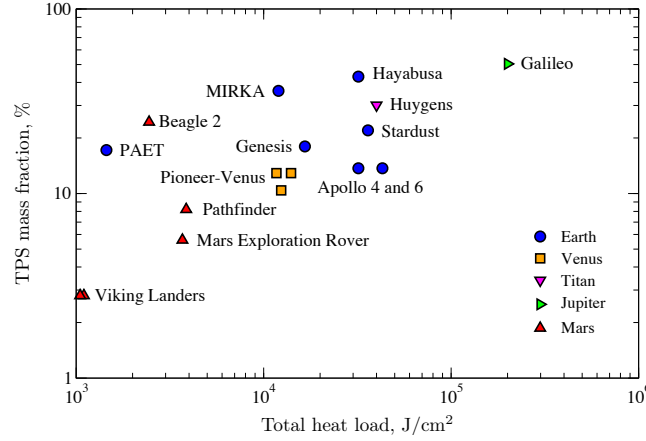


Figure 1.4: Graph showing the percentage of TPS mass compared to the total mass for several space missions. Graph from [2] with data compiled from [4]

decreased. Regarding the temperature, it can reach values up to 10000 [K] as all the kinetic energy has been transformed into internal energy. Values of the pre- and post shock for the atmospheric entry of FIRE II on Earth are given in Table 1.2.

	$P [Pa]$	$T [K]$	$\rho [kg/m^3]$	$u [m/s]$
pre-shock	2.09	195	3.72×10^{-5}	11360
post-shock	4.53×10^{-3}	10000	6.51×10^4	649.7

Table 1.2: Pressure, temperature, density and velocity values before and after the shock. Table from [5] and data from [7]

Due to these extreme conditions, several chemical reactions can occur in the shock layer: (1) dissociations reaction of molecules, (2) ionizations of atoms or molecules and (3) “radiation due to the excitation or de-excitation of the electronic population” [5].

Moreover, because of the high enthalpy flow, the surface of the heat shield must absorb a lot of energy. The temperature at the wall can rise to 3000 [K] for the most severe conditions [5]. Hence the materials used for the protection must be designed to dissipate this energy, which is done through the degradation of the wall. The two phenomena that allow the energy dissipation are the pyrolysis and the ablation.

One example of material used for ablative TPS is PICA, which is considered as a light ablator due to its low density. It has three distinctive layers as shown in Fig. 1.6. Initially, the PICA is at a virgin state and is composed by carbon

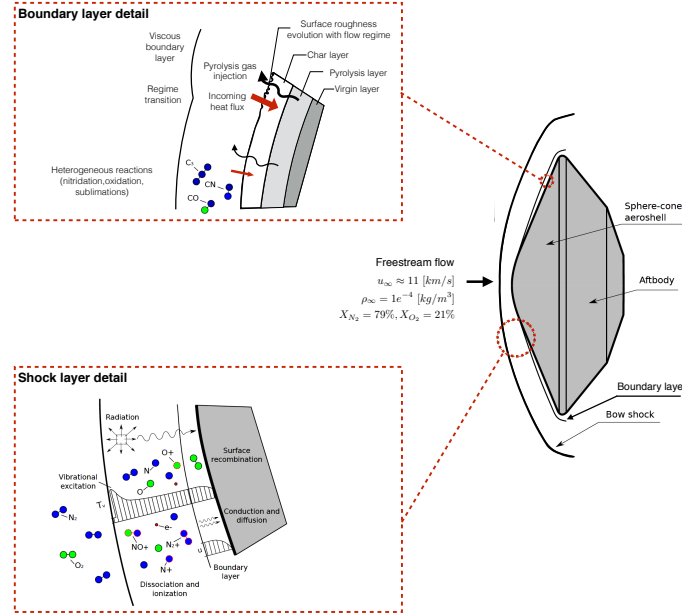


Figure 1.5: Shock and thermal layer and the phenomena that occur in case of atmospheric entry. Sketch from [5] adapted from [6]

fibers with a pyrolysing resin. When heated up, the resin is first pyrolysed which transform the resin into gases that are blown through the surface of the material. This reaction is endothermic and hence it helps for the dissipation of the energy. In addition to that, the blown flux can block a part of the convective heat flux from the shock layer.[5]

Then, when the resin is consumed, the remaining carbon fibers can react with the gas and reactions such as carbon oxidation or sublimation can occur. Thus, the char is also consumed and the material recedes at a certain rate. This rate depends on the pressure and the temperature at the surface [9]. The three stages of the PICA degradation can be seen in Figures 1.7a to 1.7c.

We also note that the erosion of the surface leads to a change of roughness which consequently has an influence on the flow regime and to a change of the aerodynamics properties as found in Wright et al. work [11]. For turbulent regime or for higher roughness, the heat load increases as depicted in Figs. 1.8a and 1.8b respectively. Hence, an essential factor for designing a TPS is the ability to predict the transition between a laminar to turbulent flow.

Eventually, the wall can act like a catalyst for atom recombination which will

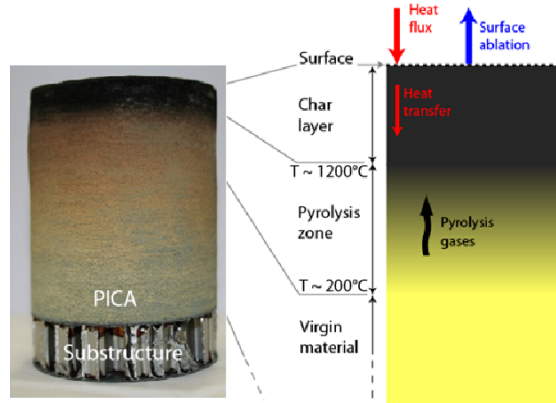
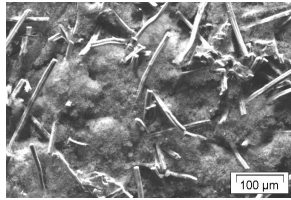
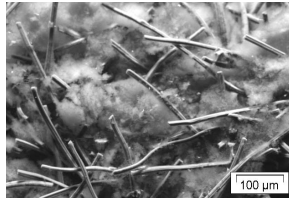


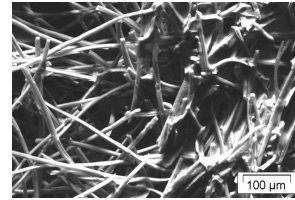
Figure 1.6: Structure of PICA extracted from Stardust. The virgin, pyrolysis and char layers are shown as well as a simplified representation of the heat and mass transfer. Picture from [8]



(a) Virgin material



(b) Pyrolysis zone



(c) Ablated material

Figure 1.7: Microscopic of (a) the virgin material, (b) the pyrolysis zone and (c) the ablated material for PICA. Pictures taken from [10]

be more detailed in chapter 2. Unlike ablation, catalysis does not degrade the wall but contribute to the heat load as the reactions are often exothermic. This aspect will be studied when running simulations in this thesis.

1.3 State-of-the-art

The sizing of the thermal protection system is decisive for atmospheric entry missions. It allows to protect the inside of the shell in order to successfully return samples, expensive equipment or even to safely land humans. Consequently, physical experiments were performed and simulations tools were developed in order to understand the physics and model it. Those experiments and simulations tools are briefly showed here.

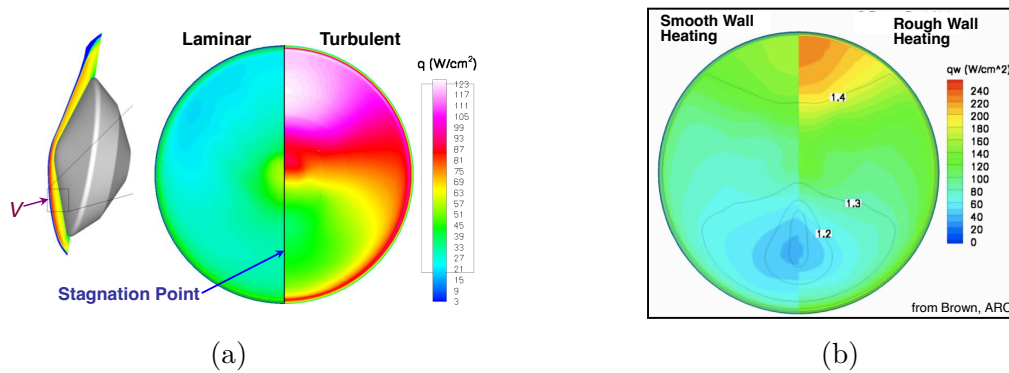


Figure 1.8: Effects of (a) the flow regime and (b) surface erosion on the heat loads. Pictures taken from [1]

1.3.1 Experiments

All the extreme conditions that occur during atmospheric entry can hardly be met on actual ground facilities. As shown in Fig. 1.9, all the existing ground facilities are classified in function of the enthalpy they can generate and their testing time. The atmospheric entry problems stands in the top right corner. Besides, flight experiments are very expensive but still necessary due to our lack of understanding. Hence, only few flight experiments were made.

We can cite the Atmospheric Reentry Demonstrator created by ESA to validate theoretical predictions used for the design of a TPS [12]. There are other examples such as the Galileo probe seen previously or the Mars Science Laboratory missions which were respectively designed to enter Jupiter and Mars atmospheres.

In addition to these experiments, two main ground tests facilities were created. Those tests allow the experimentation of some specific flight conditions. These experiments also improve the understanding of the physical phenomena.

The first test facilities are called hypersonic wind tunnels. As an example, the von Karman Institute Longshot gun tunnel [13] can generate a flow velocity up to Mach 20. This facility is used notably to study shocks and the laminar-to-turbulent transition of the boundary layer. However their testing times are really low.

On the other hand, arc jets and plasmatrons are capable of larger time-scale simulations with a relatively high enthalpy environment. Consequently, we can better understand the degradation of certain materials thanks to thermocouples. An example of such facility is the VKI plasmatron as shown in Fig. 1.10. The plasma is produced by elevating the temperature of a gas to approximately 10000 [K] using

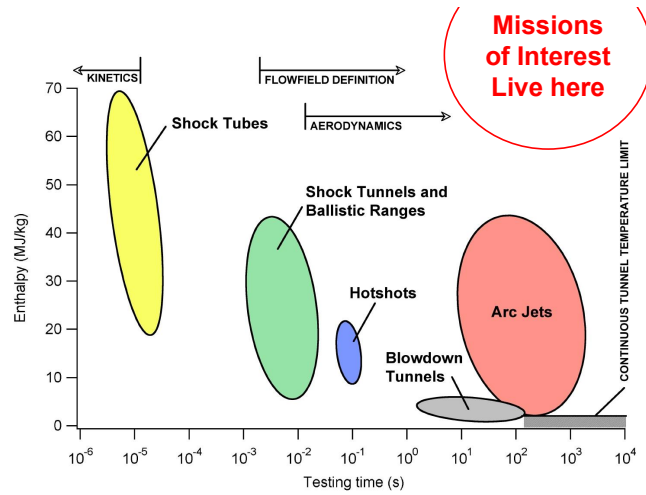


Figure 1.9: Classification of the ground facilities in function of the enthalpy generated and their testing times. Atmospheric entry stands in the top right corner. Graph from [1]

induction. The photograph in Fig. 1.10 shows a running ablation test in the VKI plasmatron.

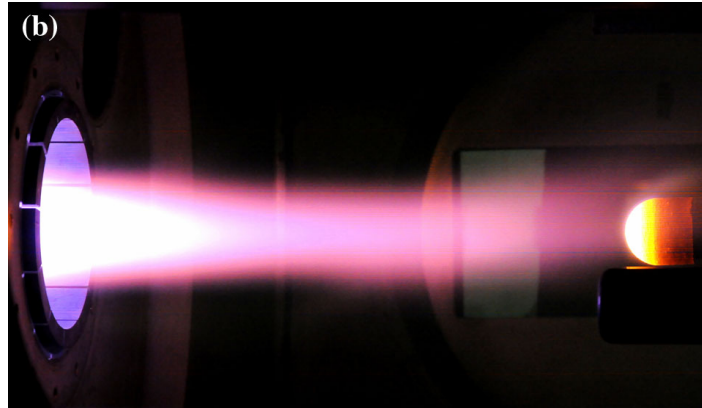


Figure 1.10: Real-time testing of the plasmatron on an ablative material. Picture from [14]

1.3.2 Numerical approaches

Different types of solver were developed to simulate the degradation of thermal protection systems. Each type had its own approach regarding the modeling of the gas-surface interactions and hence their performances and their limitations may differ. A summary of the four types of solver will be given.

Fluid solvers

Fluid solvers center their attention on solving the reactive Navier-Stokes equations while the material response is modeled. The models needed must describe all the gas-surface interactions including catalysis, pyrolysis, ablation and the heat transfer due to those phenomena. Even though the models remain simplistic, especially with the development of new light ablators, flow solvers are crucial as they can decrease the computational costs. Examples of flow solvers will be given later.

Material solvers

Unlike fluid solvers, material response solvers focus on the material while modeling the effect of the flow. In a material, the reactions occur with a very small time scale. In order to solve the material, each reaction and its effects must be captured. Consequently, material solvers allow to add more complexity in the modeling of the material side. The state-of-the-art codes and their performances are summarized by Lachaud et al. [8].

Loosely coupled solvers

Loosely coupled solvers are widely used as they combine the two previous solvers. The flow and the material are solved on separate domains but communicate through the boundaries. As the time scales of the flow and the material reactions are different, loosely coupled solvers allow the communications at given time-steps. The challenge is to use the right strategy both for the information that is passed through the boundaries and the time-steps at which the exchange will happen. Example of loosely coupled solvers can be found in these works [15, 16, 17].

Unified or strongly coupled solvers

With the unified approach, the flow and the material are solved in the same domain. This is computationally expensive as the same time step must be used for all the domain even in unnecessary regions. However, it is proven to be very accurate especially in the presence of a highly porous medium like with low density ablators. The complexity of such solvers is often significant resulting in the development of only a limited number of them [5, 18, 19].

1.3.3 State-of-the-art CFD tools

CFD tools are still widely used as they are powerful. Despite the fact that they are less accurate for atmospheric entry problem when it comes to capture the gas-surface interactions, they remain useful in the early stage of the design of the

TPS as they are computationally less expensive than high fidelity codes. Indeed, the boundary condition at the gas-surface interface is often modeled simplistically. The same observation is true for material response code as well. Hence a weak or strong coupling between the two solvers was found to be a more suitable solution.

However, CFD tools continue to develop. The Data-Parallel Line Relaxation (DPLR) [20] developed by NASA could only solve steady-state flow with simplistic gas-surface interactions and on structured grids. In some cases it could be coupled with a material response code like DPLR/TITAN [16]. DPLR finds the solution along normal lines from the boundaries. Another tool developed by NASA is LAURA [21]. Unlike DPLR, this tool can use point and line relaxation methods to find the solution at steady-state. We can also cite FUN3D solver [22], successor of LAURA, as it was developed to solve problems on an unstructured mesh and US3D [23] which can be seen as the successor of DPLR as well.

Then solvers that could capture the turbulent effects were developed like the USM3D solver [24] as those phenomena impact the heat flux.

Other enhancements on the description of the thermodynamic state of the mixture were also made. LeMANS code developed at The University of Michigan [25] can account for a multi-temperature models to describe the state of the mixture.

Eventually, other CFD tools have improved their boundary conditions such as the HALO3D code. Huang et al. [26] implemented a boundary condition taking into account the catalytic reactions of the wall which is also one of the main interest of this thesis.

1.4 Objectives

Cenaero developed an in-house code capable of solving the flow and the material in an unified manner [5]. Even though this approach was proven to be more rigorous and precise, it was computationally expensive. In order to have quicker simulations for ablative materials, Cenaero is continuing its development by first implementing improved boundary conditions for their material response code [27]. Then comes the main objective of this thesis which is to implement the proper boundary conditions for the fluid solver. Those conditions were obtained by solving the mass and energy balance at the interface of the degrading material. The thermochemical and transport properties needed for the balance were evaluated thanks to an external library named *Mutation*⁺⁺ [2]. The latter also allows to model quantities such as the production rate due to catalysis or ablation. Eventually, the mass and energy balance

were implemented in two different ways: by imposing a Dirichlet boundary condition obtained by solving the mass and energy balance or by imposing a Neumann boundary condition obtained by isolating the diffusive flux from the balances. In addition to verifying the accuracy of those two methods, their convergence and stability will be studied in the same optic of finding the less computationally expensive method. The tests simulations will range from pseudo-1D problems to 2D problems.

This thesis is structured into four chapters including this introduction. The second chapter aims to write the governing equations to solve such problems. The description of the thermochemical and transport models were also given followed by the derivation of the mass and energy balance and the modeling of the gas-surface interactions such as catalysis, pyrolysis and ablation adapted for a flow solver. Chapter 3 is dedicated to the practical implementation of the boundary conditions within Argo. A brief summary of the *Mutation*⁺⁺ library will also be given as it was mainly used in this work. The results will be presented and discussed in Chapter 4. The pseudo-1D tests cases are performed in order to verify the constitutive equations of the mass and energy balance implemented in Argo. The 2D simulations have a double goal. First the simulation of more concrete problems can be performed. The physical response of a non-catalytic, catalytic and radiative wall are observed. Then the performance of the two types of boundary conditions impositions will be compared. Eventually, the conclusions and the perspectives of this work will be discussed.

Chapter 2

Physical modeling

The first objective of this chapter is to describe the physical models as well as the thermodynamic and transport models for a multi-species flow. For high entry velocities and temperatures, the multi-component Navier-Stokes equations must be solved to keep track of every species present in the mixture as the latter is not at equilibrium. The second part of this chapter aims to derive suitable boundary conditions for a fluid solver. The mass and energy balance around the surface must be derived with some assumptions as no material solver will be used. Indeed, the main objective of the thesis is to improve the fluid solver of Argo.

2.1 Introduction

As no ground test has the capacity to reproduce the exact same conditions of atmospheric entry, the development of simulating tools is necessary in order to design a suitable thermal protection system. However, this task is also complex as various physical and chemical processes can occur. Indeed, during an atmospheric entry, shocks can happen at a certain distance from the wall and temperatures can reach 10000 [K] within the layer. At these temperatures, some air species can be dissociated or ionized. The latter will not be studied in this thesis. Therefore, a multi-component formulation for the Navier-Stokes equations is needed in order to track every species.

Furthermore, the interactions between the gas and the surface must also be taken into account. The surface can radiate energy, have catalytic properties that will favor some chemical reactions, have a pyrolysis layer and can be deformed due to ablation. As some of those phenomena occur in the material side, they have to be modeled to be implemented in a fluid solver.

2.2 Reactive Navier-Stokes equations

The gas-surface interactions mainly occur at altitudes where continuum mechanics can be applied. Hence, the Navier-Stokes equations can be used. In fact, for higher altitudes, we must use rarefied gas flows methods such as the Direct simulation Monte Carlo (DSMC) [28].

The system of equations considered in this work is constituted by a mass conservation equation for each species present in the mixture, the momentum and the energy conservation equations.

2.2.1 Mass equations

The mass equations for each species are written as follows:

$$\frac{\partial \rho_i}{\partial t} + \nabla \cdot (\rho_i \mathbf{u}) = -\nabla \cdot \mathbf{J}_i + \dot{\omega}_i, \forall i \in \{1, N_s\}, \quad (2.1)$$

where N_s is the number of species, ρ_i is the density of the species, $\mathbf{u}$ is the velocity, $\mathbf{J}_i$ is the diffusion flux and $\dot{\omega}_i$ is the chemical production term [5].

2.2.2 Momentum equations

The momentum equations can be written as follows:

$$\frac{\partial \rho \mathbf{u}}{\partial t} + \nabla \cdot (\rho \mathbf{u} \mathbf{u}) = -\nabla P + \nabla \cdot \boldsymbol{\tau}, \quad (2.2)$$

where the total density of the mixture ρ is obtained by summing all the species densities, P is the total pressure of the mixture given by summing all the species partial pressures $P_i = \frac{\rho_i R T}{W_i}$ with R the universal gas constant, T the temperature and W_i the molecular mass of a species. $\boldsymbol{\tau}$ is the viscous stress tensor. Note that the external forces and the shear stress were neglected in this thesis [29].

2.2.3 Energy equations

The energy equation can be written as follows:

$$\frac{\partial \rho E}{\partial t} + \nabla \cdot (\rho H \mathbf{u}) = -\nabla \cdot \mathbf{q} + \nabla \cdot (\boldsymbol{\tau} \cdot \mathbf{u}) + \dot{\omega}_T, \quad (2.3)$$

where $E = e + \frac{\mathbf{u}^2}{2}$ is the total energy, $H = E + \frac{P}{\rho}$ is the total enthalpy, $\mathbf{q}$ is the heat flux and $\dot{\omega}_T$ is the contribution of the chemical production term $\dot{\omega}_i$ to the energy [5].

2.2.4 Thermodynamic

In order to get a determined system of equations, quantities such the energy and the enthalpy must be computed. An extensive explanation is beyond the scope of this thesis but the reader can refer to those works [5, 29, 2]. However, the main assumptions used in this thesis will be given.

First, a single temperature model is used to describe the energy mode meaning that the four energy modes (translational, rotational, vibrational and electronic) have a common temperature. This will have an effect on how thermodynamic and transport terms are evaluated.

The total enthalpy of the mixture is evaluated as follows:

$$H = \sum_{i=1}^{N_s} Y_i h_i \quad (2.4)$$

where Y_i is the mass fraction and h_i is the enthalpy of one species. The latter depends on the temperature and is given by [5]:

$$h_i(T) = \underbrace{\int_{T_0}^T c_{p,i} dT}_{sensible} + \underbrace{h_{f,i}^0}_{chemical}, \quad (2.5)$$

where $c_{p,i}$ is the specific heat at constant pressure and $h_{f,i}^0$ is the formation enthalpy. The separation of the sensible and chemical enthalpy has been commonly used for reactive flows as it can lead to simplification [5]. However, as catalytic reactions will be used in this thesis, the total enthalpy must be used to take into account the contribution of the chemical reactions to the energy.

Thus, the integration of $c_{p,i}$ is given by [29]:

$$h_{i,sensible} = R_i T \left(-\frac{a_{0,i}}{T^2} + a_{1,i} \frac{\ln T}{T} + a_{2,i} + \frac{a_{3,i}}{2} T + \frac{a_{4,i}}{3} T^2 + \frac{a_{5,i}}{4} T^3 + \frac{a_{6,i}}{5} T^4 + \frac{a_{7,i}}{T} \right), \quad (2.6)$$

with $R_i = \frac{R}{W_i}$. The coefficients $a_{k,i}$ are computed with the *Mutation*⁺⁺ [2] library using the NASA-9 thermodynamic tables [30] which are adapted for a wide range of temperatures.

2.2.5 Transport

The transport quantities such as the diffusion, the heat flux and the viscosity must also be evaluated and thus their properties must be modeled. Indeed, the

interaction between the species has an effect on the transport properties. Similarly to the thermodynamic properties, only the diffusion and the heat flux properties will be summarized in this work as they will be used for the main subject which is modeling the mass and energy balance. For a comprehensive description, readers can refer to Schrooyen [5] and Bellas-Chatzigeorgis [29] works.

First, the diffusion $\mathbf{J}_i$ in eq. (2.1) is given by:

$$\mathbf{J}_i = \rho Y_i \mathbf{V}_i = -\rho \sum_{j=1}^{N_s} D_{ij} \mathbf{d}_j, \quad (2.7)$$

where $\mathbf{V}_i$ is the diffusion velocity, D_{ij} are the multi-component diffusion coefficients and $\mathbf{d}_j$ are the driving forces [5]. The latter can be expressed in function of the molar fractions $X_i = \frac{W}{W_i} Y_i$ as $\mathbf{d}_j = \nabla X_j$ where W is the mixture molecular weight. Concerning the multi-component diffusion coefficients, they can be computed with the *Mutation*⁺⁺ library.

Evaluating the diffusive flux can be complex and computationally expensive as the Stefan-Maxwell equations must be solved [29]. Hence, we can model the diffusion with the Fick law and the Ramshaw projection. The projection is used to ensure that all species diffusion sum up to zero in order to keep a conservation of mass. The formulation is given by:

$$\mathbf{J}_i = -\rho D_{i,m} \frac{W_i}{W} \nabla X_i + \rho Y_i \sum_{k=1}^{N_s} D_{k,m} \frac{W_k}{W} \nabla X_k, \quad (2.8)$$

“where $D_{i,m}$ is the average diffusion coefficient of species i in the mixture” [5]:

$$D_{i,m} = \frac{1 - Y_i}{\sum_{j \neq i} \frac{X_j}{D_{i,j}}}. \quad (2.9)$$

Note that in Argo some particular cases for the diffusion coefficients are implemented in which case, $D_{i,m}$ can be simplified. Nevertheless, in this thesis only the *Mutation*⁺⁺ library was used.

Eventually, the general expression of the heat flux in eq. (2.3) is given by [29]:

$$\mathbf{q} = -\left(\underbrace{\lambda^T \nabla T^T}_{\text{Translational}} + \underbrace{\sum_M \lambda^M \nabla T^M}_{\text{internal modes}} \right) + \sum_{i=1}^{N_s} h_i \mathbf{J}_i, \quad (2.10)$$

where λ^T is the translational thermal conductivity, λ^M are the thermal conductivities for the other internal energy modes M and the last term is the contribution

of the diffusion. Furthermore, as in this thesis, a single temperature model was assumed, the heat flux can be written as follows:

$$\mathbf{q} = -\lambda^{Tot} \nabla T + \sum_{i=1}^{N_s} h_i \mathbf{J}_i, \quad (2.11)$$

where λ^{Tot} is the sum of all the thermal conductivities. Note that the Dufour effect was neglected [5] meaning that concentration gradients do not induce a gradient of temperature.

2.2.6 Chemical model

In this thesis, different air mixtures were used across the simulations. In Argo, the chemical production term $\dot{\omega}_i$ must be evaluated. When considering a flow solver, reactions between the gaseous species can occur as the mixture may not be at equilibrium and they are called homogeneous reactions. The focus of this section is to only describe these reactions.

The set of N_r homogeneous reactions for N_s species is given as:

$$\sum_{i=1}^{N_s} \nu'_{i,r} A_{i,k} \rightleftharpoons \sum_{i=1}^{N_s} \nu''_{i,r} A_{i,k}, \forall r \in \{1, N_r\}, \quad (2.12)$$

where $\nu'_{i,r}$ and $\nu''_{i,r}$ are the stoichiometric coefficients for the reactant and the product of the species.

The chemical production $\dot{\omega}_i$ is then given by:

$$\dot{\omega}_i = W_i \sum_{k=1}^{N_r} (\nu''_{i,k} - \nu'_{i,k}) \left[k_{f,k} \prod_{j=1}^{N_s} \tilde{\rho}_j^{\nu'_{j,k}} - k_{b,k} \prod_{j=1}^{N_s} \tilde{\rho}_j^{\nu''_{j,k}} \right] \quad (2.13)$$

“where $\tilde{\rho}$ is the molar density. $k_{f,k}$ and $k_{b,k}$ are respectively the forward and backward reaction rates” [5]. The former is given by

$$k_{f,k}(T) = A_k T^{n_k} \exp\left(-\frac{E_{a_k}}{RT}\right), \quad (2.14)$$

where the coefficients A_k , n_k and the activation energy E_{a_k} depend on the reaction. For the mixtures and reactions considered in this thesis, these quantities were proposed by Park and given in Tables 2.1 and 2.2.

Eventually, the backward reaction rate is calculated as follows using the equilibrium criteria:

$$k_{b,k}(T) = \frac{k_{f,k}(T)}{K_{C,k}(T)}, \quad (2.15)$$

where $K_{C,k}$ is the equilibrium constant found using:

$$\ln(K_{C,k}(T)) = - \sum_{i=1}^{N_s} (\nu''_{i,k} - \nu'_{i,k}) \left[\frac{W_i g_i(P_{ref} T)}{RT} - \ln \frac{P_{ref}}{RT} \right], \quad (2.16)$$

with P_{ref} a reference pressure and g_i is the Gibbs energy.

Air mixtures and reactions

The different air mixtures used in this thesis are the *air2*, *air5* and *airCarbon11*. The *air2* mixture is constituted of oxygen and dioxygen and its homogeneous reactions are given in Table 2.1. M denotes a generic species present in the mixture.

	A_k	n_k	$E_{a,k}$
$O_2 + M \rightleftharpoons O + O + M$	2.75×10^{13}	-1	59500

Table 2.1: Homogeneous reaction considered for *air2* mixture. The coefficients and the activation energy for the Arrhenius type law are given by [31]

The *air5* mixture contains five species: N , N_2 , NO , O , O_2 and its mechanisms are given in Table 2.2. The *airCarbon11* contains additional species which are C_2 , C_3 , CO , CO_2 , CN and C_b . The subscript b indicates that this species is solid and not gaseous. In this thesis, *airCarbon11* has the same gas homogeneous reactions than *air5*. However, what differentiates the two mixtures is the gas-surface interactions that will be described later. Indeed, *airCarbon11* contains species that can result from the ablation of solid carbon.

Eventually, inert mixtures can be used later for simpler simulations. This simply means that no homogeneous or gas-surface reactions can take place.

2.3 Surface Balance

In this section, the boundary conditions at the wall will be derived. As explained in the introduction chapter, the aim is to develop a fluid solver without coupling it with a material solver. Thus, the phenomena that occur inside the material must

	A_k	n_k	$E_{a,k}$
$N_2 + M \rightleftharpoons N + N + M$	7.0×10^{21}	-1.6	113200
$O_2 + M \rightleftharpoons O + O + M$	2.0×10^{21}	-1.5	59360
$N_2 + O \rightleftharpoons NO + N$	5.70×10^{12}	0.42	42938
$NO + O \rightleftharpoons O_2 + N$	8.4×10^{12}	0	19400

Table 2.2: Homogeneous reaction considered for *air5* and *airCarbon11* mixtures. The coefficients and the activation energy for the Arrhenius type law are given by [31]

be modeled. Besides, some reactions in the thermal boundary layer of the flow can be favored by the presence of the wall (catalysis) and the surface can re-radiate a part of the energy. A good understanding and a precise modeling of the gas-surface interactions lead to design the thermal protection system properly. However, for fluid solvers this tasks can be more complex and the limitations and hypotheses of the models will be discussed in this section.

The boundary conditions can be obtained by doing a mass and energy balance. This will be detailed in the following.

2.3.1 Mass balance

In order to solve the mass balance, a control volume is attached to the surface between the boundary layer and the solid material. The surface of the material, in case of ablation, is receding at a certain speed. Then all the contributions entering or leaving the control volume are shown in Fig. 2.1.

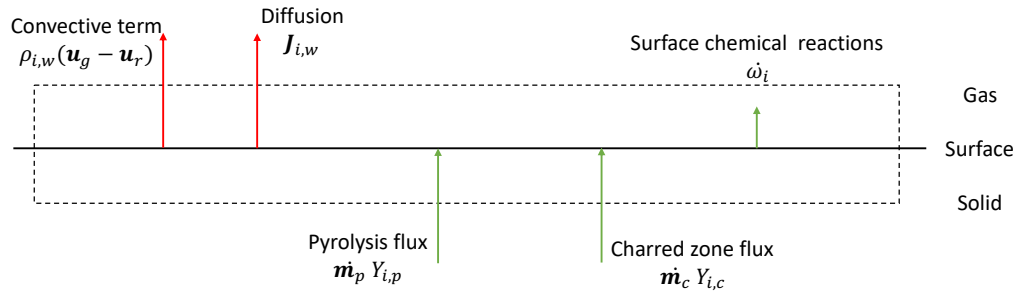


Figure 2.1: Representation of the mass balance at the gas-solid interface. Sketch inspired from [32, 9]

Therefore, the mass balance can be written for each species present in the

mixture as follows

$$\left[\rho_{i,w}(\mathbf{u}_g - \mathbf{u}_r) + \mathbf{J}_{i,w} - \dot{\mathbf{m}}_p Y_{i,p} - \dot{\mathbf{m}}_c Y_{i,c} \right] \cdot \mathbf{n} = \dot{\omega}_i \quad \forall i \in \{1, N_s\}, \quad (2.17)$$

Note, that in this thesis, the mechanical removal and hence the injection of solid degraded material (spallation) is not taken into account. Hence, when speaking of pyrolysis or ablation, only the gas products are considered [29]. The subscripts w , p and c refer to respectively the gaseous species at the surface, in the pyrolysis zone and in the char zone where the terms must be evaluated.

The source term $\dot{\omega}_i$, which represent the creation or destruction of the species at the surface has two contributions (catalysis and ablation):

$$\dot{\omega}_i = \dot{\omega}_{i,abl} + \dot{\omega}_{i,catal}. \quad (2.18)$$

The first term at the left hand side of eq. (2.17) , $\rho_{i,w}(\mathbf{u}_g - \mathbf{u}_r)$, represents the convective part where $\mathbf{u}_g$ is the blowing velocity of the gas due to pyrolysis and ablation. Indeed, the species at the surface are blown towards the boundary layer by the injection of the pyrolysis and ablation gas products. In order to evaluate this velocity, “the momentum equation should normally be solved” [29]. Nevertheless, another hypotheses can be made which is “imposing a non-slip condition on the surface and imposing a null normal pressure gradient” as done in Bellas-Chatzigeorgis work [29]. One can hence retrieve the blowing velocity as follows:

$$u_g = \frac{\dot{m}_{blow}}{\sum_{i=1}^{N_s} \rho_{i,w}}, \quad (2.19)$$

where $\dot{m}_{blow}$ is the mass flux due to ablation and pyrolysis:

$$\dot{m}_{blow} = \dot{m}_c + \dot{m}_p. \quad (2.20)$$

The pyrolysis mass flux can be found by solving the gas-phase mass conservation equation given in eq. (2.1). This approach was not used here and the modeling of pyrolysis will be discussed later. The recession velocity $\mathbf{u}_r$, is the speed at which the surface of the material is consumed. It is given as follows:

$$\mathbf{u}_r = \frac{\dot{m}_c}{\sum_{i=1}^{N_s} \rho_{i,c}} = \frac{\sum_{i=1}^{N_s} \dot{\omega}_{i,abl}}{\rho_c}. \quad (2.21)$$

The second term of the mass balance the represent the diffusive part of the mass flux given by eq. (2.8) where the quantities in the equation such as the gradients are evaluated at the surface.

The last two terms represent the mass fluxes of the pyrolysis and ablation from the porous material.

2.3.2 Energy balance

The energy balance is found similarly by attaching a control volume to the surface and by taking into account all the energy contributions shown in Fig. 2.2.

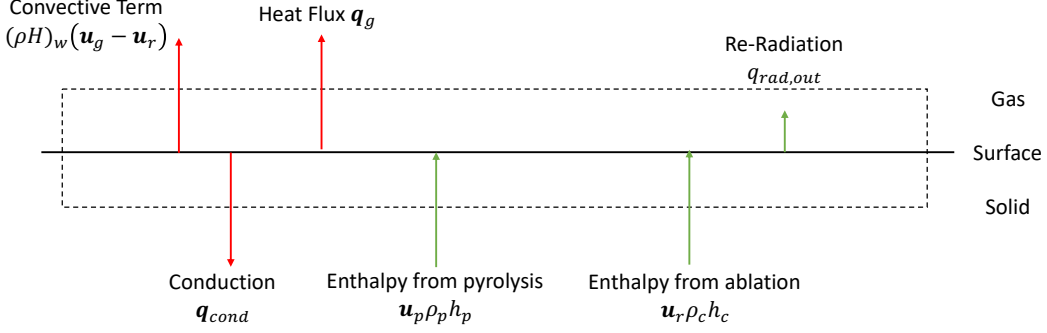


Figure 2.2: Representation of the energy balance at the gas-solid interface. Sketch inspired from [32, 9]

The energy balance can be written as:

$$\left[(\rho H)_w (\mathbf{u}_g - \mathbf{u}_r) + \mathbf{q}_g + \mathbf{q}_{cond} - \mathbf{u}_p \rho_p h_p - \mathbf{u}_r \rho_c h_c \right] \cdot \mathbf{n} = q_{rad,out}, \quad (2.22)$$

Here, the source term is the re-radiation of the wall $q_{rad,out}$. It follows the Stefan-Boltzmann law:

$$q_{rad,out} = \sigma \varepsilon (T_w^4 - T_{env}^4), \quad (2.23)$$

where $\sigma \approx 5.67 \times 10^{-8} [W/(m^2 K^4)]$ is the Stefan-Boltzmann constant, T_w is the temperature of the surface, T_{env} is the temperature of the environment towards which the radiation happens and ε is the emissivity of the surface. In this work, as the surface temperature of TPS can reach several thousands of degrees, the environment temperature has been neglected. Furthermore, as the emissivity of the materials used for TPS is generally high ($\varepsilon \approx 0.86$ for carbon ablators), the effect of radiation is significant.

Similarly to the mass equations, the first term is the energy contribution due to the convective part. The surface enthalpy is given by summing up the enthalpy of each species at the wall:

$$H_w = \sum_{i=1}^{N_s} Y_{i,w} h_{i,w}. \quad (2.24)$$

Note that the enthalpy h_p and h_c are also found by summing up the enthalpy of each species but for respectively the pyrolysis and the charred zone gases:

$$h_p = \sum_{i=1}^{N_s} Y_{i,p} h_{i,p}, \quad h_c = \sum_{i=1}^{N_s} Y_{i,c} h_{i,c}. \quad (2.25)$$

The second term is the heat flux of the gas. As seen in eq. (2.11), it has two part which are the conductivity and the energy from the diffusion. The radiation of the species was neglected.

The conduction inside the material must also be determined. In general, a material response code is needed. However, as a fluid solver must be used, $\mathbf{q}_{cond}$ must be evaluated by using some hypotheses. Two approaches will be described.

The first idea is that, in case of a steady-state ablation with pyrolysis, the conduction can be approximated. The second idea is used when the conductivity of the material is low and no pyrolysis reactions occur, the conduction term can be neglected[29].

This first approach was proposed by Turchi [32] and has two objectives. It allows to model the pyrolysis for a fluid solver and to evaluate the conduction term.

For a steady-state ablation, the recession rate of the pyrolyzing resin is equal to the recession rate of the consumed char. For these conditions, the profile of the temperature inside the material remains the same. Besides, the heat wave due to conduction is supposed to not having reached the virgin material [32]. We can find the conduction by solving the energy balance inside the material. The control volume begins at the surface and goes to the virgin layer. The subscripts c represents the charred material and V represents the virgin solid material. The conduction is thus given by [29, 32]:

$$q_{cond,steady} = \mathbf{u}_p \rho_p h_p - \mathbf{u}_r (\rho_V h_V - \rho_c h_c). \quad (2.26)$$

Then one can define the parameter ϕ [32]:

$$\phi = \frac{\rho_V}{\rho_{C_b}} - 1, \quad (2.27)$$

where ρ_{C_b} is the density of the remaining solid carbon in the char zone. By assuming gas equilibrium inside the porous material, the mass fractions in the pyrolysis and the char zones are both equal to the equilibrium composition $Y_{i,p} =$

$Y_{i,c} = Y_{i,eq}$ and the mass and energy equations become [29]:

$$\left[\rho_{i,w}(\mathbf{u}_g - \mathbf{u}_r) + \mathbf{J}_{i,w} - \dot{\mathbf{m}}_c \phi Y_{i,eq} \right] \cdot \mathbf{n} = \dot{\omega}_i \quad \forall i \in \{1, N_s\} \quad (2.28)$$

$$\left[(\rho H)_w(\mathbf{u}_g - \mathbf{u}_r) + \mathbf{q}_g + \dot{\mathbf{m}}_c(\phi + 1)h_V \right] \cdot \mathbf{n} = q_{rad,out}. \quad (2.29)$$

Note that for this thesis, pyrolysis was not taken into account and we assumed to have a low material conductivity. Bellas-Chatzigeorgis [29] also found that $\mathbf{u}_r \ll \mathbf{u}_g$. The mass and energy balances considered in this work become:

$$\left[\rho_{i,w} \mathbf{u}_g + \mathbf{J}_{i,w} \right] \cdot \mathbf{n} = \dot{\omega}_i \quad \forall i \in \{1, N_s\} \quad (2.30)$$

$$\left[(\rho H)_w \mathbf{u}_g + \mathbf{q}_g \right] \cdot \mathbf{n} = q_{rad,out}. \quad (2.31)$$

2.3.3 Surface chemical models

In this part, the various surface chemical models will be described. First, we will explain the model used for the catalytic reactions then for the ablation.

Catalysis

The surface of the thermal protection system can have catalytic properties. Indeed, in the presence of the solid wall, the recombination of certain species can be promoted. As the catalyst is the solid wall, these reaction are named heterogeneous catalysis despite the fact that the dissociated species that will recombine are and remain gaseous. This phenomenon is crucial for the design of TPS as most of the catalytic reactions release a significant amount of energy consequently heating up the material. Furthermore, unlike ablation or pyrolysis, the catalytic reactions do not degrade the material but the wall is nevertheless needed.

Two main models were developed and used in the state-of-the-art: (1) the gamma model [33] which is commonly used in this domain and (2) the finite rate catalysis model which can be more precise.

The first approach will be detailed as the simulations in this thesis were performed using the gamma model. This theory is based on defining a probability of recombination γ for each dissociated species. We can first consider a generic homo-nuclear species A with its recombination reaction:



the recombination coefficient γ_A is defined as follows:

$$\gamma_A = \frac{F_{A,rec}}{F_A^\downarrow}, \quad (2.33)$$

“where $F_A^\downarrow$ is the flux of species A impinging the surface and $F_{A,rec}$ is the flux of species recombining at the surface” [29]. The recombination coefficient γ_A must take a value between 0 for a non-catalytic wall and 1 for a fully catalytic wall. In the latter, all the dissociated species at the wall will recombine.

Then, the chemical production $\dot{w}_{A,cat}$ and $\dot{w}_{A_2,cat}$ are given by[29]:

$$\dot{w}_{A,cat} = \gamma_A m_A F_A^\downarrow = \gamma_A m_A n_A \sqrt{\frac{k_B T_s}{2\pi m_A}} \quad (2.34)$$

$$\dot{w}_{A_2,cat} = -\gamma_A m_A F_A^\downarrow = -\gamma_A m_A n_A \sqrt{\frac{k_B T_s}{2\pi m_A}}, \quad (2.35)$$

where m_A is the mass of species A , $k_B \approx 1.38 \times 10^{-23} [J/K]$ is the Boltzmann constant and T_s is the wall temperature.

Eventually, hetero-nuclear catalytic reactions could also occur. The recombination of oxygen and nitrogen into NO is an example. The generic formulation is the following:



and with a chemical production expressed as [29]:

$$\dot{w}_{AB,cat} = -\gamma_{AB} m_A F_A^\downarrow - \gamma_{BA} m_B F_B^\downarrow, \quad (2.37)$$

with $\gamma_{AB} F_A^\downarrow = \gamma_{BA} F_B^\downarrow$ such that the mass remains conserved.

One recalls that the recombination coefficient for homo-nuclear species must stay between 0 and 1, in addition to that, if hetero-nuclear reactions (with species present in other catalytic reactions) occur, the conditions on the recombination coefficients become [29]:

$$0 \leq \gamma_A + \gamma_{AB} \leq 1 \quad (2.38)$$

$$0 \leq \gamma_B + \gamma_{BA} \leq 1 \quad (2.39)$$

Indeed, if those conditions are not satisfied such that $\gamma_A + \gamma_{AB} > 1$ for example, this means that more than the available dissociated species A will recombine leading to the non-conservation of the mass equations.

Ablation

Similarly to catalysis, several models are used to evaluate the chemical rates due to ablation: (1) two phenomenological ablation models depending on the reaction

considered and (2) the finite rate ablation model.

The first two models are implemented in *Mutation*⁺⁺ in order to get the reaction rates of the two following generic reactions [29, 2]:



where A is a gaseous species, and the subscript b is to indicate the solid species. Equation (2.40) is for ablation reactions such as carbon oxidation $O + C_b \rightarrow CO$, and eq. (2.41) is for sublimation where the solid is directly transformed into gas. The coefficient α is the number of atoms of the solid.

For the first type of equation, we also define a recombination probability β which plays the same role as γ seen previously. For the oxidation and nitridation reactions considered in this work, the β coefficients are given by Park in Table 2.3

Reaction	β
$O + C_b \rightarrow CO$	$0.63 \exp(-1160/T_s)$
$N + C_b \rightarrow CN$	$0 - 1$

Table 2.3: Phenomenological model for oxidation and nitridation. Coefficient β from Park et al. [31]

For nitridation, Park gave only a range of values. However, in this work, $\beta = 0.003$ is given by Helber [34].

Eventually, for the sublimation, the chemical production is given by [29, 2]:

$$\dot{\omega}_{abl,C_3} = \beta_{C_3}(\rho_{C_3,equil} - \rho_{C_3})\sqrt{\frac{k_B T_s}{2\pi m_{C_3}}}, \quad (2.42)$$

where $\rho_{C_3,equil}$ is the density obtained at equilibrium on the surface which can be computed thanks to Park [31]:

$$\rho_{C_3,equil} = W_{C_3} 1.9 \times 10^7 T_w^{-1} \exp\left(-\frac{59410}{T_s}\right).$$

However, in *Mutation*⁺⁺, we must provide the coefficients of the Arrhenius type law to get the saturation pressure. For C_3 , it reads [29]:

$$p_{C_3,sat} = 5.19 \times 10^{15} \exp\left(-\frac{90908}{T_s}\right). \quad (2.43)$$

2.4 Conclusion

In this chapter, the chemically reactive Navier-Stokes equations were derived. The thermodynamic properties were also described and a single temperature model was used. Then, transport properties were needed in order to evaluate the diffusion of the species and the heat fluxes. Furthermore the boundary conditions needed for the closure of the Navier-Stokes equations were derived and added to Argo in this work. We showed that with certain assumptions, a fluid solver only can be used and that the material response could be modeled. Nevertheless, those hypotheses remain simplistic but still useful for practical situations. Eventually, the surface chemistry and the models used for the catalytic and ablative reactions were detailed.

Chapter 3

Numerical methods

In this chapter, the practical implementation of the mass and energy balance in the Argo code and the numerical methods used will be presented. First, the discontinuous Galerkin methods will be explained as well as how the different boundary conditions are imposed. Two types of boundary conditions can be imposed: Dirichlet and Neumann. The former needs an auxiliary solver of the mass and energy balance in order to find the values to impose whereas for the latter, the diffusive flux can be isolated from the mass and energy balance and hence it can be directly imposed. Eventually, a brief description of the use of *Mutation*⁺⁺ will be given.

3.1 Argo

“Argo is a multi-physics code based on a discontinuous Galerkin method” [5]. Several module are implemented in Argo and can be used depending on the problem notably *DGFluid* which can solve incompressible and compressible flows and *DGAblation*, which is based on the latter and is the module of interest for this work. This module aims to solve ablation problems for high enthalpy flows. The new boundary conditions will be implemented in this block in addition to the unified approach. A more detailed description of the capabilities of Argo is given in Schrooyen work [5].

3.2 Discontinuous Galerkin method

Before showing the discontinuous Galerkin formulation, eqs. (2.1) to (2.3) from the previous chapter can be written by separating the convective and diffusive terms as follows:

$$\frac{\partial \mathbf{U}}{\partial t} + \nabla \cdot \mathbf{F}^c = \nabla \cdot \mathbf{F}^d + \mathbf{S}, \quad (3.1)$$

“where $\mathbf{U}$ is the vector of conservative variables $(\rho_i, \rho \mathbf{u}, \rho E)$ ” [5] and with

$$\mathbf{F}^c = \begin{pmatrix} \rho_i \mathbf{u} \\ \rho \mathbf{u} \mathbf{u} + P \mathbf{I} \\ \rho \mathbf{u} H \end{pmatrix}, \quad \mathbf{F}^d = \begin{pmatrix} -\mathbf{J}_i \\ \boldsymbol{\tau} \\ \boldsymbol{\tau} \cdot \mathbf{u} - \mathbf{q} \end{pmatrix}, \quad \mathbf{S} = \begin{pmatrix} \dot{\omega}_i \\ \mathbf{0} \\ \dot{\omega}_T \end{pmatrix}. \quad (3.2)$$

Then, we define $\mathcal{L}_m(\tilde{\mathbf{u}})$ for every component $m \in \{1, N_v\}$ of the solution state $\tilde{\mathbf{u}}$ [5]:

$$\mathcal{L}_m(\tilde{\mathbf{u}}) = 0 \quad (3.3)$$

$$= \frac{\partial \tilde{u}_m}{\partial t} + \frac{\partial}{\partial x^k} F_m^{c,k}(\tilde{\mathbf{u}}) - \frac{\partial}{\partial x^k} F_m^{d,k}(\tilde{\mathbf{u}}, \nabla \tilde{\mathbf{u}}) - S(\tilde{\mathbf{u}}, \nabla \tilde{\mathbf{u}}) \quad (3.4)$$

where N_v is the number of variables and $F_m^{d,k}$ is defined as follows:

$$F_m^{d,k} = -D_{m,n}^{k,l}(\mathbf{u}) \frac{\partial \tilde{u}_n}{\partial x^l}, \quad (3.5)$$

with $D_{m,n}^{k,l}$ linking the diffusive flux to the gradients of the solution.

Then, for the discontinuous Galerkin method, the spatial domain is decomposed into Ω_e distinct and non-overlapping elements. The solution on one element is approximated by using orthogonal shape-functions ϕ_i belonging to a functional space $\mathcal{V}$:

$$\tilde{u}_m \approx \sum_{i=1}^N U_i \phi_i, \quad (3.6)$$

where N is the number of degrees of freedom (also named control points) on the element. The latter depends on the order p of the shape-functions and U_i is the value at the control point i . In Argo, the shape-function are the Lagrange polynomials expressed on an element of reference. Hence a mapping is needed to express the solution on the actual domain. Moreover, for discontinuous Galerkin, the continuity of the solution on two adjacent elements is not imposed. This can be shown in Fig. 3.1 for two one-dimensional elements.

Eventually, the weak form of Equation (3.3) is solved. The weak formulation is obtained by multiplying $\mathcal{L}_m$ by a test function $v \in \mathcal{V}$ and by integrating over the

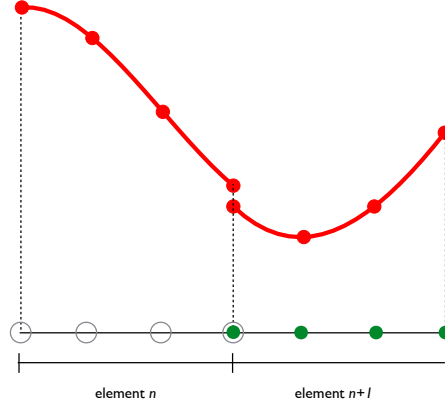


Figure 3.1: Representation of discontinuous Galerkin functions on two adjacent one dimensional elements. At the interface, no continuity constraint is imposed. Figure from [5]

whole domain:

$$\begin{aligned}
\int_{\Omega} v \mathcal{L}_m(\tilde{\mathbf{u}}) &= 0 \\
&= \sum_{\Omega_e} \int_{\Omega_e} v \frac{\partial u_m}{\partial t} d\Omega_e \\
&\quad - \sum_{\Omega_e} \int_{\Omega_e} \frac{\partial v}{\partial x^k} F_m^{c,k}(\mathbf{u}) d\Omega_e + \sum_{I_i} \oint_{I_i} [v]^k n^k \mathcal{H}_m(\mathbf{u}^+, \mathbf{u}^-, \mathbf{n}) dS \\
&\quad + \sum_{\Omega_e} \int_{\Omega_e} \frac{\partial v}{\partial x^k} F_m^{d,k}(\mathbf{u}) d\Omega_e - \sum_{I_i} \oint_{I_i} \langle D_{mn}^{kl} \frac{\partial \mathbf{u}_n}{\partial x^l} \rangle [v]^k dS \\
&\quad - \theta \sum_{I_i} \oint_{I_i} \langle D_{mn}^{kl} \frac{\partial v}{\partial x^l} \rangle [u_m]^k dS + \alpha \sum_{I_i} \oint_{I_i} [v]^k [u_m]^k dS \\
&\quad - \sum_{\Omega_e} \int_{\Omega_e} v S(\mathbf{u}, \nabla \mathbf{u}) d\Omega_e,
\end{aligned}$$

“where I_i are interfaces between adjacent elements and $\mathcal{H}_m$ is the flux at the interface” [5]. We also define the following operators [5]:

$$[a] = a^- n^- + a^+ n^+ \quad (3.7)$$

$$\langle a \rangle = \frac{a^- + a^+}{2} \quad (3.8)$$

The coefficient α and θ come from the Interior Penalty method implemented in Argo to discretize the diffusive term. In this work, $\theta = 0$ was used and α depends on the mesh size [35].

For more comprehensive details about how the interfaces fluxes for the convective part is evaluated in Argo, the reader can refer to these works [5, 35]. However, we note that $\mathcal{H}_m$ depends on the values $+$ and $-$ at the interface which by convention are defined as in Fig. 3.2.

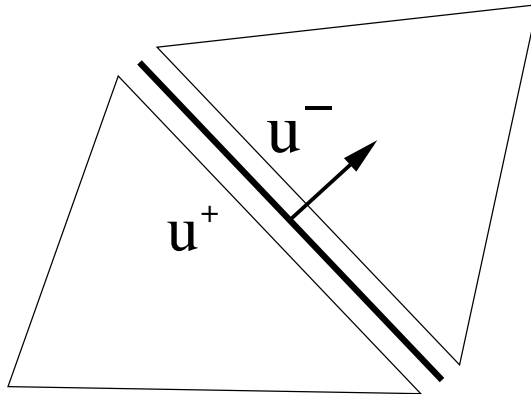


Figure 3.2: Conventional representation of the value $+$ and $-$ on an interface between two elements. Figure from [35]

Our interest in this thesis is to determine those values at the boundary where gas-surface interactions occur.

3.3 Boundary conditions

In this thesis, two types of boundary conditions for the mass and energy balance were used namely Dirichlet and Neumann. In both cases, a choice for the outer values $\mathbf{U}^-$ and for the diffusive flux $\mathbf{F}^d \cdot \mathbf{n}$ must be made.

Before detailing these methods, the mass and energy balance from eqs. (2.30) and (2.31) will be given. Indeed, the choice for the boundary conditions will depend on the balance. Considering only the gas-surface interactions studied in the results, we can recall:

$$\left[\rho_{i,w} \mathbf{u}_g + \mathbf{J}_{i,w} \right] \cdot \mathbf{n} = \dot{\omega}_i \quad \forall i \in \{1, N_s\} \quad (3.9)$$

$$\left[(\rho H)_w \mathbf{u}_g + \mathbf{q}_g \right] \cdot \mathbf{n} = q_{rad,out}. \quad (3.10)$$

Then, we can write using eq. (2.11) for $\mathbf{q}_g$:

$$\left[\rho_{i,w} \mathbf{u}_g + \mathbf{J}_{i,w} \right] \cdot \mathbf{n} = \dot{\omega}_i \quad \forall i \in \{1, N_s\} \quad (3.11)$$

$$\left[(\rho H)_w \mathbf{u}_g - \lambda^{Tot} \nabla T + \sum_{i=1}^{N_s} h_{i,w} \mathbf{J}_{i,w} \right] \cdot \mathbf{n} = q_{rad,out}. \quad (3.12)$$

In order to verify the implementation step-by-step, we first implemented the mass balance equations and we imposed the temperature at the wall. The conditions for the Dirichlet and the Neumann type of imposition is given in Table 3.1.

BC type	Convective terms	Diffusive terms
Dirichlet	$\mathbf{u}^-$, P_i^- and T^- are given; $\mathbf{U}^+ = \mathbf{U}^-$ for the rest	/
Neumann	$\mathbf{u}^-$ and T^- are given; $\mathbf{U}^+ = \mathbf{U}^-$ for the rest	$\mathbf{F}_{mass}^d \cdot \mathbf{n}$ is given

Table 3.1: Additional boundary conditions implemented in Argo when solving the mass balance only. Notations from [5]

where $\mathbf{u}^-$ is the velocity vector, P_i^- are the partial pressures for each species obtained by solving the mass balance equations and T^- is the given wall temperature chosen prior the simulations. The resolution of the mass and energy balance will be detailed in the next section.

For Neumann, $\mathbf{F}_{mass}^d \cdot \mathbf{n}$ is given by isolating the diffusive flux $\mathbf{J}_{i,w}$ from the mass balance equations in eq. (2.17):

$$\mathbf{F}_{mass,i}^d \cdot \mathbf{n} = -\rho_{i,w} \mathbf{u}_g \cdot \mathbf{n} + \dot{\omega}_i \quad \forall i \in \{1, N_s\}. \quad (3.13)$$

Eventually, when the temperature at the wall is an unknown, T^- is given by the solution of the energy equation for Dirichlet and by giving $\mathbf{F}_{energy}^d \cdot \mathbf{n}$ as well for Neumann as shown in Table 3.2.

BC type	Convective terms	Diffusive terms
Dirichlet	$\mathbf{u}^-$, P_i^- and T^- are given; $\mathbf{U}^+ = \mathbf{U}^-$ for the rest	/
Neumann	$\mathbf{u}^-$ is given; $\mathbf{U}^+ = \mathbf{U}^-$ for the rest	$\mathbf{F}_{mass}^d \cdot \mathbf{n}$ and $\mathbf{F}_{energy}^d \cdot \mathbf{n}$ are given

Table 3.2: Additional boundary conditions implemented in Argo when solving the mass and energy balance. Notations from [5]

The diffusive energy flux is given by isolating $-\lambda^{Tot}\nabla T$ from the energy equation in eq. (2.22):

$$\mathbf{F}_{energy}^d \cdot \mathbf{n} = -\left[(\rho H)_w \mathbf{u}_g + \sum_{i=1}^{N_s} h_{i,w} \mathbf{J}_{i,w}\right] \cdot \mathbf{n} + q_{rad,out}. \quad (3.14)$$

3.4 Solving the mass and energy balance

In order to impose a Dirichlet boundary condition, the mass and energy balance must be solved at each iteration independently from the whole flow solver. Hence, a Newton-Raphson solver has been implemented. NR-solver is an iterative solver and therefore a first guess is needed and its choice can be crucial for the convergence.

In our case, the unknown vector $\mathbf{x}$ is constituted by the molar fraction X_i of each species $i \in \{1, N_s\}$ in the mixture and T_s , when the temperature is not imposed. Indeed, simplifying the system allows us to focus on a specific aspect of the models used and to rigorously verify the implementation step-by-step. It will be shown in the next chapter that solving the mass balance alone allows us to study the effect of different types of wall-catalycity and that solving the energy equation alone let us focus on the effect of the surface's re-radiation. In this work, a single temperature state is used and thus there will be at maximum one energy equation.

In order to solve a system using a NR-solver, a functional $\mathbf{f}(\mathbf{x}_t) = \mathbf{0}$ is defined by the mass and energy balance equations seen in eqs. (3.11) and (3.12). The latter is a vector of the same size of $\mathbf{x}_t$. Then the solution of the next iteration is given as follows:

$$\mathbf{x}_{t+1} = \mathbf{x}_t - \mathcal{J}^{-1}(\mathbf{x}_t) \cdot \mathbf{f}(\mathbf{x}_t) \quad (3.15)$$

where $\mathbf{x}_{t+1}$ is the solution found after one iteration from the previous solution $\mathbf{x}_t$ and $\mathcal{J}$ is the Jacobian of the system. The Jacobian is defined as follows:

$$(\mathcal{J}(\mathbf{x}_t))_{i,j} = \frac{\partial f_i(\mathbf{x}_t)}{\partial x_j}. \quad (3.16)$$

However, it is not always possible to compute the analytical derivatives hence the Jacobian is evaluated by using finite differences:

$$\mathcal{J}_{i,j} = \frac{\mathbf{f}_i(\tilde{\mathbf{x}}_t^j) - \mathbf{f}_i(\mathbf{x}_t)}{\epsilon} \quad (3.17)$$

where ϵ must be chosen arbitrarily small and $\tilde{\mathbf{x}}_t^j$ is the state vector where the j -th quantity is the perturbed.

The inverse of the Jacobian is needed, hence all the equations must be linearly independent. However, as all the N_s species were considered and that the constraint in eq. (3.18) must always be valid, the system is not of full rank and the inversion is not possible at this point.

$$\sum_{i=1}^{N_s} X_i = 1 \quad (3.18)$$

There are two ways to deal with this issue. We can solve for $N_s - 1$ species with the constraint in eq. (3.18). This approach was not used here. Or, we can perturb the Jacobian [2, 29] as follows:

$$\mathcal{J} = \mathcal{J} + \alpha \mathcal{I} \quad (3.19)$$

where α is an arbitrary constant and $\mathcal{I}$ is the identity matrix. The choice of α is important. It cannot be too small because it will not perturb the system enough and it cannot be too big as it will influence the solution. The choice made for the implementation in this work is the following:

$$\alpha = \max_{i \neq N_s+1} \left(\text{diag}(\mathcal{J})_i \right), \quad (3.20)$$

where $\text{diag}(\mathcal{J})$ is the diagonal of the Jacobian. Note that the diagonal element corresponding to the energy equation was not taken into account. Indeed, the order of magnitude of the energy balance is way bigger than the mass balance. Thus, the coefficient α given by eq. (3.20) will slightly affect the sub-system containing the mass equations without affecting the energy equation. This choice was taken from the *Mutation*⁺⁺ solver [2] and proved to be effective.

Eventually, as the boundary conditions require the partial pressures P_i for the species. It is given by multiplying X_i by the total pressure P .

3.5 *Mutation*⁺⁺

Even though Argo has its own internal library to compute some thermodynamic and transport properties, it also uses *Mutation*⁺⁺ for more accurate results. In this work, the latter was used to evaluate the reaction rates for homogeneous reactions, to compute the transport and thermodynamics properties for a non-equilibrium mixture and to evaluate the reaction rates for the gas-surface interactions such as

catalysis and ablation.

The user's input for the simulations must be given in three different files:

1. Mixture: This file contains the species present in the mixture as well as the information regarding the state of the mixture, the database used for the evaluation of the thermodynamic properties and the type of the gas-surface interaction. In this thesis, a chemically non-equilibrium mixture with a single temperature state was used.
2. Mechanisms: In this file, the corresponding homogeneous reactions with their kinetics coefficients are specified.
3. Gas-surface interactions: Eventually, the gas-surface interactions considered are given in this file. We can define some coefficients (such as the recombination coefficients γ) to produce different reactions and observe the physical response obtained accordingly.

Eventually, *Mutation*⁺⁺ provides test codes to verify gas-surface interactions when given the fluid-side state at a certain distance from the wall and the temperature of the wall when the latter is imposed. These tests alone do not allow to verify the convergence to a steady-state solution as the mass and energy balance are solved only once with one given state for the fluid. Nevertheless, these tests provides a preliminary check for the implementation of the constitutive equations and the implementation of the auxiliary NR-solver.

Chapter 4

Results

This chapter aims to verify the implementations of the mass and energy balance developed in Argo. Two approaches were implemented and described in Chapter 3 which are the Dirichlet and the Neumann imposition of the mass and energy balance. A series of tests will be conducted and will range from pseudo-1D to 2D cases with various boundary conditions. Then the convergence and the stability of these two types of imposition will be studied.

4.1 Introduction

The implementation of the Dirichlet imposition after solving the mass and energy balance can be compared to the *Mutation*⁺⁺ test codes [2]. This first step will ensure that the equations of the gas-surface interactions are well implemented in Argo. As *Mutation*⁺⁺ has a one dimensional finite volume solver, a pseudo-1D test was created for the Argo simulations such that the results of the Argo code can be comparable to the *Mutation*⁺⁺ ones.

In fact, Argo uses the discontinuous Galerkin method such that the mass and energy balance must have been adapted. However, it is still possible to create a simple test case to get as close as possible from a finite volume solver. As shown in Fig. 4.1, the mesh has only one square element with 4 nodes and the simulations will be done using first order shape-functions. Besides, the same state is imposed in each vertical vertex. In contrast, *Mutation*⁺⁺ only needs two points: one describing the fluid state and one describing the wall state.

The test codes in *Mutation*⁺⁺ allow to verify, given the state on the fluid side and the temperature at the wall when the latter is imposed, if the Newton-Raphson solver converges correctly when solving the mass and energy balance. Hence, these

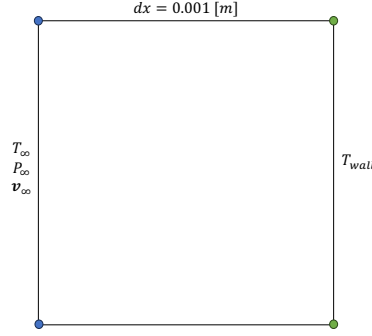


Figure 4.1: Mesh used to simulate pseudo-1D problems in Argo. Order $p = 1$ shape-functions were used.

tests do not verify the steady-state solution taking into account the air homogeneous reactions for example.

More complex tests will then be conducted. This will show which case and method of imposition really converges in Argo and will subsequently show the physical effects of the different boundary conditions (non-catalytic vs catalytic wall, imposed wall temperature vs energy equation).

As one of the thesis objectives is to accelerate the simulations, the convergence and stability of the different imposition methods will be studied. As the Neumann imposition method cannot directly be compared to *Mutation*⁺⁺ solutions, we will also compare the solutions of the Neumann with the Dirichlet imposition. Indeed the former does not solve the mass and energy balance at each iteration but the diffusion flux is directly imposed.

For all the tests and simulations, different air mixtures can be used. Their homogeneous reactions, also called air mechanisms, were given in section 2.2.6. The gas-surface interactions were also described in section 2.3.3. However, in order to study the effects of different gas-surface interaction properties on the solution, such as the catalycity at the wall, variants of the previous mixtures were also used. In these variants, either the air mechanisms were neglected (for inert mixtures), either the recombination coefficients γ were changed to arbitrary values ($\gamma = 1$ for example to impose a fully catalytic wall).

As a reminder, only three catalytic reactions were taken into account: (1) O_2 recombination, (2) N_2 recombination and (3) NO formation. In Table 4.1, the different properties for the gas-surface interaction for testing the catalytic reactions

are given.

mixture name	(1)	(2)	(3)	composition
<i>air2</i>	$\gamma_O = 1$	/	/	O, O_2
<i>air5_inert</i>	$\gamma_O = 0$	$\gamma_N = 0$	$\gamma_O = 0; \gamma_N = 0$	O, O_2, N, N_2, NO
<i>air5</i>	$\gamma_O = 0.001$	$\gamma_N = 0.001$	$\gamma_O = 0.003; \gamma_N = 0.002$	O, O_2, N, N_2, NO
<i>air5*</i>	$\gamma_O = 1$	$\gamma_N = 1$	$\gamma_O = 0; \gamma_N = 0$	O, O_2, N, N_2, NO

Table 4.1: Air mixtures used for simulations

For the ablating wall, we will only use the three ablation reactions and the coefficients discussed in section 2.3.3. Besides, no catalytic reactions were taken into account for the *airCarbon11* mixture and the air mechanisms are the same as the *air5* mixture.

Eventually, all the boundary conditions considered in this section are: (1) non-catalytic wall with imposed temperature, (2) catalytic wall with imposed temperature, (3) catalytic & ablative wall with imposed temperature, (4) non-catalytic wall with energy eq., (5) catalytic wall with energy eq. and (6) catalytic & ablative wall with energy equation.

4.2 Pseudo-1D cases

In this section, the results of the Argo code will be compared against *Mutation*⁺⁺ test codes on pseudo-1D cases.

4.2.1 Mass equations

First, the lists of cases to verify the mass equations are given in Tables 4.2, 4.4 and 4.7. The tables give the free-stream conditions, the distance to the wall, the temperature at the wall and the mixture used. The composition of the free-stream fluid is given by equilibrating the mixture at the free-stream conditions.

For the catalytic wall, the tests aimed to compare the difference of the solutions between Argo and *Mutation*⁺⁺ for a simple realistic air mixture. The mixture used is *air5*.

	T_∞	p_∞	$\mathbf{v}_\infty$	dx	T_{wall}
case 1	5000	1000	$\mathbf{0}$	0.001	3000

Table 4.2: Boundary conditions for a catalytic wall with imposed temperature

The results are given in Table 4.3. The Argo code gives a solution of the same order of magnitude than *Mutation*⁺⁺ with a relative error of at most $\approx 3 \cdot 10^{-6}$.

	X_N	X_O	X_{NO}	X_{N_2}	X_{O_2}
Mpp	$2.264 \cdot 10^{-1}$	$3.055 \cdot 10^{-1}$	$2.508 \cdot 10^{-3}$	$4.653 \cdot 10^{-1}$	$3.106 \cdot 10^{-4}$
Argo	$2.264 \cdot 10^{-1}$	$3.055 \cdot 10^{-1}$	$2.511 \cdot 10^{-3}$	$4.653 \cdot 10^{-1}$	$3.111 \cdot 10^{-4}$
absolute error	$2.867 \cdot 10^{-6}$	$2.110 \cdot 10^{-6}$	$2.975 \cdot 10^{-6}$	$1.561 \cdot 10^{-6}$	$4.408 \cdot 10^{-7}$

Table 4.3: Molar fractions and absolute errors for case 1: catalytic wall with imposed temperature

Then, for the ablative wall, different temperatures can be imposed in order to see the presence of certain species or not as some chemical reactions only occur at a certain temperature. As an example, the carbon sublimation occurs around 3000 [K] for the conditions imposed [9].

For the following cases, a different mixture (*airCarbon11*) was used in order to have the species resulting from the ablation. Besides, an excess of carbon at the wall is imposed such as the latter does not limit the reactions.

	T_∞	p_∞	$\mathbf{v}_\infty$	dx	T_{wall}
case 2.1	3000	1000	$\mathbf{0}$	0.001	2000
case 2.2	5000	1000	$\mathbf{0}$	0.001	4000

Table 4.4: Boundary conditions for ablative wall and imposed temperature

The results are shown in Tables 4.5 and 4.6. Only non-null values were shown. We can depict that for the hotter conditions, sublimated carbon is the main species resulting from ablation whereas carbon monoxide is the main resulting one for the cooler case. However, the relative errors seen for the cooler conditions are not negligible.

	X_N	X_O	X_{NO}	X_{N_2}	X_{O_2}	X_{C_3}	X_{CN}	X_{CO}
Mpp	$1.096 \cdot 10^{-4}$	$1.276 \cdot 10^{-1}$	$1.945 \cdot 10^{-2}$	$5.977 \cdot 10^{-1}$	$4.426 \cdot 10^{-2}$	$3.628 \cdot 10^{-8}$	$1.432 \cdot 10^{-6}$	$2.109 \cdot 10^{-1}$
Argo	$1.081 \cdot 10^{-4}$	$1.025 \cdot 10^{-1}$	$1.912 \cdot 10^{-2}$	$5.832 \cdot 10^{-1}$	$4.354 \cdot 10^{-2}$	$3.209 \cdot 10^{-8}$	$2.108 \cdot 10^{-6}$	$2.516 \cdot 10^{-1}$
e	$1.381 \cdot 10^{-6}$	$2.512 \cdot 10^{-2}$	$3.307 \cdot 10^{-4}$	$1.452 \cdot 10^{-2}$	$7.203 \cdot 10^{-4}$	$4.195 \cdot 10^{-9}$	$6.809 \cdot 10^{-7}$	$4.069 \cdot 10^{-2}$

Table 4.5: Molar fractions and absolute errors for case 2.1: ablative wall cooler conditions

	X_N	X_O	X_{NO}	X_{N_2}	X_{O_2}	X_{C_3}	X_{CN}	X_{CO}
Mpp	$1.970 \cdot 10^{-3}$	$2.729 \cdot 10^{-3}$	$8.024 \cdot 10^{-6}$	$2.526 \cdot 10^{-3}$	$1.049 \cdot 10^{-7}$	$9.927 \cdot 10^{-1}$	$1.059 \cdot 10^{-7}$	$2.158 \cdot 10^{-5}$
Argo	$1.971 \cdot 10^{-3}$	$2.725 \cdot 10^{-3}$	$8.026 \cdot 10^{-6}$	$2.527 \cdot 10^{-3}$	$1.049 \cdot 10^{-7}$	$9.927 \cdot 10^{-1}$	$1.325 \cdot 10^{-7}$	$2.694 \cdot 10^{-5}$
e	$5.175 \cdot 10^{-7}$	$4.579 \cdot 10^{-6}$	$2.217 \cdot 10^{-9}$	$6.959 \cdot 10^{-7}$	$2.898 \cdot 10^{-11}$	$2.020 \cdot 10^{-6}$	$2.654 \cdot 10^{-8}$	$5.358 \cdot 10^{-6}$

Table 4.6: Molar fractions and absolute errors for case 2.2: ablative wall in hotter conditions

4.2.2 Energy equation

The list of cases to verify the mass and energy equations is given in Table 4.7. The aim of these tests is to see how the wall temperature changes with the gas-surface interactions. Four cases are proposed and use respectively: a non-catalytic wall such that only the re-radiation of the wall is taken into account, two different sets of recombination coefficients for a catalytic wall and eventually an ablative wall. In case of radiation, the emissivity must also be given. The values were taken from *Mutation*⁺⁺ test codes. However, $\varepsilon = 0.86$ is a more realistic value for a carbon wall.

	T_∞	p_∞	$\mathbf{v}_\infty$	dx	$T_{wall,guess}$	ε	mixture
case 3	5000	1000	$\mathbf{0}$	0.001	5000	1	<i>air5_inert</i>
case 4	5000	1000	$\mathbf{0}$	0.001	5000	0.86	<i>air5</i>
case 5	5000	1000	$\mathbf{0}$	0.001	5000	0.86	<i>air5*</i>
case 6	5000	1000	$\mathbf{0}$	0.001	2200	0.86	<i>airCarbon11</i>

Table 4.7: Boundary conditions for energy equation, first temperature guess and emissivity values

For the inert mixture, its composition does not change as no reaction is possible and both codes found $T_{wall} = 1652 [K]$.

Furthermore, when adding catalysis, we already observe in Tables 4.8 and 4.9 that energy is released and that the physical effects are not negligible. This energy is higher in case of higher recombination coefficients which translates to higher wall temperature: $1733 [K]$ for a partially catalytic wall against $2293 [K]$ for a fully catalytic wall.

In Table 4.10, the results for the ablative case are shown. Note that the wall temperature guess for the Argo simulation was chosen to be much closer than the real temperature. The Argo code did not converge for guesses lower than $1500 [K]$ and higher than $2200 [K]$. This particular case shows the importance of the choice of the first guess.

	X_N	X_O	X_{NO}	X_{N_2}	X_{O_2}	T_{wall}
Mpp	$2.242 \cdot 10^{-1}$	$3.036 \cdot 10^{-1}$	$4.844 \cdot 10^{-3}$	$4.663 \cdot 10^{-1}$	$9.612 \cdot 10^{-4}$	1733
Argo	$2.242 \cdot 10^{-1}$	$3.036 \cdot 10^{-1}$	$4.844 \cdot 10^{-3}$	$4.663 \cdot 10^{-1}$	$9.612 \cdot 10^{-4}$	1733
$ e $	$4.933 \cdot 10^{-9}$	$4.404 \cdot 10^{-9}$	$5.341 \cdot 10^{-9}$	$2.340 \cdot 10^{-9}$	$1.504 \cdot 10^{-9}$	$2.186 \cdot 10^{-3}$

Table 4.8: Molar fractions, temperature at the wall and absolute errors for case 4: catalytic wall

	X_N	X_O	X_{NO}	X_{N_2}	X_{O_2}	T_{wall}
Mpp	$4.484 \cdot 10^{-2}$	$7.081 \cdot 10^{-2}$	$1.579 \cdot 10^{-3}$	$6.784 \cdot 10^{-1}$	$2.043 \cdot 10^{-1}$	2293
Argo	$4.484 \cdot 10^{-2}$	$7.081 \cdot 10^{-2}$	$1.579 \cdot 10^{-3}$	$6.784 \cdot 10^{-1}$	$2.043 \cdot 10^{-1}$	2293
$ e $	$5.633 \cdot 10^{-8}$	$8.148 \cdot 10^{-8}$	$1.677 \cdot 10^{-10}$	$1.049 \cdot 10^{-7}$	$1.063 \cdot 10^{-7}$	$2.928 \cdot 10^{-3}$

Table 4.9: Molar fractions, temperature at the wall and absolute errors for case 5: catalytic wall

	X_N	X_O	X_{NO}	X_{N_2}	X_{O_2}	X_{C_3}	X_{CN}	X_{CO}	T_{wall}
Mpp	$2.113 \cdot 10^{-1}$	$1.279 \cdot 10^{-1}$	$1.287 \cdot 10^{-3}$	$3.841 \cdot 10^{-1}$	$1.668 \cdot 10^{-5}$	0	$3.673 \cdot 10^{-3}$	$2.717 \cdot 10^{-1}$	1998
Argo	$2.114 \cdot 10^{-1}$	$1.279 \cdot 10^{-1}$	$1.288 \cdot 10^{-3}$	$3.842 \cdot 10^{-1}$	$1.668 \cdot 10^{-5}$	$2.832 \cdot 10^{-8}$	$3.673 \cdot 10^{-3}$	$2.716 \cdot 10^{-1}$	1998
$ e $	$5.242 \cdot 10^{-6}$	$1.989 \cdot 10^{-6}$	$2.175 \cdot 10^{-7}$	$8.265 \cdot 10^{-6}$	$2.547 \cdot 10^{-9}$	$2.832 \cdot 10^{-8}$	$3.401 \cdot 10^{-7}$	$1.150 \cdot 10^{-4}$	0.251

Table 4.10: Molar fractions, temperature at the wall and absolute error for case 6: ablative wall

Eventually, the absolute error for the catalytic wall is very small and hence the equations are verified. Besides, for the ablative wall, when solving the energy equation, the biggest error is $|e| = 1.15 \cdot 10^{-4}$ which is smaller than the cases with imposed temperature even though the found temperature at the wall $T_{wall} = 1998 [K]$ is close to the imposed temperature $T_{wall} = 2000 [K]$.

4.3 Flow past a cylinder

In this section, one will focus on the results obtained in a 2D case. First, we will show the effect of having a catalytic cylinder wall with imposed temperature and then we will study the solutions obtained by solving the energy equation as well. The overall configuration is given in Fig. 4.2.

The boundary conditions imposed are: a velocity inlet, a pressure outlet, an adiabatic and slip top wall and a symmetry at the bottom. For the cylinder, we can impose one of the boundary conditions given in section 3.3.

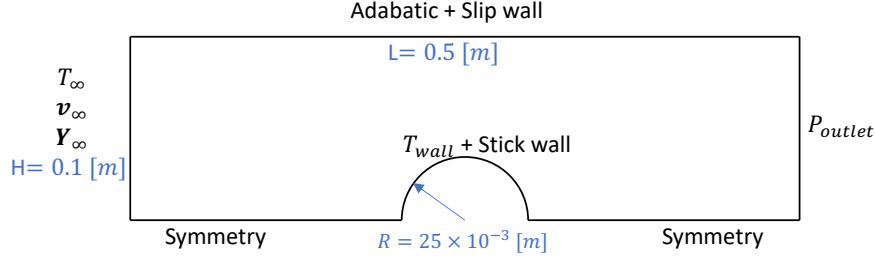


Figure 4.2: Boundary conditions used to simulate 2D problems with Argo

The initial conditions used for the non-catalytic wall with imposed temperature are given in Table 4.11.

T	p	$\mathbf{v}$
3439	25000	$\mathbf{0}$

Table 4.11: Initial conditions for a non-catalytic wall with imposed temperature

For the initial conditions of any other cases, we take the steady-state solution obtained with a non-catalytic wall and imposed wall temperature. This will be discussed in the next section on convergence and stability.

Eventually, different meshes were used for the different simulations. For simpler cases as for 2-species air mixture, a coarse mesh was used (see Appendix A Fig. A.1). For the 5-species mixtures, the mesh (in Appendix A Fig. A.2) was used when solving for a non catalytic wall with imposed temperature and finally a finer mesh was necessary for the other cases and a zoom on the boundary layer is shown in Fig. 4.3:

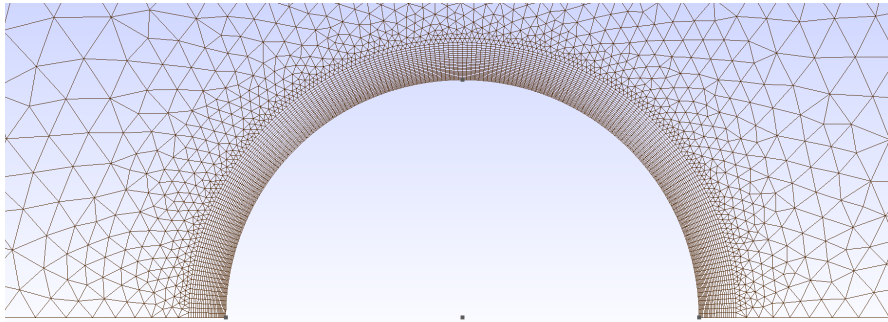


Figure 4.3: Mesh used for 5-species mixtures with a catalytic wall with and without imposing the temperature. Order $p = 2$ shape-functions were used.

Eventually, if it is not specified otherwise, the solutions shown in the following are obtained with the two types of boundary imposition.

4.3.1 Catalytic wall

In order to see the effect of a catalytic wall while imposing the temperature, two sets of simulations were made with three different air mixtures. The boundary conditions are given in Table 4.12.

wall catalycity	mixture	T_∞	u_∞	p_{outlet}	T_{wall}
non-catalytic and catalytic	<i>air2</i>	3439	15	25000	750
non-catalytic and catalytic	<i>air5</i> and <i>air5*</i>	3439	15	25000	1400

Table 4.12: Imposed values for simulations with a catalytic wall with imposed temperature

In Figs. 4.4 and 4.5, the results of a non- and fully catalytic wall with *air2* mixture are given. The figures show respectively the air composition along the stagnation line and the composition around the cylinder. It can be depicted that at the wall, all the oxygen was recombined to form dioxygen.

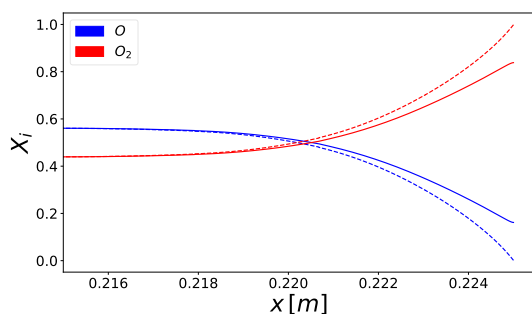


Figure 4.4: Molar fractions at stagnation line for *air2* mixture. Dashed lines are used for a non-catalytic wall and plain lines for a fully catalytic wall

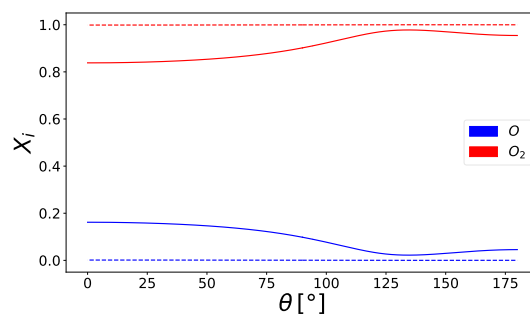


Figure 4.5: Molar fractions around the cylinder for *air2* mixture. Dashed lines are used for a non-catalytic wall and plain lines for a fully catalytic wall

Then we can see the effect of the different recombination coefficient using 5-species mixtures. In Figs. 4.6 and 4.7, we can depict that catalytic reactions happened as the presence of N_2 , O_2 and NO increased. We also depict how bigger recombination coefficients affect the molar fractions. The non-, partially and fully catalytic wall mixture composition are represented respectively by plain, dotted

and dashed lines.

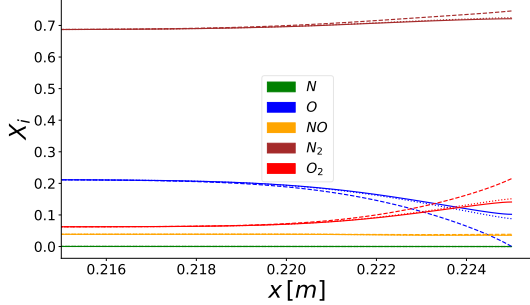


Figure 4.6: Molar fractions at stagnation line for 5-species air. The non-, partially and fully catalytic wall mixture composition are represented respectively by plain, dotted and dashed lines.

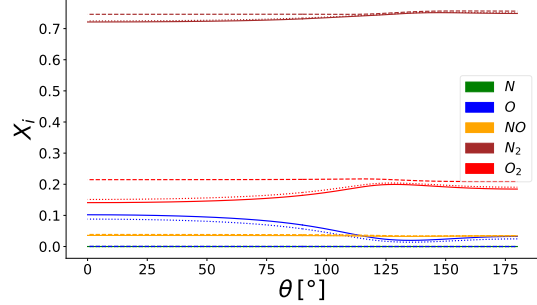


Figure 4.7: Molar fractions around the cylinder for 5-species air. The non-, partially and fully catalytic wall mixture composition are represented respectively by plain, dotted and dashed lines.

The heat flux around the cylinder can be observed for all the cases in Figs. 4.8 and 4.9. First, we note that in case of a catalytic wall, the heat flux is bigger as oxygen recombination and nitrogen recombination are exothermic reactions.

The difference of heat flux is higher for mixture with higher recombination coefficients. Indeed, at the stagnation point ($\theta = 0^\circ$), heat fluxes obtained with a partially and a fully catalytic wall are respectively 5% and 33% higher than the heat flux with a non-catalytic wall for the 5-species mixtures. Hence, imposing a non-catalytic wall can lead to underestimating the heat flux and under-sizing the TPS. In practice, when designing a TPS, we must stay conservative in our predictions due to our lack of understanding of the physical problem. As an example, Wise et al. [36] used a super-catalytic wall and assumed to have a turbulent regime in order to design the Mars 2020 capsule. This allowed to get a big safety margin and to take into account the fact that the models used for other phenomena are not perfect.

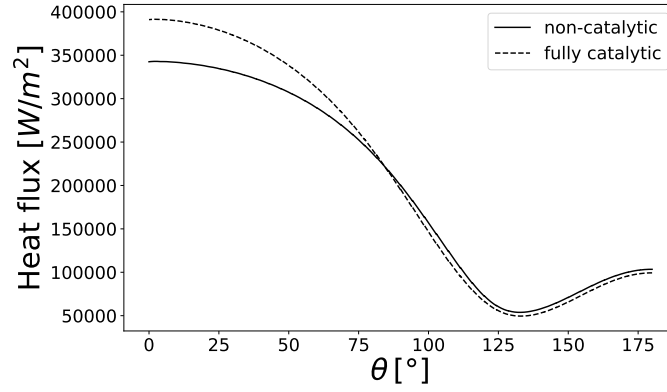


Figure 4.8: Heat flux around the cylinder for *air2* mixture. The dashed line is used for a non-catalytic wall and the plain line is used for catalytic wall

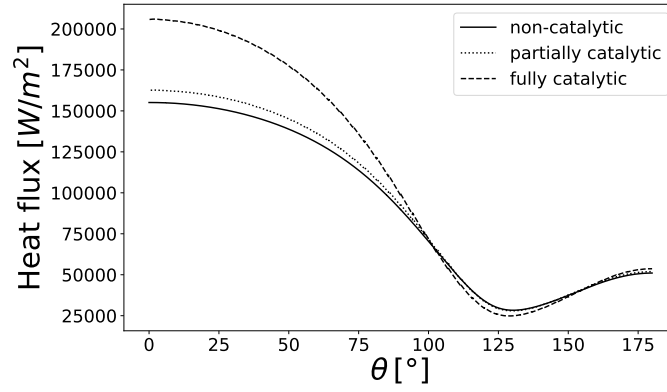


Figure 4.9: Heat flux around the cylinder for 5-species air. The non-, partially and fully catalytic wall are represented respectively by plain, dotted and dashed lines.

4.3.2 Solving the energy equation

More simulations were made to study the effects of solving the energy equation. The first objective is to find the right wall temperature and to understand how certain chemical reactions affects the temperature. The values imposed, the first guesses and the different mixtures are given in Table 4.13.

wall model	mixture	T_∞	u_∞	p_{outlet}	T_{wall}	$T_{wall,guess}$	ε
non-catalytic	<i>air5_inert</i>	3439	15	25000	/	1400	0.86
catalytic	<i>air5*</i>	3439	15	25000	/	1400	0.86

Table 4.13: Imposed values and guess values for solving the energy equation

The boundary conditions tested are an inert wall and mixture with only radiation and a catalytic wall with radiation. Note that for the latter case, Argo converged only when imposing a Dirichlet boundary condition. In Figs. 4.10 and 4.11, we can see the molar fractions along the stagnation line and around the cylinder.

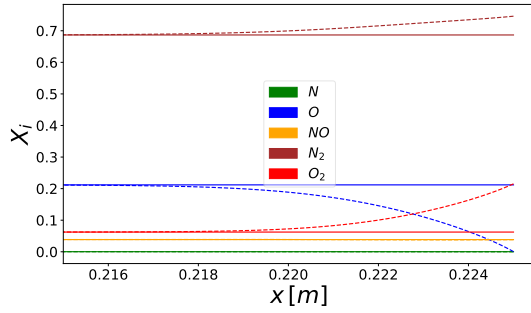


Figure 4.10: Molar fractions at stagnation line for 5-species air. The inert and *air5** mixtures are represented respectively by plain and dashed lines.

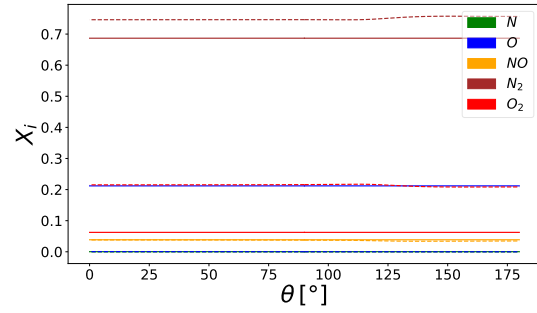


Figure 4.11: Molar fraction around the cylinder for 5-species air. The inert and *air5** mixtures are represented respectively by plain and dashed lines.

In Figs. 4.12 and 4.13, the temperature and the heat flux around the cylinder are given. We can depict that solving the energy equation for an inert wall gives smaller temperatures compared the fully catalytic wall: 1220 [K] vs 1430 [K]. This can be explained by the fact that catalytic reactions can generate large amount of energy.

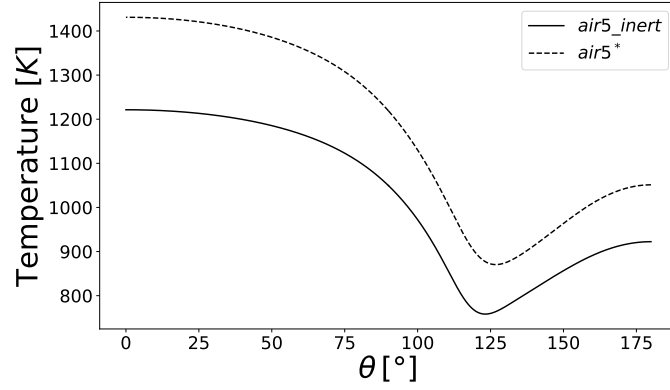


Figure 4.12: Temperature around the cylinder for 5-species air. The inert and *air5** mixtures are represented respectively by plain and dashed lines.

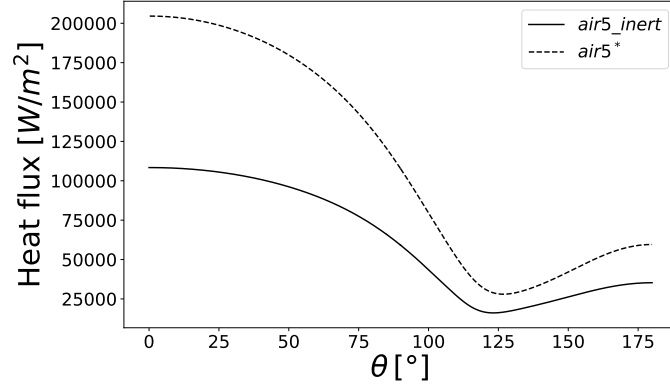


Figure 4.13: Heat flux around the cylinder for 5-species air. The inert and *air5** mixtures are represented respectively by plain and dashed lines.

The temperature and heat flux decrease can be explained by the detachment of the flow. A recirculation zone behind the cylinder is present which explains the increase of the shown quantities.

Furthermore, the temperature on the whole domain for the inert and fully catalytic mixtures are shown in Figs. 4.14 and 4.15 in order to better understand the heat flux at the wall.

Eventually, we can compare the heat flux at the wall for the fully catalytic case with and without the imposed wall temperature. This will show the error that is made when we use simpler models. In Fig. 4.16, when the energy equation is

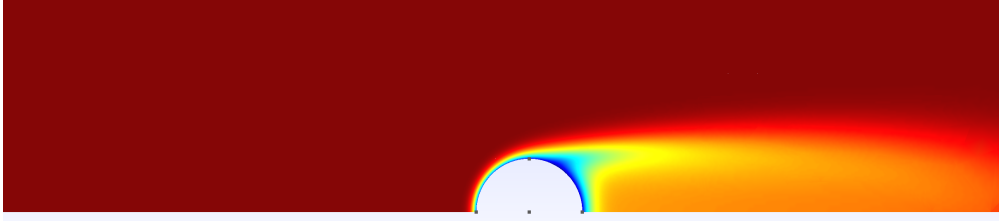


Figure 4.14: Temperature solution for the *air5_inert* mixture solved with the energy balance

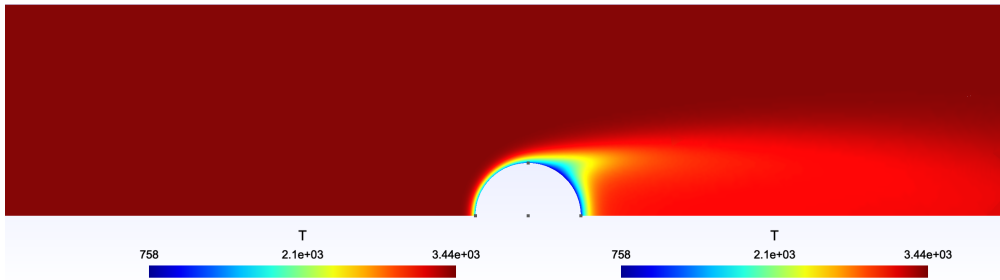


Figure 4.15: Temperature solution for the *air5** mixture solved with the energy balance

solved, the heat flux at the stagnation point is lower and then from a certain angle, the heat flux is higher. This means that when imposing the temperature, we are more conservative around the stagnation point and less conservative everywhere else.

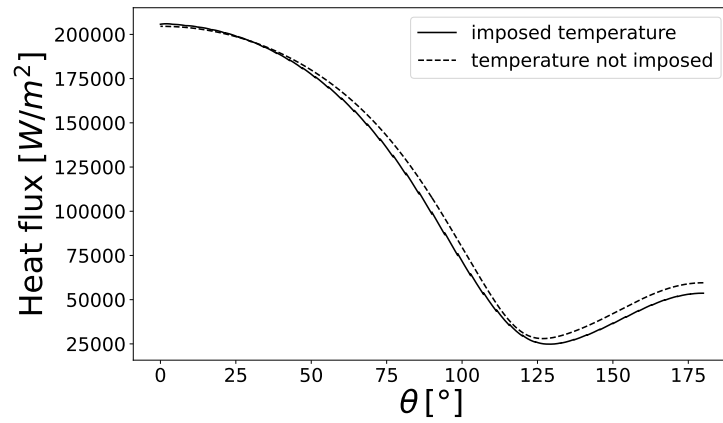


Figure 4.16: Heat flux around the cylinder for 5-species air. The fully catalytic with imposed temperature and without imposed temperature are represented respectively by plain and dashed lines.

4.4 Convergence and stability

In this section, the convergence and the stability of the two methods implemented in Argo will be discussed. First, we will compare the results obtained with the Neumann imposition against the Dirichlet for which the constitutive equations were verified previously. Then we will compare how fast each methods converges.

The boundary conditions that converged with the Dirichlet imposition are: (1) catalytic wall with imposed temperature, (2) non-catalytic wall with energy equation and (3) catalytic wall with energy equation. Imposing a Neumann boundary condition converged only for the first and second cases which will be tested in this section for different mixtures.

When solving for a reacting wall, whatever the reactions considered at the wall, the initial conditions are obtained by solving the equivalent non-catalytic case first. As an example, to solve the catalytic wall with an imposed temperature, the initial conditions are given by the solution of the non-catalytic simulation with the same imposed wall temperature. For the energy equation, as one must first guess the temperature, the initial conditions are obtained by solving the non-catalytic wall and by imposing the guess temperature.

This manipulation was used to smooth the initial conditions for the reacting wall simulations and to help with the convergence. Besides, for the non-catalytic wall with imposed temperature cases, we could use p-multigrid methods [35]. This consists in solving the problem with a lower order first and then the order is increased. This allows to converge faster as for lower order, the computational cost is lower and the problem is simplified. Besides, the solution state obtained when beginning with the higher order polynomials is already closer to the steady-state solution.

In this thesis, as the order of the polynomials was $p = 2$, a 3-levels order sequencing was used such that the solution is first converged using order zero shape-functions, then order one and finally order two. For order zero, the diffusive part of the problem is neglected as it depends on gradients which are null. When solving a non-catalytic wall, the diffusive part is less important compared to a catalytic wall. Consequently, p-multigrid methods did not worked for a reacting wall as all surface balance equations highly depend on diffusive terms. This pre-conditioning has proven to be effective as no solution was found when solving the mass and energy balance with the initial conditions shown in Table 4.11.

Eventually, the linear solver used in this section is GMRES.

4.4.1 Neumann and Dirichlet solution comparison

Before showing the performances of the two methods, we will first ensure that both give the same results. In Fig. 4.17, we can depict the two solutions for the catalytic wall with *air5* mixture. The iso-values represent the Dirichlet imposition solution whereas the filled iso-values represent the Neumann solution.

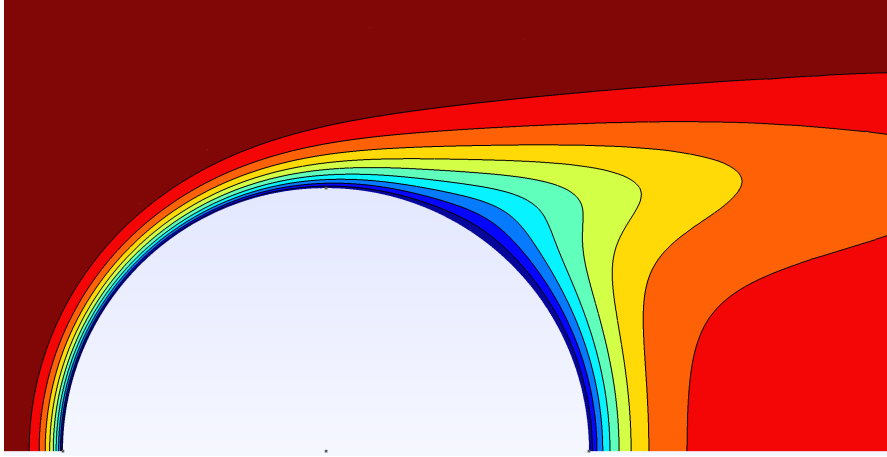


Figure 4.17: The iso-values represent the solution using Dirichlet imposition solution whereas the filled iso-values represent the solution using Neumann imposition.

Then, a radiative wall case was also simulated with an inert mixture and can therefore be compared. In Fig. 4.18, the solution of the two methods are overlapped and no difference is seen.

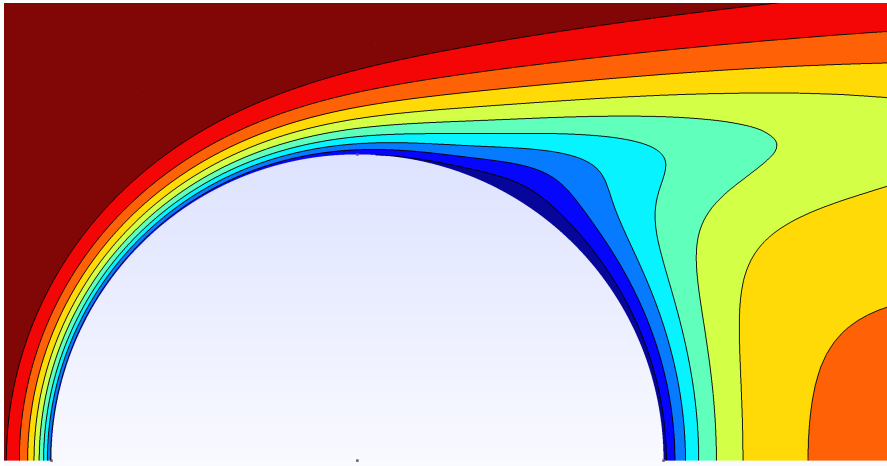


Figure 4.18: The iso-values represent the solution using Dirichlet imposition solution whereas the filled iso-values represent the solution using Neumann imposition.

For these cases, as the two methods give the same solution, their convergence and stability can be compared.

4.4.2 Neumann and Dirichlet convergence comparison

The convergence can be studied with different objectives:

- having a catalytic wall and imposed wall temperature with *air2* and *air5* mixtures. The tests aim to compare the Dirichlet and Neumann impositions methods using a simple then a more complex air mixture.
- having a catalytic wall and imposed wall temperature with *air5* and *air5** mixtures. The tests aim to see the effect of higher recombination coefficients on the the convergence and stability of the Neumann imposition.
- solving the energy equation with *air5_inert* mixture. The tests aim to compare the Dirichlet and Neumann impositions methods using a different boundary condition. Only re-radiation of the wall is taken into account.

We can observe in Fig. 4.19 that for the first case, the Dirichlet imposition seems faster. This is due to the fact that the CFL strategy had to be changed for the Neumann method. When the CFL was not limited, the code did not converge. Indeed, imposing diffusive fluxes with air mixtures having big recombination coefficients was found to be unstable.

For steady-state and implicit codes, as it is the case in this thesis, the CFL is an unphysical time-step used to compute the next iteration based on the previous iteration and the current one. The CFL hence represents the step to do in direction of descent in a minimization problem. For stiff problems, taking a big step can lead to instabilities and a small step can lead to very slow convergence. Consequently, at the beginning of the simulations, a small CFL is chosen and depending on the rate of convergence, the CFL is incremented or decremented. Thus, adapting the CFL generally allows to converge faster.

Then for the *air5* mixture, the Neumann method seems more suitable as it converged more quickly and reached lower residuals as shown in Fig. 4.20. Note that the imposed wall temperature is $T_{wall} = 750 [K]$.

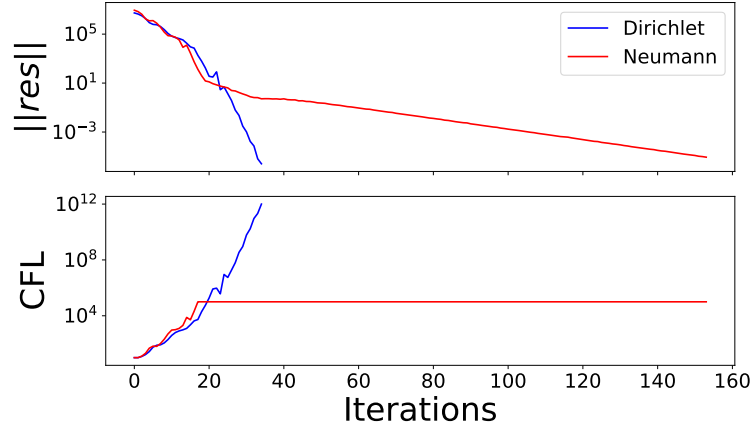


Figure 4.19: Norm of the residuals and CFL vs iterations for the *air2* mixture with imposed wall temperature

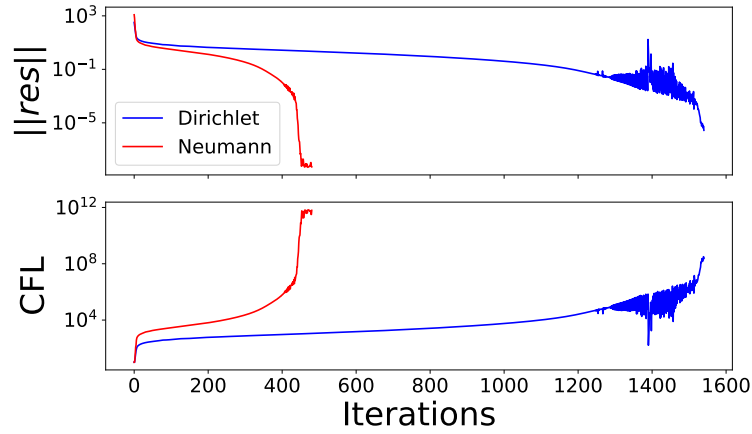


Figure 4.20: Norm of the residuals and CFL vs iterations for the *air5* mixture with imposed wall temperature

Then we can compare the use of the *air5* and the *air5** mixtures for the Neumann in Fig. 4.21. Note that for this test, the imposed wall temperature is $T_{wall} = 1400 [K]$. First of all, we can see that more iterations were needed to converge with the *air5* mixture compared to the previous case in Fig. 4.20 when the wall temperature was lower. Then, for the other mixture, the CFL had to be limited once again. The results shown are obtained without fine-tuning the CFL but those give an idea that we must be more conservative when using a more reacting mixture with the Neumann imposition.

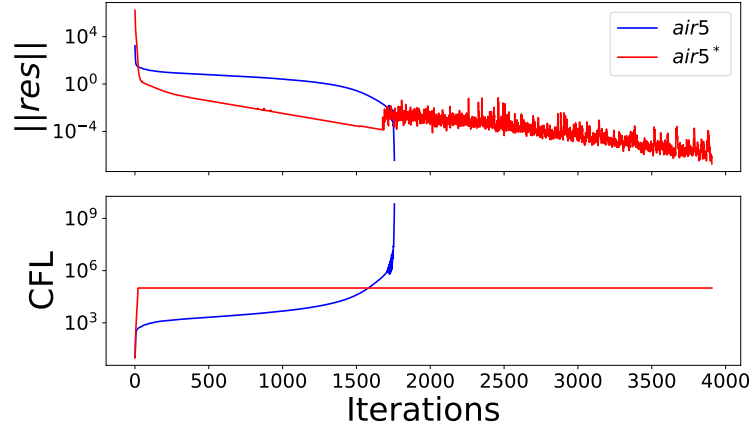


Figure 4.21: Norm of the residuals and CFL vs iterations for the *air5* and *air5** mixtures with imposed wall temperature using the Neumann imposition

The convergence for the last case studied is shown in Fig. 4.22. It also shows that the Neumann method seems more efficient. It can be explained by the fact that when imposition a Neumann boundary condition, there is no jump in the solution at the interface as the $+$ and $-$ values are set to be equal as seen in section 3.3.

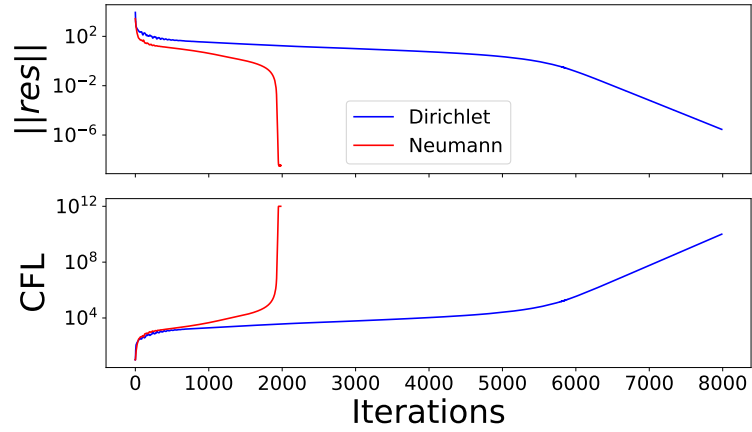


Figure 4.22: Norm of the residuals and CFL vs iterations for the *air5_inert* mixture with wall radiation

4.5 Conclusions

In conclusion, the constitutive equations for mass and energy balance implemented in Argo were first verified. Argo gave consistent results when only catalysis was taken into account with and without imposing the wall temperature. Concerning the ablation, Argo was not able to find the same solution and had a relative error of at most $\approx 2.5 \cdot 10^{-2}$ for certain species. However, in some cases (ablation in hotter conditions, or when solving the energy balance as well), Argo seemed able to find the correct values. These first tests also allowed to have a first insight on what should happen physically. For example, the temperature found with Argo when having a fully catalytic wall was higher as catalysis is often exothermic and releases energy.

The 2D simulations allowed to observe the physical effects of different gas-surface interactions on a larger scale. We saw the importance of finding and applying suitable boundary conditions as the Thermal Protection System (TPS) must be designed based on the results obtained during simulations. When we have a lack of understanding, we may use the worst scenario to design the TPS. Hence, simulations with a fully catalytic wall can be made to have the upper-bound limit of the heat flux transmitted to the material. Finally, catalytic reactions and re-radiation of the wall compete against each other regarding the main utility of TPS which is dissipating the energy. Indeed, the temperature obtained at the wall were smaller when only radiation was considered compared to the case with catalytic reactions.

Eventually, for the cases that converged with the two types of imposition, the Neumann method was found to have a slight advantage. Even though, this method seems faster, we must stay aware that it can be unstable for highly reactive wall conditions. Imposing the Dirichlet boundary condition on the other hand, allowed us to converge for the case using a catalytic wall with an unknown wall temperature.

We must also note that in this thesis, no fine-tuning for the CFL strategies was made. Besides, only one type of linear solver (GMRES) was used to compare the convergence.

Chapter 5

Conclusions and perspectives

5.1 Achievements

In this work, an improvement of the boundary conditions in case of atmospheric entry for a flow solver has been added. The boundary conditions take into account the surface catalytic properties and the surface radiation. It was implemented in an extension of the fluid module (*DGAblation*) of the multi-physics solver Argo. The latter is “based on discontinuous Galerkin methods which combines the advantages of finite element and finite volume methods” [5]. In order to evaluate the thermodynamics and transport properties, Argo is linked to the external library *Mutation*⁺⁺. This library also allows to evaluate the reaction rates of catalysis, ablation and chemically nonequilibrium flows.

Moreover, two different types of boundary condition impositions have been implemented: Dirichlet and Neumann. The aim was to further improve the computational efficiency.

The results presented in chapter 4 showed the capabilities of the flow solver. First, the constitutive equations for the mass and energy balanced were verified for a simple pseudo-1D case. The tests accounted for a non-catalytic, catalytic and ablative wall with and without imposing the wall temperature.

Then, 2D problems were solved. The mixture composition and the heat transfer at the wall were obtained for mixtures with different catalytic properties ranging from non-catalytic to fully catalytic. Furthermore, solving the energy balance allowed to evaluate the temperature at the wall taking into account the energy release due to catalytic reactions and the re-radiation of the surface. Finally, the convergence of the Neumann-type imposition was, for the numerical simulations

considered, found to be slightly better but can be unstable for highly reactive flows.

Eventually, this work adds up to previous developments in Argo. Indeed, Schrooyen implemented a high-fidelity solver that solves the material and the flow in the same domain [5]. It was proven to be accurate especially for highly porous materials. Then, more recently, a material solver with improved boundary conditions was added to Argo [27].

5.2 Perspectives

Improving the boundary conditions to incorporate some of the gas-surface phenomena marks an initial stride towards the development of the Argo code. However, several enhancements can still be made.

First, pyrolysis reactions were not taken into account. These reactions are crucial for heat dissipation as they are endothermic. Hence, the temperature found in the previous results can be over-estimated.

Then, regarding the ablation, no 2D-problems were studied in this work. The code showed a lack of convergence capability when passing from pseudo-1D to 2D simulations. The ablation is important as the surface deformation can lead to a change of shape and roughness. These phenomena can alter the aerodynamics properties and the flow regime which can in return lead to a higher heat load.

Regarding the Neumann-type boundary conditions, it did not converge for all the cases resolved with the Dirichlet imposition. Indeed, the catalytic wall solved without imposing the temperature failed to converge with the former method. As it proved to be more slightly more efficient than the Dirichlet imposition for tested cases, it is worth continuing the implementation for the others.

Besides, when taking into account the ablation, both methods failed to converge. Even the preliminary pseudo-1D tests showed non-negligible differences against *Mutation*⁺⁺ tests codes, especially when the wall temperature was imposed. The ablation models, adapted to fit the discontinuous Galerkin methods, must hence be corrected.

In summary, this work paves the way for future improvements. This first flow solver implementation was made with simplistic boundary conditions and can be further optimized.

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Appendix A

Meshes

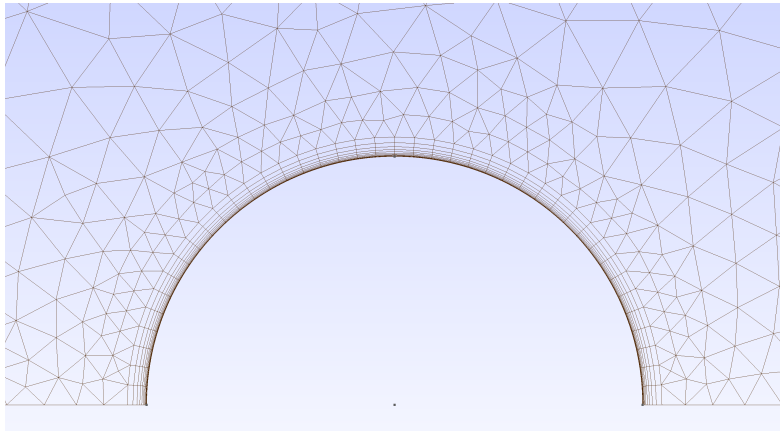


Figure A.1: Mesh used for 2-species mixtures. Order $p = 2$ shape-functions were used.

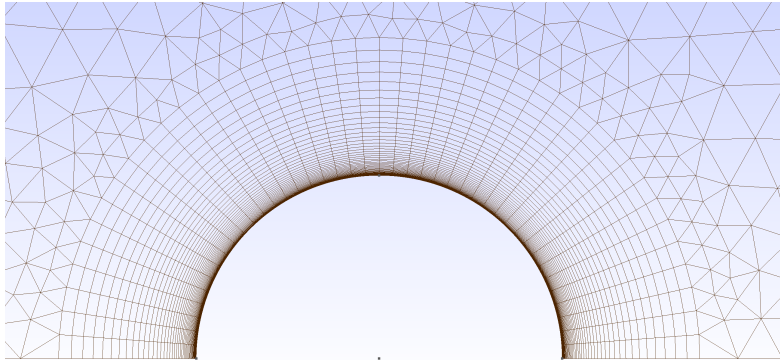


Figure A.2: Mesh used for 5-species mixtures with a non-catalytic wall with imposed wall temperature. Order $p = 2$ shape-functions were used.

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