Plasma chemistry in divertor relevant plasmas

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Plasma Chemistry in Divertor Relevant Plasmas

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Table of contents:

A. Framework & Overview of the Research

1 Introduction

1.1 The energy challenge and nuclear fusion
1.2 Tokamaks and magnetic confinement fusion
1.3 The divertor
1.4 Plasma detachment and impurity seeding
1.5 Studying divertor physics by means of linear plasma generators
1.6 This thesis
1.7 How to read this thesis
1.8 List of publications and conference contributions.

2 Experimental set-up and numerical models

2.1 Experimental set-up
2.1.1 Divertor simulator Magnum-PSI
2.1.2 Diagnostics
2.2 Codes
2.2.1 Global plasma model
2.2.2 Eunomia code
2.2.3 Coupling B2.5 and Eunomia

3 Experiments on plasma detachment in linear machines

3.1 Plasma detachment in linear plasma device Magnum-PSI
3.2 Plasma characterization in Magnum-PSI
3.3 Plasma detachment with impurity seeding (N₂, Ar and He)
3.4 Nitrogen seeding experiments
3.5 Power limitation effects
3.6 Impurities seeding experiments in linear plasma machine GAMMA10/PDX
3.7 Conclusions

4 Global modelling of divertor-relevant plasma scenarios

4.1 Global modelling of a H₂ + N₂ plasma
4.1.1 Plasma chemical reactions
4.1.2 Definition of the environment
4.1.3 Global model results: N-MAR as a new recombination path
4.1.4 Comparison between the full and the reduced global models
4.1.5 H₂/N₂ plasma chemistry for different plasma parameters
4.1.6 The role of molecular ion H₃⁺

4.2 Global modelling of a H₂ – He plasma
4.3 Global modelling of a H₂ – Ar plasma
4.4 Conclusions

5 Spatially-resolved simulations of detached-like plasma in the presence of different impurities
5.1 Numerical simulations for divertor-relevant plasma physical-chemistry
5.2 Simulating N₂ seeding in detached-like conditions in linear plasma machine with EUNOMIA code
5.3 B2.5-EUNOMIA simulations of plasma detachment in Magnum-PSI with different impurities
5.4 Conclusions

6 Conclusions and outlook

Bibliography

B. Publications

7 Studying the influence of nitrogen seeding in a detached-like hydrogen plasma by means of numerical simulations
7.1 Abstract
7.2 Introduction
7.3 Global modelling with Plasimo code
7.3.1 Governing equations
7.3.2 Chemical model
7.3.3 Plasma chemical reactions
7.4 Global model results
7.4.1 Plasimo results: new reaction paths in the presence of nitrogen
7.4.2 Centre of the plasma beam
7.4.3 Divertor-relevant H₂/N₂ plasma chemistry for different plasma parameters
7.4.4 The role of molecular ion H₃⁺
7.4.5 Periphery of the plasma beam
7.4.6 Comparison between the full and the reduced global models
7.5 Eunomia code
7.5.1 Eunomia grid and geometry
7.5.2 Implementation of the reduced model into Eunomia
7.6 Eunomia results
7.7 Summary and conclusions
7.8 Acknowledgments
7.9 Bibliography

8 Experimental evidence of enhanced recombination of a hydrogen plasma induced by nitrogen seeding in linear device Magnum-PSI.
8.1 Abstract
8.2 Introduction
8.3 Experimental set up and diagnostics
8.4 Plasma detachment in linear machine Magnum-PSI
8.5 Nitrogen seeding experiments
8.6 Helium and nitrogen seeding: a comparative study
8.7 Summary and conclusion
8.8 Acknowledgments
8.9 Bibliography

9 Investigating the effect of different impurities on plasma detachment in linear plasma machine Magnum-PSI.
9.1 Abstract
9.2 Introduction
9.3 Experimental set up and diagnostics
9.4 Plasma detachment with hydrogen seeding
9.5 Plasma detachment with impurities seeding (N₂, Ar, He)
9.6 Global model
9.7 EUNOMIA code
9.8 Coupling B2.5-EUNOMIA
9.9 Implementation of the codes
9.10 Simulating plasma detachment in Magnum-PSI by means of B2.5-EUNOMIA codes
9.10.1 Modelling results
9.11 Conclusion
9.12 Acknowledgment
9.13 Bibliography

Summary
Sommario
Samenvatting
Curriculum Vitae
Acknowledgments
Part A

Chapter 1

Introduction

1.1 The energy challenge and nuclear fusion

The world population prospect, released by the UN in 2017, estimates a population increase up to 12 billion people by 2100[1]. The industrialization, which started at the end of 18th century and currently ongoing, has led to a steep increase of carbon dioxide released in the atmosphere, reaching a concentration beyond the level of 400 ppm in 2017[2]. Maintaining such trend among mankind would imply unbearable exploitation of natural resources and intolerable atmospheric emissions due to energy consumption. CO₂ and other greenhouse gases are currently causing a broadly acknowledged irreversible climate change. This is characterized by temperatures enhancement which would lead to more frequent extreme meteorological events, increased desertification, disappearance of considerable amount of animal and vegetal species and rising of sea levels. All these phenomena would heavily affect the habitability of several regions, leading to, eventually, uncontrolable mass migration. Actions have been taken by international institutions and by collective agreements between governments to control and eventually limit such trend; worth mentioning the ratification of Kyoto protocol[3] and the Paris agreement[4]. Moreover, the recent report from the intergovernmental panel on climate change[5] stated the vital importance of limiting the global temperature increase below 1.5°C. The future energy system will likely be run by electricity generated from wind and solar electricity. The intermittent nature of these energy sources causes a strain on the electricity grid and therefore a discrepancy between supply and demand. This poses the need of a sustainable energy source where energy storage and transport form an integral part of the system. However, it remains debatable whether renewable energy production can match the required base load. A recent study [6] of the current German energy production system highlights that only ~40% of the base load can be assured by renewable sources. Given so, CO₂-free electricity production has to be additionally provided. This need will become even more relevant if considering the increasing demographic trend towards urban establishments. A strong growth in the number of megacities, together with extremely high energy needs, is foreseen to occur by the end of the century. For these reasons, a new energy source has to be developed and should be capable to satisfy the following criteria: the energy source has to be clean, safe, economically favorable and accessible on a global scale[7].

One of the main candidates to fulfil all the above-mentioned requirements is controlled nuclear fusion[8]. The principle is as follows: two light particles combine to create a heavier particle, releasing tremendous amounts of energy. The most reactor-relevant fusion reaction is where two hydrogen-isotopes nuclei, deuterium and tritium, merge generating an atom of helium and a highly energetic neutron, as can be seen in figure 1. To achieve such process on earth, a very high kinetic energy has to be provided to the reactants; in fact, this energy has to overcome the coulomb repulsion force between the two positively-charged nuclei.
The fuels necessary for nuclear fusion are easily accessible: deuterium is naturally present in ocean water with an isotopic abundance of 0.015%, while tritium, which does not occur spontaneously, can be produced in the power plant itself[9], by means of lithium, as follows:

\[ ^6\text{Li} + n \rightarrow ^3\text{H} + ^4\text{He} \]  \hspace{1cm} (1.1)

For a GW-scale power plant the quantities of D and Li needed to fuel the reactor for one year consist of approximately just 100 and 300 kg respectively. The availability of them on our planet may be sufficient to provide fusion energy for millions of years[10].

To achieve self-sustaining nuclear fusion, a so-called Lawson criterion has to be satisfied i.e. \( n_i T_i \tau_e \geq 3 \times 10^{21} \text{m}^{-3} \text{keV} \) [11] (one eV corresponds to roughly 11600 K) which is the triple product of ion density \( n_i \), ion temperature \( T_i \) and energy confinement time \( \tau_e \). On earth, this can only be done by heating a plasma up to 150 million K i.e. ten times hotter than the core of the Sun. The main challenge towards realizing fusion electricity is posed by maintaining a very hot plasma in a vessel that has to be kept fairly cold in order to preserve its components. This can be done by applying a magnetic confinement. A plasma is, in fact, characterized by the presence of free charged particles i.e. ions and electrons, therefore is sensitive to magnetic fields due to the charges of its constituents. Exploiting such feature, thus applying strong magnetic fields in a fusion plasma, allows to achieve the pressure gradients needed to maintain relatively cold plasma edges with a core hot enough for the nuclei to fuse and to reach the \( T_i \) needed to fulfil the Lawson criterion. In practice, this can be done with the so-called magnetic confinement fusion (MCF), where charged particles are magnetically confined inside a fusion reactor.

### 1.2 Tokamaks and magnetic confinement fusion

Since the beginning of the 1950’s, Soviet scientists conceived the concept of magnetic confinement nuclear fusion. They came up with the design of a donut-shaped plasma reactor, called Tokamak[12]. A schematic representation of such set up can be seen in figure 2. The magnetic configuration in a tokamak is designed as follows: a toroidal magnetic field, generated by external currents, is applied to produce a torus shaped geometry. Without any further magnetic component, the plasma would drift towards the external wall due to a \( \nabla B \) drift. A toroidal current in the plasma is provided by an inner poloidal field coil which generates a poloidal magnetic field. To “shape” and stabilize the plasma, outer poloidal field coils are used. As a result, a helical-shaped magnetic field configuration is obtained. A key-feature characterizing plasma confinement is that perpendicular transport is orders of magnitude lower than the parallel one. Once there is enough confinement, ohmic heating can provide further power, although the resistivity of the plasma diminishes with increasing \( T_e \) according to the Spitzer
relation, where $\rho \sim T_e^{-\frac{3}{2}}$ [13]. Additional heating is therefore needed to achieve the temperatures required to fuse nuclei; this is provided by means of microwave-induced heating and neutral beam injection [14]. Once enough energy is provided to the plasma, D-T reaction takes over.

The basic requirement is that the energy produced has to be higher than the energy provided to the system. The so-called fusion gain parameter, $Q$, often used to determine the efficiency of a fusion reactor can be expressed as $Q = \frac{P_{fus}}{P_{heating}}$.

Figure 2. Schematic of a Tokamak with field coils and the generated magnetic field lines. Picture taken from [15].

ITER tokamak, which stands for International Thermonuclear Experimental Reactor, is the largest experimental fusion project so far and is currently being built in the south of France. This machine is designed to achieve $Q \approx 10$ i.e. producing 500 MW with a power input of 50 MW. Heat and particles are inevitably expelled from the confined plasma towards the walls giving rise to so-called plasma-surface-interaction (PSI). Predictions tell us that such heat load are not tolerable for any existing material. Unmitigated that heat and particle flux to the walls would lead to a phenomenon called “sputtering”, where particles of the solid material are ejected from its surface. The contamination with wall materials in the core plasma would cause a cooling of it due to high radiation of high-Z species at those temperatures, consequently compromising the fusion performance.

To avoid deterioration of the reactor walls, a temperature gradient between the core and the plasma edge is necessary to be set in place. To keep the PSI region far enough from the plasma core, a so-called divertor configuration [16] has been designed. This thesis will focus on the understanding of ITER-relevant divertor-plasma scenarios. A more detailed description on the divertor region and the governing physics is given hereafter.

1.3 The divertor

The concept of the divertor originates in early 50s [17] and the original motivation was to reduce the impurity content in the main plasma, hence isolating a specific region where (inevitable) exhaust products can be extracted from the vessel. Such a concept has been then further developed aiming to divert the heat (and particle) flux ejected from the plasma core towards a defined area. To do so, an additional magnetic field created by current coils, placed below the divertor, intersects with the separatrix, i.e. the last-closed-flux-surface, creating a so-called “magnetic null” i.e. the x-point in figure 3.
The plasma core is confined by closed magnetic field lines. The region of the plasma edge with open field lines is called scrape-off-layer (SOL). In the SOL, plasma is driven towards the divertor target and gives rise to the complex PSI occurring in a tokamak. The points where plasma faces divertor components are called strike points. Pumps located behind divertor targets take away gas particles.

By means of the divertor, a separation between the core plasma and the edge is now created and the two scenarios can be, to a certain extent, considered decoupled. In the divertor, plasma is much cooler compared to the core i.e. between 10,000 and 100,000 K and a high content of neutral particles is expected due to ion recycling at the target and/or impurity seeding.

![Diagram of the divertor concept. The main advantage of this configuration is to keep plasma-surface-interaction far from the plasma core, limiting impurity contamination of it. The high neutral pressure originates in the divertor region facilitates the removal of the helium ash.](image)

Even at those relatively-low temperatures, given the high flux density ($>10^{24} \text{m}^{-2}\text{s}^{-1}$), a power density greater than 10 MWm$^{-2}$ is expected to occur during tokamak operation. It is worth to be stressed that the technological limit for plasma-facing-components in steady-state operation is set at 10 MWm$^{-2}$[18]. Moreover, transient events such as ELMs (Edge localized modes) in ITER are foreseen to lead to power loads of $\approx 1 \text{GWm}^{-2}$. The material chosen for divertor plates in ITER is Tungsten (W). It has been chosen due to its high melting point i.e. 3695 K, low neutron damage, high sputtering threshold[19] and low fuel retention [20]. Nevertheless, modelling predictions show that, in order to maintain fusion performance in the plasma core, the tolerable fraction of W has to stay below $10^{-5}$[21]. Such limit cannot be respected in normal operation, where SOL plasma is “attached” to the divertor target and would certainly cause sputtering and/or melting of W. Therefore, it is mandatory to reduce the heat flux to the target. The heat flux can be expressed as:

$$ q_t = \frac{P_{\text{sol}} - P_{\text{rad}} - P_{\text{neut}}}{A_w} \text{Wm}^{-2} \quad \text{(1.2)} $$

Where $P_{\text{sol}}$ is the power ejected by the core that enters the SOL, $P_{\text{rad}}$ is the radiated power in the SOL, $P_{\text{neut}}$ is the power converted from ions to neutrals by means of volume recombination and $A_w$ is the “wetted” area of the target that interacts with the plasma. To reduce $q_t$ to tolerable values, therefore, the following actions may be carried out:

- Making more resilient materials capable to withstand the foreseen heat load occurring during ITER operation.
- Increase radiation from the core, hence reducing the power delivered to the SOL ($P_{\text{sol}}$).
- Enlarge the wetted area, with, for instance flux expansion as in [20].
• Enhancing the radiated power along the SOL ($P_{\text{rad}}$) by means of impurities injected in the upstream region of the SOL, where temperatures are in the order of $\approx 100$ eV, with the goal of dissipating enough power before it reaches the target.
• Finally, the energy brought intrinsically by the incoming ions can be dissipated in the volume phase via so-called volume recombination.

The scope of this thesis lays on the understanding of these volume processes in complex scenarios characterized by a multitude of different species, in order to highlight new mechanisms that would lead to neutralization of ions before reaching the divertor plate. In a tokamak, a regime where a synergy between radiative losses and volume recombination occurs is mandatory to be achieved and controlled. This operational regime is called plasma detachment, and it will be described in the next section.

1.4 Plasma detachment and impurity seeding

When an ion impacts on a solid surface it recombines and is then re-emitted in the form of neutral atom or, in case of molecular gases e.g. H$_2$ and N$_2$, as thermalized molecules. Some of those particles undergo ionization in the plasma volume and can be transported back to the wall, giving rise to another cycle. This process is defined as plasma recycling and occurs in tokamaks as well as in laboratory plasmas. The ionization mean free path ($\lambda_{\text{mfp}}$) of such neutrals strongly depends on parameters (density and temperature) of the plasma they interact with. In divertor-relevant conditions, $\lambda_{\text{mfp}}$ is generally shorter than the plasma volume, therefore particles are ionized in the vicinity of the target. In this way the recycling region is close to the divertor plate, causing an amplified particle flux to the wall. This regime is called high-recycling regime and is characterized by a high-density and low-temperature plasma and high ion fluxes to the target[22]. Such regime is already an improvement compared to basic operations of tokamak edge, given that the energy carried by the plasma can be spread over more particles and, therefore, temperature decreases. Nevertheless, this is not enough to achieve scenarios tolerable for the divertor material.

In order to protect the wall and hence achieve fusion, another regime is necessary to be achieved: plasma detachment. The first observation of plasma detachment occurred in [23], where an increase in the upstream density in ASDEX tokamak led to a so-called roll over of the ion saturation current measured at the divertor target. Such plasma regime is characterized by a strong reduction of both particle and heat fluxes to the divertor target. Given that, the harsh conditions to which the material has to undergo during attached operation are mitigated and the integrity of the plate is preserved [24].

Detachment is driven by a synergy of three different mechanisms i.e. radiative cooling, momentum loss due to ion-neutral interaction and volume recombination[25]. The different regions that are built up during detachment (figure 4):

• A region where high enough $T_e$ leads to impurity radiation, hence cooling down the plasma.
• An ionization region, where H atoms and H$_2$ molecules (in vibrational excited state) coming from the wall are ionized. This constitutes a further energy sink for the incoming plasma.
• A recombination region, where ions are converted to neutrals in the volume phase, before they reach the target plate. The increased neutral density leads to momentum loss due to plasma-neutrals collision events.
To provide further insights into the processes leading to the reduction of ion flux and therefore the potential energy carried with it, a zero-dimensional particle and power balance similar to [26] is reported hereafter. The ionization of neutrals in a tokamak equals the sum of plasma flux to the wall and the (volume) recombination sinks as follows:

$$\Gamma_{\text{ion}} - \Gamma_{\text{wall}} - \Gamma_{\text{rec}} = 0$$  \hfill (1.3)

The overall plasma-edge power balance can be written as:

$$Q_{\text{SOL}} = Q_{\text{imp}} + Q_{\text{ion}} + Q_{\text{neut}} + \gamma T_{\text{wall}} \Gamma_{\text{wall}}$$  \hfill (1.4)

Where $Q_{\text{SOL}}$ is the power coming from the LCFS into the SOL, $Q_{\text{imp}}$ the radiation due to impurities, $Q_{\text{ion}}$ is the power loss related to neutrals ionization, $Q_{\text{neut}}$ the energy transferred to neutrals and then eventually to the walls after charge-exchange (CX) or elastic ion-neutral reaction. The last term is the power transported to the wall with $T_{\text{wall}}$ the temperature at the wall location. $Q_{\text{ion}}$ can be related to the ionization “cost” (4.52 eV to dissociate molecular hydrogen plus 13.6 eV per hydrogen atom ionization[27]) and re-written as $Q_{\text{ion}} = E_{\text{ion}} \Gamma_{\text{ion}}$. Similarly, $Q_{\text{neut}}$ can also be related to $E_{\text{ion}} \Gamma_{\text{ion}}$ using the effective energy cost, and can be then defined as $Q_{\text{neut}} = E_{\text{neut}} \Gamma_{\text{ion}}$ with $E_{\text{neut}}$ typically 5 eV [28]. Combining equations 1.3 and 1.4, we obtain:

$$\Gamma_{\text{wall}} = \frac{Q_{\text{SOL}} - Q_{\text{imp}} - (E_{\text{ion}} + E_{\text{neut}}) \Gamma_{\text{rec}}}{(E_{\text{ion}} + E_{\text{neut}} + \gamma T_{\text{wall}})}$$  \hfill (1.5)

May be seen from equation 1.5 that the key ingredients to reduce $\Gamma_{\text{wall}}$ are (1) enhancing radiative plasma cooling due to impurities i.e. $Q_{\text{imp}}$ and (2) increasing volume recombination. The leading candidate for impurity seeding in ITER is nitrogen [29]. It has been chosen due to its radiative properties in SOL-like plasma parameters range, while radiating less at higher temperature, as can be seen in figure 5. Moreover, given its low Z number, the plasma fuel dilution in case of core contamination is limited compared to high Z impurities e.g. neon and argon.
Figure 5. Radiative loss functions for possible divertor seeding gases N, Ne, Ar with \( n_e \approx 10^{20} \text{ m}^{-3} \). Notably, nitrogen is the best radiator at low temperatures, while radiates less at high temperature compared to argon and neon. Picture obtained via ADAS[30] taken from [31].

In this thesis we will focus on the effect of nitrogen and other impurities on the volume recombination occurring in the divertor region. This will be carried out by means of both plasma-chemistry and plasma-physics approaches. To do so, numerical simulations have been done together with dedicated experimental campaigns in the linear device Magnum-PSI. An overview on the main features of linear plasma machines is given in the next section.

1.5 Studying divertor physics by means of linear plasma generators

Linear plasma machines, sometimes referred to as divertor simulators, have been extensively used in the last three decades to study fundamental aspects of divertor plasmas. The main advantages posed by them are (1) the capability of sustaining a steady-state divertor-relevant plasma for a long time (2) the relative low cost compared to a tokamak and (3) the excellent diagnostic accessibility[32]. A detailed overview of the most relevant linear machines worldwide and their contribution on the understanding of specific plasma-driven phenomena can be found in [33].

The first gaseous divertor concept experiments date back to [34] and proved, for the first time, the possibility of strongly reduce the power load on a plate by increasing the background neutral pressure inside the vessel. Similar findings have been described in [35] at PISCES-A linear machine. Those results have been explained by a combination of two factors i.e. the enhanced radial transport due to ion-neutral elastic collisions and volume recombination processes originated by neutral atoms and molecules. A breakthrough publication from de Graaf et al. [36] highlighted for the first time a plasma recombination mechanism led by the presence of molecular hydrogen. Although the plasma in such study was not magnetized, that finding constitutes a fundamental achievement in the understanding of plasma-neutral interaction, hence, divertor-relevant as well. The process has been defined as Molecular-Activated-Recombination (MAR). MAR mechanisms have been further investigated by comparing spectroscopy measurements at the NAGDIS linear machine with collisional radiative models, confirming the importance of molecular-activated-recombination mechanisms [37]. Experiments and simulations concerning the radiation efficiency led by different impurities upstream in the SOL have been done in GAMMA10/PDX [38]. Such machine is capable to achieve high \( T_e \) (~100 eV), although at low electron densities. Linear plasma devices are often used as simulator of the SOL, but a direct comparison between a tokamak and a linear machine would be misleading; while in a divertor the source for ionization (ionization front in figure 4) is driven by power coming from upstream that ionizes recycled neutrals, in linear devices charged particles are produced in the plasma source
itself. The plasma physics explored with Magnum-PSI is therefore limited to the portion of divertor plasma between the ionization region and the target plate. In that portion most of the recombination processes occur due to low $T_e$ i.e. $< 5$ eV, therefore the plasma chemical processes are the same. Exploiting numerical codes, together with plasma diagnostics, allows one to pinpoint the most relevant physical-chemical processes occurring in the vicinity of the target during detachment, highlighting new relevant physics (and chemistry) that would be difficult to determine in the intrinsically more complex tokamak environment. Detachment experiments have been carried out by means of the newly-renovated Magnum-PSI: a unique linear machine capable to mimic the PSI foreseen to occur in ITER. The results will be discussed in details in the next chapters.

1.6 This thesis

It has been shown that plasma-surface-interaction in the divertor region poses one of the biggest challenge towards the realization of such technology. To reduce the heat and particle flux to the divertor plate, a so-called detached plasma regime has to be achieved and controlled. It has been also reported that injection of impurities, in either mid-plane SOL and/or divertor, facilitates onset of detachment. The main reason impurities are used is because of their radiative properties, leading to a cooling of $T_e$ in the divertor plasma down to values where volume recombination can extensively contribute to ion neutralization, reducing the heat and particle flux to the target.

Although several studies with state-of-the-art code packages e.g. [39], [40] have been carried out and constantly provide fundamental insights into the dynamics of SOL and detachment physics, very few attention has been paid to the plasma chemical processes occurring in the divertor within an impurity-seeded plasma detached regime. Those processes may actively contribute to enhance recombination in the volume phase, preventing intolerable particle flux that would lead to material deterioration. In this thesis, we aim to fill this lack of knowledge by means of both numerical simulations with three different codes and experiments in divertor simulator Magnum-PSI. We will strive to answer the following research questions:

1) What is the influence of nitrogen-driven plasma chemistry on plasma detachment?
2) What is the influence of other impurities i.e. argon and helium on plasma detachment?
3) Is it possible to reproduce experimental results in Magnum-PSI with dedicated codes?

Even though this thesis is entirely “framed” within the field of plasma physics for nuclear fusion, a plasma-chemical approach has been adopted in order to provide new insights into divertor-relevant scenarios and to further bridge the gap between fusion-edge plasmas and low temperature ionized gases from a different prospective.

1.7 How to read this thesis

This thesis is divided into two main parts: part A, which describes the framework of this study together with an overview of the main findings, and part B, where peer-reviewed publications are reported.

In chapter 2 of part A, an overview of Magnum-PSI and the diagnostics used for the experimental campaigns is provided. Moreover, a description of the numerical codes adopted is also given i.e. (1)
the main features of global plasma modelling, (2) the spatially-resolved Monte Carlo code Eunomia (standalone) suited for the transport of neutrals in linear machines and (3) the fluid code B2.5, which solves plasma equations and has been used coupled together with Eunomia.

Chapter 3 constitutes an overview of the experimental results, starting with plasma detachment experiments in Magnum-PSI followed by results from impurity seeding experimental campaigns. In particular, the effect of different impurities on plasma parameters and their impact on PSI will be discussed. Moreover, results from impurity seeding campaign in linear plasma machine GAMMA10/PDX [41] are also reported. Given that such machine operates in plasma regimes different from Magnum-PSI, a comparison between the two experimental findings would allow us to cover a wider range of plasma parameters.

Chapter 4 sets up extended global models for H₂-N₂, H₂-Ar and H₂-He is described in details. Insights into the population distribution of molecular ions in a H₂-N₂ plasma is given for different plasma parameters, and newly-addressed ion-recombination paths are presented and discussed. The reduced plasma chemical data-sets achieved are listed, highlighting the most relevant processes occurring in the volume phase for each seeding scenario. Moreover, a parallel study on the importance of H₃⁺ is discussed.

In Chapter 5, results from numerical simulations for Eunomia standalone and B2.5-Eunomia are presented. Trends obtained experimentally are qualitatively compared to the codes outputs. The aim is to provide further insights into the plasma physics and chemistry occurring in a detached-like hydrogen plasma with impurity seeding.

Finally, chapter 6 is focused on answering the research questions exposed in section 1. Research outlook is provided as well.

Part B consists of three peer-reviewed publications:

- Global modelling of H₂-N₂ plasma and implementation of the reduced set of plasma chemical equations in Eunomia. Eunomia simulation results with the new chemistry are presented and discussed.
- Experimental evidence of synergetic effects led by H₂+N₂ seeding in a detached-like hydrogen plasma in Magnum-PSI. Eunomia runs have been also performed and presented. The discrepancy between the heat flux (and plasma pressure) between H₂+He and H₂+N₂ is discussed.
- The influence on detached-like plasma parameters led by the seeding of three different impurities i.e. N₂, He and Ar, together with H₂, is studied by means of both experiments, global models and B2.5-Eunomia.

1.8 List of publications and conference contribution

First author publications on which this thesis is based:

enhanced recombination of a hydrogen plasma induced by nitrogen seeding in linear device Magnum-PSI, Nuclear Materials and Energy, 19, 87-93, 2019.


Other first author publications:


Co-authored publications:

- Y. Hayashi et al., Application of ion sensitive probe to high density plasmas in Magnum-PSI, Plasma and Fusion Research, 14, 1202135, 2019.
- K. Jesko et al., Gas puff experiments at Magnum-PSI from the perspective of power exhaust, in preparation for submission.

Conference contributions:

- 22-23 January 2019: Physics@Veldhoven (Veldhoven, NL) – Oral presentation.
- 6-8 November 2018: FuseNet PhD event at ITER (Cadarache, FR) – Poster.
- 23 – 24 January 2018: Physics@Veldhoven (Veldhoven, NL) – Poster.
- 26-30 June 2017: European Physical Society Conference (Belfast, NIR) – Poster.
- 23 – 24 January 2017: Physics@Veldhoven (Veldhoven, NL) – Poster.
- 19 – 23 September 2016: Taming the Flame Workshop (Leiden, NL) – Attendee.
- 19 – 20 January 2016: Physics@FOM (Veldhoven, NL) – Poster.
Chapter 2

Experimental set-up and numerical models

In this section the instruments adopted to carry out the work of this thesis are presented. Concerning the experimental set-up, a broad description of the linear plasma machine will be followed by the diagnostics utilized in this study. Secondly, description and insights into the codes will be provided in the following order: (1) global models for complex plasma chemistries, (2) Eunomia and (3) B2.5-Eunomia coupled.

2.1 Experimental set-up

2.1.1 Divertor simulator Magnum-PSI

Magnum-PSI, which is the acronym for Magnetized plasma Generator and NUMerical modelling for Plasma-Surface Interaction, is a linear plasma device designed with the scope of reproducing PSI foreseen to occur in ITER divertor[42]. The machine is divided in three different chambers separated by skimmers i.e. source, middle and target chambers. Those environments are differentially pumped[43], so that the neutral fraction in the target chamber is dominated by ion recycling at the target, rather than neutrals coming from upstream chambers[44]. The plasma beam is generated by means of a cascaded arc source[45] located in the source chamber. A superconducting magnet generates a magnetic field that confines the plasma, hence the beam travels throughout the three chambers and eventually encounters the plate in the target chamber, as can be seen in figure 1. In this work, the plates used in the experiments consist of a tungsten circular target with a diameter of 3 cm and thickness of 1 mm.

Figure 1. Design of linear plasma machine Magnum-PSI. The numbers correspond to: 1. Plasma source 2. Skimmers separating the three chambers 3. Plasma beam 4. Target 5. Superconducting magnet.

The uniqueness of the machine consists on generating steady-state divertor-relevant low-temperature high-density plasmas for a very long time (up to hours). Plasma parameters range is $T_e \leq 5 \text{ eV}$, $n_e \geq 10^{20}$ m$^{-3}$ with particle flux up to $10^{25}$ m$^2$s$^{-1}$, leading to heat loads onto the plate up to 10 MW/m$^2$[46]. A pulsed source can also be used to produce ELM-like events achieving heat loads $> 1 \text{ GW/m}^2$[47]. In this work, only steady-state scenarios have been explored. For dedicated detachment studies, two gas seeding valves are located in the target chamber. In such way, one can tune the background neutral pressure according to the degree of plasma detachment needed for the experiments. One valve has been used to inject molecular hydrogen, while the second one has been adopted to seed the different impurities specifically for this research i.e. N$_2$, Ar and He. The applied magnetic field has been set at 1.2 T for all the experiments presented in this thesis.
Magnum-PSI also allows a very good diagnostics accessibility for what concerns both plasma and material characterization. A lateral view of the device is shown in figure 2. In the next section, a list of the diagnostics used for this thesis is reported.

2.1.2 Diagnostics

To measure fundamental plasma parameters i.e. $T_e$ and $n_e$, a Thomson Scattering (TS) system has been used, and details can be found in [48]. The laser has been kept fixed at 3 cm in front of the target. The target location has been kept fixed among all the experiments described in this thesis.

Moreover, a two-channel fiber-optic spectrometer (AvaSpec-ULS2048) with a bandwidth coverage between 299 and 579 nm has been used to investigate of molecules and radicals during N$_2$ seeding experiments. Of particular interest is the signal at 336 nm, corresponding to the NH$^*$ (A$^3\Pi$→X$^3\Sigma^-$) transition. The intensity of the band at 336 nm has been calculated as $\frac{1}{t_{(\text{exposure})}} \int I(\lambda) d\lambda$, hence integrating the intensity over the width of the profile. The location of OES is the same as TS i.e. 3 cm in front of the target.

A residual gas analyzer (SRS-RGA), located at the end of the vacuum pump of the target chamber, has been adopted as well. The aim is to evaluate the formation of ammonia and, therefore the conversion efficiency of N$_2$ to NH$_3$. The analyzer consists of an ionizer, a quadrupole mass filter and a detector. Peaks at m/q 15.16 and 17 amu, corresponding to NH, NH$_2$ and NH$_3$ species, have been monitored in this study.

The heat flux to the W target has been diagnosed by means of calorimetry. To determine the amount of power or energy absorbed by the target, the water flow, water input temperature and water output temperature have been measured. With this information the temperature rise is known and the energy deposited on the solid can be calculated as follows: $P(W) = \text{flow} \left(\frac{kg}{s}\right) dT (K) 4200 \left(\frac{J}{kg\cdot K}\right)$, then divided by the surface area ($m^2$). The mass flow is equal to 0.4 kg/s, $dT$ is the temperature difference (in K) of the water before and after the heating occurring when flowing through the heated target and 4200 $\frac{J}{kg\cdot K}$ is the specific heat of water.

2.2 Codes

In the sections presented hereafter a description of the codes used to carry out numerical simulations on the plasma physics and chemistry occurring during impurity seeding in a detached-like hydrogen
plasma is given. At first, insights into the global plasma modelling provided by Plasimo simulation package[49] are provided. This will be followed by an overview on the main features of Monte Carlo code Eunomia[50], an in-house code suited for the transport of neutral particles in linear plasma machines. Finally, plasma equations solved by the fluid-code B2.5 [51] are presented and the coupling between B2.5 and Eunomia is described.

2.2.1 Global plasma model

In Global Plasma Model [52], the plasma is homogeneously distributed throughout the simulation volume, resulting in a 0-dimensional model that describes the plasma chemistry[53]. The physical parameters are calculated from the ignition to the achievement of steady-state species density[54]. In such codes, no transport is included and the aim is to study the species density distribution and how the reaction rates influence it. The outcome of the simulation is obtained by solving a system of coupled differential equations i.e. the energy balance, the quasi-neutrality condition and the particle balance. The electron energy balance is solved simultaneously. The electron energy distribution function (EEDF) is assumed to be Maxwellian. The solution describes the evolution of species as a function of time. The input parameters, to be defined a-priori, are input power and density of precursor gases (H₂ and N₂, H₂ and Ar, H₂ and He). Plasma parameters \( n_e \) and \( T_e \) are provided as outputs. This kind of codes are computationally less expensive compared to spatially-resolved hybrid models. Therefore, one is allowed to include extensive plasma chemical data sets without implying any relevant enhancement of the computational effort [55]. Although the limitations given by the absence of transport phenomena in a 0-D simulation, fundamental plasma chemical processes can be highlighted, providing detailed insights into the most relevant atomic and molecule-induced processes governing the volume collisions in a detached-like plasma environment. For each species, the chemical composition and the energy level has to be defined. Every reaction is described by the chemical equation of the species involved and the respective reaction rate.

The source terms are formulated from the reaction rates, thus the time-dependent evaluation of number densities of the chemical species is calculated as follows:

\[
\frac{dn_k}{dt} = \sum_r (v^p_k - v^d_k) k_r(t) \prod n^{p_d}_k = S_k \tag{2.1}
\]

where \( v^p_k \) and \( v^d_k \) are the stoichiometric coefficients of the reactants \((d)\) and the products \((p)\) of the reaction, \( k_r(t) \) is the rate coefficient, \( n_k \) is the density of species \( k \) and \( S_k \) is the source term for the \( k \) species.

The electron energy balance is defined as:

\[
\frac{d(\frac{3}{2}n_e e T_e)}{dt} = P_{\text{input}}(t) - Q_{\text{inelas}} - Q_{\text{elas}} \tag{2.2}
\]

where \( n_e \) and \( T_e \) are the electron density \([m^3]\) and temperature \([eV]\) respectively, \( e \) the elementary charge, \( P_{\text{input}} \) the input power density, \( Q_{\text{inelas}} \) and \( Q_{\text{elas}} \) the energy losses from inelastic and elastic collisions between electrons and heavy particles.

In electron-induced collisions with heavy particles, the energy difference between left and right hand side of the reaction is due to energy loss by the electron. The total inelastic source term can be written as:

\[
Q_{\text{inelas}} = \sum_r E_r n_r n_e k_{r\text{eac}} = E_e R \tag{2.3}
\]

With \( E_e \) the electron energy transfer (one per reaction) and \( R \) the triple product of the reaction rate times reactant densities i.e. \( n_r \) and \( n_e \).
Quasi-neutrality must be fulfilled, implying that plasma is neutrally charged. The electron density is therefore calculated from:

\[ n_e = \sum_i n_i q_i e \]  

(2.4)

Where \( n_i \) is the density of the ionic species \( i \), \( q_i \) its charge and \( e \) the elementary charge.

The power supplied to the gas is entirely consumed by the plasma: lost and supplied power must balance. The input power density is then used to create ion - electron pairs by means of inelastic electron - neutral processes.

The chemical equations in the model regard a wide range of mechanism types, i.e. dissociation, ionization, dissociative ionization, dissociative recombination, neutral-neutral, ion-neutral and elastic collisions. The rate coefficient for electron-neutral elastic and ionization processes is gained by averaging the product of cross section and velocity over the electron energy distribution function. The relation can be written:

\[ k_i = \int_{E_{th}}^{\infty} \sigma_i (E) v(E) f(E) \, dE \]  

(2.5)

With \( E_{th} \) the threshold energy of the collision, \( E \) the electron energy, \( f(E) \) the electron energy distribution function, \( v(E) \) the electron velocity and \( \sigma_i \) the cross section of collision \( i \). The rates of the remaining classes of reactions have been taken from the most comprehensive databases available in the literature such as the astrochemical database UMIST[56], the cross sections included in LxCat[57], NIST database[58] and Anichich’s extensive reaction rates review[58]. Such rates are expressed in the generalized Arrhenius form:

\[ k(T_e) = A \times \left( \frac{T_e}{1 \text{eV}} \right) \times \exp\left( -\frac{E_a}{T_e} \right) \]  

(2.6)

Where \( A \) is in \( \text{cm}^3\text{s}^{-1} \) and \( E_a \), the activation energy of the reaction, with \( T_e \), in eV. The temperature of neutrals in the simulations (\( T_e \)) has been set at 0.2 eV. Such value has been estimated by numerical simulations[59] in to be in the temperature range of molecules in the Pilot-PSI device, precursor of Magnum-PSI and characterized by very similar plasma parameters in terms of \( T_e \) and \( n_e \). The plasma chemical table implemented for this work are listed in chapter 4.

2.2.2 Eunomia code

Eunomia code is a spatially-resolved Monte Carlo code designed for the transport of neutrals in linear plasma machines, and was firstly described in [50]. The code is conceptually very similar to the well-established Eirene code[60]. The driving motivation that led to the development of such code is the need of a kinetic description of neutral particles in ITER-divertor relevant plasma scenarios. In Eunomia-standalone, plasma equations are not solved, therefore a static plasma background is assumed and the temperature and density profiles are provided as input. The essential concept of the code is to follow many independent random walks of neutral test-particles, which represent many real neutral particles. The code solves the equilibrium density, temperature and flow velocity of neutrals and is based on the particle approximation method. Throughout the random paths, test-particles interact with background neutrals, background plasma species and with the walls.

The code estimates the solution of the modified Boltzmann equation by sampling test-particles random paths, hence describing the statistical behavior of a gas. The general form of the Boltzmann equation, for species \( i \), is:
\[ \frac{d}{dt} + \mathbf{v} \cdot \nabla \mathbf{r} + \frac{F(r,v,i,t)}{m} \cdot \nabla \mathbf{v} \] \[ f(r,v,i,t) = \left( \frac{df(r,v,i,t)}{dt} \right)_{\text{coll}} \] (2.7)

With \( f \) the probability density function of species \( i \) in the dimensional space defined by velocity \( \mathbf{v} \) and position \( \mathbf{r} \). The second and third term between square brackets represent terms for diffusion and external forces. On the right-hand side of the equation, the collision term is added. In Eunomia, only neutral particles are simulated and gravity force is neglected. Thus, \( F(r,v,i,t) = 0 \), being no external forces on the traced particles. In the code, particle sources and sinks are included i.e. gas puffing, plasma volume recombination to neutrals, recombination at the walls and absorption due to pumping. The modified Boltzmann equation, solved by the code, can be then written as:

\[ \mathbf{v} \cdot \nabla f(r,v,i) = \sum_j C(r,v,i,j) + S(r,v,i) \] (2.8)

Being \( \sum_j C(r,v,i,j) \) the collision term including the totality of inelastic and elastic processes \( j \) and \( S(r,v,i) \) the source/sink term for neutrals. The change of momentum is inherently included.

The spatial environment is constituted by a grid based on a generic linear plasma machine, as can be seen in figure 3. The cells have flexible areas and become smaller moving close to the target, providing higher resolution and further spatial information on the key region where PSI are expected to occur. At each wall, test-particles can be either reflected or absorbed. The walls can act as a recombination surface for atomic hydrogen as follows: \( \text{H}_w + \text{H}_w \rightarrow \text{H}_2^{(v)}_{\text{bulk}} \), producing a molecular hydrogen in vibrational excited state entering the volume phase. The distribution over the different vibrational excited states is based on a given temperature \( T_{\text{vib}} \), which relates as \( n_{\text{H}_2(v)} \propto e^{-E_v/kT_{\text{vib}}} \). Particles impinging on the axis of symmetry undergo through specular reflection. In figure 3, the blue line corresponds to the plasma beam axis of symmetry, the orange line is the plasma source, the green lines are the walls of the vessel and the red one is the target.

![Figure 3](image_url)

*Figure 3. The grid adopted in this work for Eunomia-standalone simulations. To improve the resolution and the statistics, the cells becomes smaller close to the center of the plasma beam and in the vicinity of the target.*

Test-particles travel upon the grid, where background properties for neutrals and plasma particles are averaged on each cell. The rate coefficients of the collisions are calculated accordingly at the beginning of each cycle. The random walks of test-particles, which undergo through different processes
interacting with both neutrals and charged particles, are used by the code to calculate the new background, which will be updated for the next cycle. That is done by tracking large number of individual test-particles, hence generating proper statistics for the newly-calculated backgrounds. In Eunomia, this process is called scoring. Plasma sources and sinks and neutrals distribution will eventually converge to equilibrium within few cycles. In this study, 20 iterations have been adopted. The code calculates density, flow velocity and temperature for each species of the neutral background, while sinks and sources for charged particle are solved simultaneously. Random paths of test particles generate information on those quantities and once a source is simulated, the ‘scored’ data are converted into actual physical quantities, corresponding to the new background. To calculate the density of each species, Eunomia has to know the amount of real particles represented by each test particle; this is given a-priori and is provided to the code as an input. The simulation of a source gives the number of test-particles in a certain cell, which is then converted to real particles as follows:

\[ N_{rp} = \Gamma_{rp} \tau_{rp} \]  

(2.9)

With \( N_{rp} \) the amount of real particles, \( \Gamma_{rp} \) the influx of them per second and \( \tau_{rp} \) the average life time of a real particle. The latter is calculated from the average life time of a test particle, \( \tau_{tp} \). Such value is estimated by the sum of the residence time in different cells, divided by the number of simulated test-particles i.e.:

\[ \tau_{rp} \approx \tau_{tp} = \frac{1}{N_{tp}} \sum C \tau_C \]  

(2.10)

With \( \tau_C \) calculated as \( \sum_i \tau_{c,i} \) where \( \tau_{c,i} \) is the time a test particle visits cell \( C \). Finally, the total number of real particle per cell is given by:

\[ N_{rp,c} = \frac{\Gamma_{rp} \tau_C}{N_{tp}} \]  

(2.11)

Regarding the number of collisions in a cell, particles sources and sinks, ion heat, ion momentum and electron energy, the same scaling is adopted by the code.

In a Monte Carlo code, test particles collisions are random processes. Differently from what occurs in PIC codes used in the field of nuclear fusion e.g. [61], where test particles collide with each other, in Eunomia a different approach is used. In fact, test particles are meant to collide with either plasma or neutral background. In the code only two-body collisions are implemented and they assume the following form:

\[ A + B \rightarrow C + D \]  

(2.12)

Where A is the simulated test particle and B its collision partner. C and D are the products of the reaction. Ion-neutral collisions lead to momentum, particle and energy sources and sinks. These information are then used by the coupled fluid code i.e. B2.5, as will be discussed in more details in the next section. In the code, short-living species are not simulated and are assumed to instantaneously recombine. Molecular-activated-recombination (MAR) [36], which are two two-step processes initiated by molecular hydrogen in vibrational excitation, read as follows:

1) \[ H_2(v) + H^+ \rightarrow H_2^+ + H \]
\[ H_2^+ + e^- \rightarrow H + H^* \]

2) \[ H_2(v) + e^- \rightarrow H^- + H \]
\[ H^- + H^+ \rightarrow H + H^* \]
The two products of the first-step process respectively are $H_2^+$ and $H^-$. Those species are not simulated by the code and are assumed to promptly undergo through step two. Electronically excited state of hydrogen atom, $H^*$, are assumed to go through relaxation or ionization, hence a third step is required. Considering the high-density plasma characterizing our simulated scenarios, radiative processes for $H^*(n \geq 3)$ can be neglected, according to the van der Mullen assumption[62]. Therefore, for the first excited level $H^*(n = 2)$, a fraction will excite further to $H^*(n \geq 3)$ and eventually ionize, otherwise it will be de-excite to the ground state. This probability is calculated as:

$$pH = \frac{A_{2,1}}{n_e k_{2u}(T_e) + A_{2,1}}$$

(2.13)

With $n_e k_{2u}(T_e)$ the excitation rate of $H^*(n = 2) + e^- \rightarrow H^*(n \geq 3) + e^-$, and $A_{2,1}$ the de-excitation coefficient.

Neutral-neutral collision cross sections are treated by means of BGK approximation[63]. Hence, the cross section is obtained from information related to the Lennard-Jones potential, which are then used to derive the binary diffusion coefficient[64] of species $i$ in a background of species $j$ and is calculated as:

$$n_{ij} D_{ij} = \frac{3}{16} \sqrt{\frac{4\pi kT}{2m_r}} \frac{1}{\pi d_{ij}^2 \Omega(T)}$$

(2.14)

Where $d_{ij}$ equals to $\frac{d_i + d_j}{2}$ and is the binary collision diameter (m), $\Omega$ the collision integral for momentum loss, $m_r$ the relative mass and $T$ the temperature (K).

Data regarding atomic processes have been taken from ADAS[65]. Rates and cross sections for inelastic reactions have been imported from two main databases i.e. HYDHEL[66] and AMJUEL[67]. In the code vibrational excited states for molecular hydrogen are simulated, given their importance in reducing the energy threshold for processes like ion conversion, i.e. first step of MAR(1) and dissociation. Data have been taken from H2VIBR database[68], which is an extension to AMJUEL. The collision frequency for electron-induced reaction $a$, is calculated by Eunomia as: $\nu_{e,c}(T_e) = n_e \langle \sigma v \rangle_c(T_e)$ i.e. by the product of collision rate and electron density. The collision frequency for heavy-particles processes is solved by the code as: $\nu_{h,c}(E_r) = n_j \sigma_c(E_r) \sqrt{\frac{2E_r}{m_r}}$, with $E_r$ the relative energy (eV), $m_r$ the relative mass, $n_j$ the density of the test-particle’s collision partner and $\sigma_c$ the cross section. In this thesis, only simulations with a hydrogen plasma beam have been carried out, while impurities have been injected in experiments (and simulations) as ground state particles. The plasma chemistry occurring during the interaction of a H$_2$ plasma with different impurities have been implemented in the codes and will be discussed in details in the chapter 4.

2.2.3 Coupling B2.5 and Eunomia

To provide a full description of Magnum-PSI experimental scenario during detachment campaigns, Eunomia code has been coupled with the multi-fluid B2.5[69], which is part of the SOLPSS.0 package. The two codes interact within each other, converging to a steady-state solution after several iteration steps. The equations solved by the program are based on Braginskii equations[70]. The code solves the continuity equation for $i$ ion which is:

$$\frac{d n_i}{dt} + \nabla \cdot (n_i v_i) = S_{n_i}$$

(2.15)
With the parallel momentum equation for ions being:

$$\frac{d}{dt}(m_i n_i v_{i||}) + \nabla \cdot (m_i n_i v_{i||} v_{i||}) = -\nabla p_i - (\nabla \cdot \Pi_i)_{||} + Z_i e n_i \nabla \phi + F_k + R_{i||} + S_{m_i v_{i||}} \quad (2.16)$$

Where $-\nabla p_i$ is the ion pressure gradient, $F_k$ the Coriolis force, $\nabla \Pi_i$ the viscosity tensor, $Z_i e n_i \nabla \phi$ the electric force, $R_{i||}$ the ion-electron friction and $S_{m_i v_{i||}}$ the ion-neutral friction. The parallel momentum balance for electrons is expressed as:

$$j_{||} = \sigma_{||} (\frac{1}{en} \nabla \cdot n T_e + \frac{0.71}{e} \nabla \phi + \nabla T_e) \quad (2.17)$$

With $\sigma_{||}$ the parallel conductivity, $\frac{1}{en} \nabla \cdot n T_e$ the pressure gradient, $\frac{0.71}{e} \nabla \phi$ the temperature gradient and $\nabla \nabla \phi$ the electric field. The definitions of radial and perpendicular current are from the sum of ion and electron momentum balance equations. The total energy for ions is calculated as:

$$\frac{d}{dt}(\frac{3}{2} n_i T_i + \frac{m_i}{2} v_i^2) + \nabla \cdot \left(\left[\frac{5}{2} n_i T_i + \frac{m_i}{2} v_i^2\right] v_i + \Pi_i \cdot v_i + q_i\right) = (Z_i e n_i E - R) \cdot v_i - Q_{ei} + S_{Ei} \quad (2.18)$$

While the electron energy conservation is given as:

$$\frac{d}{dt}(\frac{3}{2} n_e T_e) + \nabla \cdot \left(\left[\frac{5}{2} n_e T_e v_e + q_e\right] \right) = -e n_e E v_e + R_i \cdot v_i + Q_{ei} + S_{E_e} \quad (2.19)$$

In the equations, $q_{ie}$ and $q_{i}$ are the electron and ion energy fluxes, $Q_{ei}$ represents the coupling between electrons and ions i.e. the collisional equilibration term, while the terms $S_{n_i}$, $S_{m_i v_{i||}}$ and $S_{Ei}$ are sources for particles, momentum and energy due to neutrals and are calculated by the Monte Carlo. $S_{E_e}$ is the electron energy source. Boundary conditions are needed for the above-mentioned equations. Regarding the electron energy conservation equation, the heat flux at the target has to be specified as a boundary condition. It is described as follows: a thin layer, called Debye sheath[71], is located in the region where the plasma interacts with the solid surface. The sheath is collisionless and fully kinetic[72], therefore cannot be treated by the fluid model. Hence, the boundary conditions for that specific environment have to be defined separately. The Debye layer is located between the target and the simulation boundary, while a full description of sheath physics is beyond the capability of fluid code B2.5. The sheath-heat transmission coefficient ($\gamma_e$), needed for the electron energy conservation equation at the sheath entrance, is treated as follows. The distribution function of electrons at the target cannot be perfectly Maxwellian[73], and a cut-off of the Maxwellian EEDF is assumed at the sheath entrance (plasma boundary). In such way, only electrons capable to overcome the potential drop are deposited to the target. At the very surface, no electrons are going backwards (upstream), hence the cut-off electrons at the target are assumed to have a half-Maxwellian distribution. In the sheath, no particle sources or sinks are present, and $T_e$ does not change i.e. $\Gamma_w = \Gamma_{se}$ and $T_w = T_{se}$ where the subscripts “w” and “se” stand for values at the wall and at the sheath entrance respectively. The deposited parallel heat flux on the target is written as $q_w = 27 \Gamma_w \Gamma_w$, which is based on the half-Maxwellian EEDF. The energy lost by an electron passing through the sheath i.e. $\epsilon |e\Delta \phi|$ has to be added to the electron at the sheath edge. Hence, the electron-driven heat flux over the boundary is calculated as: $q_{se} = \gamma_e T_{se} \Gamma_{se}$, with $\gamma_e = 2 + \frac{|e\Delta \phi|}{T_{se}}$ which is $\approx 5$. B2.5 is self-consistently coupled with Eunomia i.e. the static plasma background characterizing Eunomia standalone is now calculated and updated by B2.5 for every cycle. A graphical representation is shown in figure 4.
In this work, a grid representing the newly-renovated linear machine Magnum-PSI, including all three differentially-pumped chambers, has been used and can be seen in figure 5. All walls are reflecting walls for the test particle, and the velocity of the reflected particle follows a cosine distribution. The outer walls thermalize the reflected particle, therefore, the velocity is rescaled to the wall temperature. The skimmers do not thermalize the particle.

Differential pumping is treated in the code as follows: a certain probability rate describing whether the test particle is terminated when crossing this boundary is specified. If that would not be the case, it gets reflected. The probability rate is updated each cycle according to the specified pressure in a determined location within the domain. To achieve the differential pumping, we have different pumps in different location (per chamber) and also different pressure location for each of the pumps.

Figure 4. Graphical representation of the iteration scheme between the two codes, reciprocally providing information on the plasma itself (B2.5 for Eunomia) and sources and sinks for particles, momentum and energy (Eunomia for B2.5). Credits: Ray Chandra.
Figure 5. Left: drawing of Magnum-PSI, where 1. is the plasma source 2. the skimmers 3. the plasma beam and 4. the target. Right: the geometry used in the simulations of the coupled codes is shown. Cells become smaller in the vicinity of the skimmers and close to the target, to improve the statistics of those regions.

The B2.5 grid for both tokamaks and linear device are represented in r-z coordinates with r=0 being the axis of symmetry. The evaluation of surface area of cell faces and of the cell volume is identical among the two geometries. Basically, a grid for a linear device is just a simplification of a tokamak grid. Given so, more processes can be implemented in a linear geometry without causing a strong increase in the computational effort compared to a tokamak scenario, allowing one to study in detail physical and chemical phenomena in a simplified simulation environment. These models are then used to highlight relevant physics occurring in experimental scenarios, where diagnostics cannot provide insights due to, for instance, limited accessibility. In B2.5-Eunomia, the default hydrogenic processes adopted by the code involve a wide range of reactions i.e. neutral-neutral and ion-neutral elastic collisions, ionization, dissociation, (de-)excitation, recombination. All 14 vibrational excited states are simulated in the code, while no v-t transitions are included. The list of reactions can be seen in Table 3.
<table>
<thead>
<tr>
<th>N.</th>
<th>Reaction</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$H + H \rightarrow H + H$</td>
<td>Elastic collision</td>
</tr>
<tr>
<td>2</td>
<td>$H + H_2 \rightarrow H + H_2$</td>
<td>Elastic collision</td>
</tr>
<tr>
<td>3</td>
<td>$H_2 + H_2 \rightarrow H_2 + H_2$</td>
<td>Elastic collision</td>
</tr>
<tr>
<td>4</td>
<td>$H + e^- \rightarrow H^+ + 2e^-$</td>
<td>Ionization</td>
</tr>
<tr>
<td>5</td>
<td>$H^+ + H \rightarrow H + H^+$</td>
<td>Charge exchange</td>
</tr>
<tr>
<td>6</td>
<td>$H_2 + e^- \rightarrow H + H + e^-$</td>
<td>Dissociation</td>
</tr>
<tr>
<td>7</td>
<td>$H_2(v) + e^- \rightarrow H_2(v \pm 1) + e^-$</td>
<td>Vibrational (de-)excitation</td>
</tr>
<tr>
<td>8</td>
<td>$H_2(v) + H^+ \rightarrow H + H_2^+$ $\quad e^- + H_2^+ \rightarrow H + H_{n=2}^*$</td>
<td>Ion conversion Dissociative recombination (MAR)</td>
</tr>
<tr>
<td>9</td>
<td>$H_2 + e^- \rightarrow H + H^-$ $\quad H^+ + H^- \rightarrow H + H_{n=2}^*$</td>
<td>Ion conversion Dissociative recombination (MAR)</td>
</tr>
<tr>
<td>10</td>
<td>$H + H^+ \rightarrow H + H^+$</td>
<td>Ion-neutral elastic collision</td>
</tr>
<tr>
<td>11</td>
<td>$H_2 + H^+ \rightarrow H_2 + H^+$</td>
<td>Ion-neutral elastic collision</td>
</tr>
</tbody>
</table>

Table 3. List of hydrogenic processes included in B2.5-Eunomia.

The main scope of this work is to underline new plasma physical-chemical processes occurring in detached-like scenarios when different gas species are puffed into the system, separately. Therefore, the role of ion-neutrals volume interaction in tokamak (ITER)-relevant divertor plasma detachment is the principal subject of this work. The coupled codes have been used to study the effect on plasma parameters led by puffing different gas species in the sole target chamber during detachment experiments. To do so, new plasma chemistry has been implemented in the code i.e. $H_2-N_2$, $H_2$-He and $H_2$-Ar. In such way, we can study the differences between seeding a highly-reactive molecular species (nitrogen and ammonia-related compounds) with a poorly-reactive atomic ones (helium or argon). Considering the complexity of the system and the intrinsic uncertainties due to necessary assumptions, transport codes should not be considered as high-fidelity predictive models but rather as tools to investigate relevant physical (and chemical) processes that would not be easily quantified experimentally. We shall consider such exercises as code experiments, similarly to [73].
Chapter 3

Experiments on plasma detachment in linear machines

3.1 Plasma detachment in linear plasma device Magnum-PSI

Detached-like plasmas in Magnum-PSI are achieved by gas seeding in the target chamber, leading to an increased background neutral pressure. A background pressure scan, ranging from 0.3 to 16.5 Pa has been carried out. In this experiment, a hydrogen plasma has been used and the neutral pressure has been enhanced by puffing pure hydrogen in the target chamber. Images taken with a Phantom camera equipped with a Balmer-α filter are shown in figure 1. The dotted line corresponds to Thomson Scattering line of sight, while the straight line represents the target location.

At background pressure of 0.3 Pa i.e. figure 1(a), light emission is observed predominantly in the vicinity of the plate. Such scenario is interpreted as ion recycling at the target, leading to a source of thermalized neutrals coming from the solid surface[74]. Those particles promptly undergo through electron-impact excitation, given the high collisionality of the high-density plasma we are working with and, therefore, the short mean-free-path. Increasing the neutral background pressure up to 6 Pa, namely figure 1(b), (c) and (d), leads to a shift of the light emitted from the vicinity of the target to throughout the portion of the observed plasma beam. Further enhancing the neutral pressure (figure 1(e) and 1(f)) causes a visible extinction of the plasma beam before it reaches the plate. The experimental detached-like scenarios chose for the work presented in this thesis are divertor-relevant, and correspond to 2 and 4 Pa, where plasma parameters are suitable for recombination i.e. $T_e < 2$ eV and $n_e > 5 \times 10^{19} \text{ m}^{-3}$.

Figure 1. background pressure scan. Images taken with Phantom camera with Balmer-alpha filter. Straight and dotted lines correspond to location of the target and TS line of sight respectively. At low background neutral pressure (a)(b), light is emitted only in the vicinity of the target in a so-called high recycling regime. Increasing pressure leads to a so-called recombining plasma, where light is emitted throughout the whole beam (c)(d). Finally (e)(f), plasma is extinguished before reaching the target.

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Figure 2. Left: total static plasma pressure as a function of the vessel background pressure. Right: peaked electron temperature as a function of neutral background pressure in the target chamber. Both values decrease exponentially while increasing the content of neutrals in the target chamber of Magnum-PSI.
The total static plasma pressure, calculated as $P_p = 2kT_e n_e$, is plotted in figure 2 as a function of the background neutral pressure in the target chamber. By increasing the amount of neutral gas in the chamber up to 16 Pa, plasma pressure drops almost to zero. Such effect is mostly due to plasma-neutral volumetric interactions that eventually lead to recombination of incoming hydrogen ions, converting charged particles to neutrals before they reach the target.

The effect of radiative cooling alone on the plasma pressure drop is excluded to be dominant in Magnum-PSI detached-like scenarios because of the constant power input coming from the plasma source. Moreover, given the plasma pressure conservation along the beam, which has been extensively studied in [75] and [28], no power limitation[76] phenomena are expected to be dominant in this type of plasma scenarios. For what concerns H$_2$-driven volume recombination, MAR [36] are initiated by hydrogen molecules in vibrational excited states and constitute of two different two-step reaction paths, i.e.:

1) $\text{H}_2(v) + H^+ \rightarrow \text{H}_2^+ + H$

$\text{H}_2^+ + e^- \rightarrow \text{H}^+ + H$

2) $\text{H}_2(v) + e^- \rightarrow \text{H}^- + H$

$\text{H}^- + H^+ \rightarrow \text{H}^+ + H$

Reaction (1) is initiated by ion conversion and is followed by dissociative recombination, while the first step of reaction (2) is dissociative attachment, which is followed by mutual neutralization. In both cases, H$^+$ is effectively converted to neutral. The efficiency of the neutralization mechanism between H$_2^+$ and H$^+$, producing H$_2$ and H$^+$, is still a matter of debate in the field of divertor physics and its detailed study is beyond the scope of this work. In the plasma environment of this case of study, molecular ion H$_3^+$ is poorly produced due to very efficient dissociative recombination of its ionic primitive H$_2^+$. Similar findings have been published by Brussard et al. [78], showing that for a magnetized hydrogen plasma the main ionic species is H$^+$. The same applied in the case of a pure nitrogen plasma, where N$^+$ is the most populated ionic species of such environment. A dedicated numerical study on the population of molecular hydrogen ions can be found in the next chapter of this thesis.

3.2 Plasma characterization in Magnum-PSI

An enhancement in radial transport with higher background neutral density has been very frequently observed in TS profiles in Magnum-PSI. A detailed analysis has been carried out in [79]. In order to evaluate the role of the side walls, the electron Hall parameter has been used[80], being electrons more mobile than ions and e-i coulomb collision the most important process causing perpendicular diffusion of plasma particles. We can express the Hall parameter for electrons as:

$$H_e = \frac{e}{2.9 \cdot 10^{-12} m_e \ln(\Lambda)} \cdot \frac{B_{T_e}^2}{n_e}$$

(3.1)

Where $B$ is the magnetic field i.e. 1.2T in these experiments, $\ln(\Lambda)$ the coulomb logarithm. For the plasma parameters used in this work, $H_e$ values are between 5.6 ($T_e = 0.8$ eV) and 37.25 ($T_e = 1.5$ eV). Therefore, plasma can be considered to be properly confined without any significant orbit losses. Moreover, when looking into typical electron density profiles, full-width-half-maximum (FWHM) are generally between 14 and 20 mm[81]. The distance between the centre of the plasma beam and the machine side walls is ≈ 28 cm[46], hence we can exclude any relevant effect on the plasma due to recombination of ion on the side walls of the machine.

To provide insights into the ion temperature in the Magnum-PSI plasma, the collision frequency for elastic ion-electron collisions has been calculated as [82]:

$$f_{ie} = \frac{1}{2} \frac{e^2}{\pi \epsilon_0 m_e \mu}$$

(3.2)
The charge-exchange (CX) frequency is calculated via HYDHEL database [66]. The collision frequency as a function of $T_e$ is reported in figure 3. It can be observed that at low $T_e$ the e-i collision frequency is orders of magnitude higher than CX. Besides showing the dominance of a process to the other, this also indicates that the high collisionality between electron and ions in our plasma may justify the assumption $T_e = T_i$, as in [83], [84].

3.3 Plasma detachment with impurity seeding (N$_2$, Ar and He)

In this section a comparative study among different impurity species and their effect on plasma detachment has been carried out. Impurities have been seeded together with H$_2$ with different mixing ratios; the overall background neutral pressure in the target chamber has been kept constant at 2 and 4 Pa, while changing the ratio as:

$$\frac{[\text{impurity}]}{[\text{H}_2] + [\text{impurity}]} \cdot 100 = 0, 5, 10, 15, 20 \%.$$  \hspace{1cm} (3.3)

Three different gas species have been puffed with hydrogen i.e. nitrogen, helium and argon. For example, a 10% argon content, for a 2 Pa case, implies the pressure of H$_2 = 1.8$ Pa and Ar = 0.2 Pa. Helium and argon are poorly reactive species, while N$_2$ and related compounds such as NH$_3$, NH$_2$, NH react with particles populating the generated hydrogen plasma e.g. H$^+$, H$_2^+$, H, H$_2$(v)[85]. In this section 3.3 we present the experimental findings regarding the influence of different impurities seeding on plasma parameters by means of the plasma pressure and the heat flux collected at the target. The injected gas mixtures are H$_2$+N$_2$, H$_2$+He and H$_2$+Ar, and the plasma pressure, calculated with Thomson scattering, is shown in figure 4. These measurements have been taken in the plasma volume, at 3 cm in front of the tungsten target. The H$_2$ gas flow through the source is fixed at 1.16*10$^{-4}$ m$^3$s$^{-1}$, the current at 120 A and the applied magnetic field is 1.2 T. The target plate is kept perpendicular to the plasma beam.

Figure 3. Collision frequency of electron-ion elastic collision and charge exchange as a function of electron temperature. The high collisionality of electron-ion elastic process may justify the assumption of considering the electron temperature equal to the ion temperature.
Figure 4. Total plasma pressure as a function of impurity content for N\textsubscript{2}, He and Ar. The neutral background pressure in the target vessel is constant at 2 Pa (left) and 4 Pa (right). Interestingly, the plasma pressure drops in the presence of nitrogen while increases with the other two species. This is the case for both background neutral pressures.

For the scans of both background pressures, the baseline scenario i.e. with only H\textsubscript{2} puffing, corresponds to the first point i.e. when no impurity was added in the mixture. Although each baseline scenario can be slightly different due to limited reproducibility of the machine, every scan is carried out maintaining the same experimental conditions among each other. At 2 Pa with N\textsubscript{2} seeding up to 20%, we observe a clear decay that leads to a plasma pressure loss of ≈ 25%. In the helium case, a different trend is achieved. Here, the plasma pressure somewhat varies around 0.21 kPa and remains almost constant. Regarding the Ar-seeding case, the behaviour is similar to the helium one: after a small decrease at 5%, \( P_{\text{plasma}} \) increases by about 10% during the scans at 10, 15 and 20% of impurity content, hence reducing the effectiveness of detachment. If on one hand the addition of a mixture of H\textsubscript{2}+N\textsubscript{2} is beneficial for plasma detachment compared to H\textsubscript{2} puffing alone, the other two species show an opposite effect, enhancing the plasma pressure in front of the target.

To unequivocally investigate the effect of these impurities on plasma recombination, heat fluxes collected at the target have been diagnosed by means of calorimetry and results are reported in figure 5. The power deposited to the tungsten disc is calculated as

\[
P(W) = \text{flow} \left( \frac{kg}{s} \right) dT(\text{K}) \times 4200 \left( \frac{J}{kg*\text{K}} \right),
\]

with \( \text{flow} = 0.4 \frac{kg}{s} \) being the amount of cooling water passing through the diagnostic per second, \( dT \) the water temperature difference before and after it has been passed through the heated component and 4200 J is the energy needed to heat up 1 litre of water by 1 K. Worth to be stressed that for the calculation of the heat flux no direct measurements of plasma parameters are used; in such way we can straightforwardly measure the actual heat transported by the plasma to the target. The power load at the target is mostly due to surface recombination of incoming hydrogen ions, where they release their potential and (part of their) kinetic energy, which causes heating of the material. In figure 5 (left), the starting value of heat load for the Ar seeding scan i.e. Ar = 0% is lower compared to H\textsubscript{2}+N\textsubscript{2} and H\textsubscript{2}+He cases by ≈ 0.7 MW*m\textsuperscript{-2}. Although the experimental settings have been kept the same, plasma conditions were not perfectly reproducible. Nevertheless, for the scope of this work, the trend obtained by puffing different ratios of different species is the most relevant feature to be highlighted and studied.

At background neutral pressure of 2 Pa, when H\textsubscript{2} is diluted with He, the measured heat load increases by ≈ 11%, from the 0% to the 20% of impurity content. Regarding N\textsubscript{2}, we obtain a net reduction of heat flux of about 12%. Such findings further confirm the beneficial effect for detachment led by the presence of N\textsubscript{2} in the seeded gas mixture. Argon puffing experiments are characterized by an enhancement of heat deposited to the surface of ≈ 12%, implying a reduced detachment efficiency.
The same experiments have been carried out with a fixed background pressure of 4 Pa and results are plotted in figure 4 (right) and 5 (right). The same behavior is observed compared to the 2 Pa case; in fact, $P_{\text{plasma}}$ increases by $\approx 15\%$ between 0 and 20% of impurity content, for both He and Ar. $H_2+N_2$ puffing led to a plasma pressure reduction of $\approx 25\%$. The heat flux is reduced by the presence of $N_2$ by 18%, while is enhanced by 16% and almost 40% with $H_2$+He and $H_2$+Ar respectively.

![Figure 5. Heat load on the W target for each impurity at different $H_2$/impurity mixing ratios at 2 Pa (left) and 4 Pa (right). Similarly to the plasma pressure plots, the presence of nitrogen leads to a net reduction of the heat collected at the target, while helium and argon show an opposite behavior.](image)

According to these results, Ar seems to be the less beneficial species among the impurities exploited in this study. Helium shows a negative impact on plasma detachment as well, while nitrogen led to an improved detached state among both 2 and 4 Pa cases. Three different impurities have been tested in ITER-relevant hydrogen plasma at the same experimental conditions for the first time. The negative outcome on plasma pressure and heat flux of Ar and He seeding may be due to dilution effect i.e. less hydrogen molecules are inserted in the system, therefore less molecule-driven ion recombination occurs in the volume phase. The presence of such low-reactive species (He and Ar) does not add any contribution on plasma recombination. Worth underlining that the overall background pressure is constant among the scans, hence the partial pressure of $H_2$ diminishes with increasing the impurity content in the seeded mixture.

In a nitrogen-seeded environment we expect plasma chemistry to be influenced by the presence of $N(x)$-$H(y)$ species. In the next paragraph, the effect on plasma parameters caused by the addition of different $H_2+N_2$ ratios puffed in the target chamber is investigated and discussed.

### 3.4 Nitrogen seeding experiments

To further understand the influence of $N_2$ and related species on the physics and chemistry occurring in such environment, optical emission spectroscopy (OES), bolometry and a residual gas analyzer (RGA) have been adopted. The RGA is placed at the end of the pump tube that connects the target chamber with the roots pump while OES is placed at 3 cm in front of the target. Moreover, electron density and temperature profiles, obtained with Thomson Scattering, can provide interesting insights on the effect of the seeded mixture on the hydrogen plasma. In figure 6 $T_e$ and $n_e$ are reported for each seeding ratio at background pressures of 2 and 4 Pa.
The full-width-half-maximum (FWHM), averaged over all H₂+N₂ seeding shots, is 16.7 mm at 4 Pa and 15 mm at 2 Pa. Such difference is due to the higher neutrals content which leads to an enhancement of elastic collisions frequency, hence increasing diffusion perpendicularly to the beam. This effect in linear plasma machines has been recently investigated with Soledge2D-Eirene simulations and can be found in [18]. The reduction of the parallel transport due to momentum-transfer processes leads to an increased radial diffusion, resulting in a broadening of the beam. When looking at the different H₂+N₂ puffing ratios, a clear trend is observed in both cases, with \( n_e \) decreasing while increasing the content of N₂ in the puffed gas mixture. Peak values of electron density decrease from \( 2.2 \times 10^{20} \text{m}^{-3} \) to \( 1.3 \times 10^{20} \text{m}^{-3} \) between N₂ = 0 % and N₂ = 20 % for the 2 Pa case and from \( 2.1 \times 10^{20} \text{m}^{-3} \) to \( 1.3 \times 10^{20} \text{m}^{-3} \) for the 4 Pa one. \( T_e \) peak values were ~1.8 eV at 2 Pa and ~1 eV at 4 Pa and remain almost constant among the totality of studied scenarios. Given no trend in electron temperature, the heat flux is governed by the particle flux. The significant \( n_e \) reduction may be due to additional recombination mechanisms introduced by the presence of N₂, and therefore NHₓ, which act as electron sink.

Recent theoretical work carried out by our group [87] highlighted new plasma chemistry recombination paths, named N-MAR, occurring in a detached-like high-density (\( n_e > 10^{20} \text{m}^{-3} \)) low-temperature (\( T_e < 3 \text{ eV} \)) hydrogen plasma in the presence of nitrogen. Such mechanisms have been found to be important converting hydrogen ions to neutrals with a two-step process as follows:

\[
\begin{align*}
\text{Ion conversion} & \quad NH_x^+ + H^+ \rightarrow NH_x^+ + H \\
\text{Dissociative recombination} & \quad NH_x^+ + e^- \rightarrow NH_{x-1} + H
\end{align*}
\]

(3.4) N-MAR 1st step

(3.5) N-MAR 2nd step

Figure 6. Electron density and temperature radial profiles with different N₂ concentrations. Background pressure has been kept constant at 2 Pa (left) and 4 Pa (right). The electron density remains constant among the different seeding scenarios, while electron density decreases with increasing the content of nitrogen in the seeded mixture. This is a clear signature of enhanced recombination taking place.
They are initiated by ion conversion between \( \text{NH}_x \) with \( 1 \leq x \leq 3 \) and \( \text{H}^+ \). The products \( \text{NH}_x^+ \) promptly undergo dissociative recombination. The ion conversion is the rate determining step of \( N\text{-MAR} \). Specifically, particular importance is attributed to \( \text{NH} \) radical, which acts efficiently as electron donor in the ion conversion with \( \text{H}^+ \). Extensive plasma chemistry simulations using global modelling [53] with Plasimo code [49] have been carried out and will be discussed in details in the next chapter. To evaluate the presence of those species, OES and RGA diagnostics have been exploited.

In figure 7 two OES spectra of 15 % \( \text{N}_2 \) and without \( \text{N}_2 \) seeding are shown (background neutral pressure fixed at 2 Pa). Figure 7a represents a pure hydrogen plasma with \( \text{H}_2 \) puffing. Balmer lines from \( \gamma \) to \( \zeta \) are highlighted and clearly distinguishable. Figure 7b shows a different scenario, in fact, Balmer lines are less intense while the \( \text{NH}^+ \) electronic transition becomes dominant. In detached-like plasma environment, excited states of \( \text{H} \) are mostly generated by means of \( \text{MAR} \) and three-body recombination[37]. The differences between the 7a and 7b graphs suggest different plasma chemistry paths to be dominant in the presence of nitrogen, or, at least, N-influenced mechanisms are competing with the ones initiated by molecular hydrogen in vibrational excited state.

![OES spectrum](image)

Figure 7. (a) OES spectrum taken with only \( \text{H}_2 \) seeding at 2 Pa. (b) OES spectrum with \( \text{N}_2 = 15\% \) at 2 Pa. In the presence of nitrogen (b), the NH band at 336 nm becomes dominant, implying a considerable production rate of that species.

The peak intensity of \( \text{NH}^+ \) \( (\text{A}^3\Pi \rightarrow \text{X}^3\Sigma^-, \Delta v = 0) \) transition band at 336 nm [88] has been calculated as \( \frac{1}{t_{(exposure)}} \int I(\lambda) d\lambda \) i.e. integrating the intensity over the width of the line profile. The spectrometer used to measure the \( \text{NH}^+ \) emission intensity consists of only a single fiber, which has a chord-integrated view through the center of the plasma. Therefore, the radial distribution of \( \text{NH} \) emissions could not be measured. Peake values have been used. Data of both OES and RGA are shown in figure 8 for neutral pressure of 2 and 4 Pa.
The intensity of the NH\(^*\) band increases linearly with increasing N\(_2\) content in both cases, showing unequivocally the presence of such species in the plasma. The peak intensity of NH\(^*\) are similar in both scenarios, even though the overall content of N\(_2\) is higher in the 4 Pa environment. The rate-determining step of ammonia synthesis in a plasma-metal interface is the dissociative chemisorption of electronically and vibrationally-excited molecular nitrogen\(^{[89]}\)\(^{[90]}\). Hence, the conversion efficiency of nitrogen to ammonia strongly depends on the following electron-impact excitation reaction:

\[
N_2 + e^- \rightarrow N_2(A^1\Sigma_u^+, \Delta v=0) + e^- ; \Delta E = 6.725 \text{ eV.} \tag{3.7}
\]

In the 4 Pa case, where \(T_e\) is \(\sim 0.9\) eV, such processes is less favorable compared to the 2 Pa scenario, which is characterized by temperature above 1.5 eV. Moreover, electron-impact dissociation of NH\(_3\), which has a threshold of \(\sim 4\) eV, is less efficient at low \(T_e\) (see figure 11), hence CX-DR cycles are the main reaction paths leading to dissociation of NH\(_3\). The conversion efficiency (%) per nitrogen atom has been studied with RGA and calculated as \(\frac{\Sigma N\text{H}_3}{N_{\text{tot}}} \times 100\). Results are showed in figure 9 and go from 6.5 % to about 4.5 % in the 2 Pa case and from 5% to 2.8% in the 4 Pa one. Such difference shall explain the values in figure 8 (left).

3.5 Power limitation effects

An important feature concerning plasma detachment is the so-called power limitation effect (sometimes referred to as power starvation) \(^{[26]}\)\(^{[91]}\). In a tokamak, given that the particle source is located in the divertor in the vicinity of the target (the mean free path for neutral ionization is smaller than the typical divertor size), the energy needed for such ionization has to be provided by power coming from further upstream. Impurities injection radiate away part of this power, hence, less power...
is available for ionization, causing an upshifting of the recombination front and the rollover of the particle flux to the target.

To study the radiated power emitted during the nitrogen seeding scan in Magnum-PSI, a bolometry system has been used. In this way, we can include/exclude plasma cooling phenomena led by relaxation of electronically excited species. Results are shown in figure 10.

![Figure 10](image)

*Figure 10. Plasma radiation during H₂-N₂ seeding scan. No significant trend is achieved: the radiated power from the plasma stays almost constant over the seeding scan. We can exclude power limitation effects to be dominant.*

The total radiated power, averaged over the 3 viewing channels, is calculated as:

$$P_{\text{rad}} = \frac{\pi l_{s,ap}^2 d_p \Delta z P_s}{R_s A_{ap}}$$

where $l_{s,ap}$ is the distance between the sensor and the aperture, $A_s$ the sensor area, $A_{ap}$ the aperture area, $d_p$ is the plasma diameter taken as the FWHM measured by Thomson scattering, $\Delta z$ the axial width. $P_s$ is the power received by the sensor of a bolometer channel and is calculated as follows:

$$P_s(t) = \frac{1}{S} \left( \Delta U(t) + \frac{\Delta U(t)}{\Delta t} \right).$$

No substantial trend in plasma radiation is collected while increasing the content of nitrogen in the puffed gas mixture, being $P_{\text{rad}}$ values within the error bars. According to those findings, we shall exclude any power-limitation\[91\] effect in Magnum-PSI plasma conditions.

Moreover, differently from a real fusion reactor where the ion source is located in the plasma volume in the divertor region, in Magnum-PSI there is a constant particle (and energy) flux coming from the plasma source. The magnetically confined plasma goes throughout the source and middle chambers without significant power dissipation (differential pumping is designed to remove neutral particles along the beam path). During normal Magnum-PSI operation, even in attached-like scenarios, $T_e$ is not sufficiently high to drive a relevant ionization source in the target chamber.

The fact that no trend is observed with bolometry further suggests that the reduced heat flux and plasma pressure drop shown in figure 4 and 5, is due to volumetric recombination processes occurring before ions reach the target. In particular, the role of NH₃ molecules interacting with the considered hydrogen plasma appears to be at least partially responsible for the observed heat and plasma pressure drops. It has been widely established since [22], and recently confirmed experimentally [25][26] and by numerical simulations [14], that ammonia is produced by means of Langmuir-Hinshelwood and Eley-Reedal processes. Hence, NH₃ is synthesized on the reactor walls and is then released in the volume phase. In figure 11 the rates of NH₃-driven mechanisms are showed up to $T_e = 10$ eV. In the temperature range considered in this study i.e. $T_e < 2$ eV, dissociative recombination are dominant. NH₃ and its protonated derivative NH₄⁺ are efficient NH sources via ion conversion and recombination. The rate coefficients plotted in figure 11 have been taken from both UMIST database[27], developed by McElroy et al., and from Anicich compilation [28] and references therein.
We have shown that, for the plasma parameters in Magnum-PSI, $N_2 + H_2$ seeding implies an enhancement of plasma detachment. This leads to beneficial effects for the target, given that the heat flux is notably reduced when such gas mixture is puffed in the target chamber. An opposite outcome has been found for what concerns $H_2 + He$ and $H_2 + Ar$, where the heat flux increased compared to only $H_2$ injection. Although Magnum-PSI is capable to achieve remarkably high and ITER-relevant electron densities, electron temperatures in detached-like condition are $< 2 \text{ eV}$.

### 3.6 Impurities seeding experiments in linear plasma machine GAMMA10/PDX

To explore the consequences of different impurities seeding in different plasma scenarios, a collaboration with the group of Professor Ezumi from the University of Tsukuba has been carried out. Gas seeding experiments have been performed in the linear plasma device GAMMA10/PDX Tandem Mirror. Information about the machine experimental set up and the diagnostics available can be found in [41]. For the scope of this thesis it is worth mentioning that such device, despite electron densities $< 10^{18} \text{ m}^{-3}$, can achieve electron temperatures up to 20 eV during detachment experiments with hydrogen plasma. Impurities have been seeded in the vicinity of the characteristic V-shaped target (tungsten). Further information on the target set-up and diagnostics can be found in [92]. Plasma parameters i.e. $T_e$ and $n_e$ have been diagnosed with Langmuir probes placed on the target surface. The ion flux has been derived from calorimetry measurements. OES has been also used to observe the NH$^+$ transition band at 336 nm. Results from Langmuir probes and calorimetry are shown in figure 12 [93]. When looking at figure 12 (a), one can observe a net reduction of $n_e$ when $N_2$ is added in combination with $H_2$ at $\sim 150$ ms, while electron temperature (figure 12(b)) doesn’t change significantly. When $N_2$ is puffed without $H_2$ both $n_e$ and $T_e$ remain basically constant. Regarding the combination of $H_2$ with other impurities (in this case noble gases), no synergy is found to occur for both $n_e$ and $T_e$, compared to only $H_2$ seeding. Interestingly, as can be seen in figure 12 (c), the particle flux to the target is drastically reduced with $H_2 + N_2$, while, again, with only $N_2$ the flux remains constant. No significant differences about the ion flux are found between only $H_2$ and Ar+$H_2$ puffing scenarios. When only Ar is injected, the flux slightly increase as a function of time, due to the absence of $H_2$-driven molecular processes.
What has been presented here concerning GAMMA10/PDX experiments is in line with what observed in Magnum-PSI detachment campaigns, where the simultaneous addition of H\textsubscript{2} and N\textsubscript{2} in the gas mixture leads to $P_{\text{plasma}}$ and $q_{\text{target}}$ drop. Furthermore, the fact that the ion flux measured in GAMMA10 with only N\textsubscript{2} seeding does not lead to any reduction suggests that N\textsubscript{2}-driven molecular processes to not occur significantly in that environment. To highlight the presence of NH\textsuperscript{+} ($A^1\Pi \rightarrow X^3\Sigma$), OES measurements have been carried out and are presented in figure 13.

![Figure 12. Time evolutions of (a) $n_e$, (b) $T_e$ and (c) ion flux for various impurity gas puffing together with H\textsubscript{2}. H\textsubscript{2} gas injected after 150 ms together with one of the impurity gases. Similarly to the results achieved in Magnum-PSI, the highest ion flux reduction occurs where H\textsubscript{2} and N\textsubscript{2} are puffed simultaneously.](image-url)
Although no quantitative conclusion can be extracted, the emission intensity increases with increasing the content of N\textsubscript{2} in the system, as it was shown for Magnum-PSI experiments. The peak at 337 nm, corresponding to the 2\textsuperscript{nd} positive N\textsubscript{2} ion is more present in this case due to the higher $T_e$, i.e. electrons have more energy to ionize N\textsubscript{2} further, compared to Magnum-PSI scenario.

Similar conclusions have been obtained in experiments conducted at PISCES-E linear machine\cite{94}, located at University of California San Diego. In that case, ammonia has been directly injected in a hydrogen plasma, and enhanced recombination has been achieved. Numerical simulations confirmed the role of NH\textsubscript{3} as electron donor in the ion conversion with H\textsuperscript{+}. Albeit plasma parameters in that case were different from the ones examined in this thesis (both Magnum-PSI and GAMMA10/PDX) i.e. $n_e$ in the order of $10^{17}$ m\textsuperscript{-3} with $T_e$ around 2.5 eV, that study underlines the relevance of N-MAR in such plasma environment as well.

### 3.7 Conclusions

Synergistic effects, beneficial for plasma detachment, have been observed in both the linear devices Magnum-PSI and GAMMA10/PDX. Magnum-PSI plasma is characterized by high density and low temperature, while the other device can achieve temperature higher by one order of magnitude, with densities two orders of magnitude lower. This complementarity let us studying experimentally the effect of impurity seeding on detachment in different plasma scenarios. In both machines $T_e$ is not affected by the presence of impurities alone or in combination with H\textsubscript{2}, while $n_e$ and particle/heat flux are notably reduced in the case of H\textsubscript{2}+N\textsubscript{2} seeding. This indicates the presence of ion-recombination mechanisms occurring in the volume phase, converting incoming hydrogen ions to neutrals before they get to the surface. When substituting H\textsubscript{2} with either helium or argon in Magnum-PSI, we observe a decrease of detachment, implying higher heat loads onto the target. This is due to dilution effect of molecular hydrogen, hence diminishing the recombination capability of the puffed gas. OES have been used to identify the presence of NH\textsuperscript{+}, which resulted to be notably produced in both experiments. Bolometry has been also used to study possible power starvation effect. Results clearly show no significant difference in radiated power when increasing the amount of injected N\textsubscript{2}, therefore, no power limitation effect are occurring in Magnum-PSI detached-like plasma environment. This is in line with the constant $T_e$ along the different scans. To fully understand the fundamental volume processes leading these scenarios and in particular the role of N-H\textsubscript{x} molecules on plasma recombination, extensive numerical simulations have been carried out and are presented in the next chapter.

---

\[\text{Figure 13. Emission spectra of NH}^* \text{ transition band observed during H}_2/N_2 \text{ seeding in GAMMA10/PDX. The gas pressure indicated in the figure are the pressure in the reserve tank for gas seeding.}\]
Chapter 4

Global modelling of divertor-relevant plasma scenarios

The interaction between a hydrogen plasma with so-called impurities i.e. N$_2$, He and Ar leads to a wide variety of processes involving several species: atomic and molecular ions, electronically excited states, vibrationally excited states and molecules in the ground state. Such interactions may lead to different consequences regarding plasma parameters and, therefore, influencing plasma detachment. To provide a full description of the plasma chemical processes occurring in such environments, global models have been set up and simulations have been carried out using PLASIMO code[49]. Although the limitations imposed by a zero-dimensional code, global models allow one to us to study a large number of different processes among several species. Simulations have been done for H$_2$+N$_2$, H$_2$+He and H$_2$+Ar and are presented hereafter.

4.1 Global Modelling of a H$_2$ + N$_2$ plasma

The chemical species implemented in the H$_2$-N$_2$ model are listed in Table 1. The aim of this exercise is to obtain a reduced set of chemical equations. It has been recently reported [95] that the N$_2^+$($A^3\Sigma$) excited state acts as intermediate for the dissociation of N$_2$ in low temperature plasma via the reaction N$_2^+$($A^3\Sigma$) + H $\rightarrow$ NH + N and to a minor extent (= 30%) via N$_2^+$($A^3\Sigma$) + e $\rightarrow$ N + N. Moreover, the two-step ionization of N$_2$ involving the A$^3\Sigma$ state has been implemented in the code as well. N$_2^+$ and NH$_2^+$, together with NH$_3$ and NH$_4^+$ are included too. Although it is now well-established that the plasma-assisted hydrogenation of nitrogen, producing NH$_3$, occurs mainly on the surface by means of the so-called Sugiyama path[90], no surface processes are included in the current model, being the identification of the most relevant volume processes the scope of this work. Regarding pure hydrogen species, H$_2$ (v = 4) has been added in the model, given the important role it plays in the ion conversion with H$^+$, which is the main ion species in our plasma.

<table>
<thead>
<tr>
<th>H$_2$ species</th>
<th>N$_2$ species</th>
<th>H$_2$-N$_2$ species</th>
</tr>
</thead>
<tbody>
<tr>
<td>H, H$_2$, H$^+$, H$_2^+$, H$_2$(v=4), H$_3^+$</td>
<td>N$_2$, N, N$_2$($A^3\Sigma$), N$_2^+$, N$^+$</td>
<td>NH, NH$_2$, NH$_3$, NH$_3^+$, NH$_2^+$, NH$^+$, N$_2$H$^+$, NH$_4^+$</td>
</tr>
</tbody>
</table>

Table 1. Species included in the model

4.1.1 Plasma chemical reactions

A wide range of plasma chemical process types has been incorporated in the model, i.e. ionization, dissociation, dissociative ionization, dissociative recombination, ion-neutral, neutral-neutral and elastic collisions. The set of the chemical equations adopted in this work is listed in table 2. The temperature of neutrals ($T_g$) in the simulations is set at 0.2 eV, according to previous numerical simulations [59].

<table>
<thead>
<tr>
<th>NR.</th>
<th>Reaction</th>
<th>Rate coefficient (cm$^3$s$^{-1}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H + e$^-$ $\rightarrow$ H$^+$ + 2e$^-$</td>
<td>$^{from}$cross section</td>
<td>[96]</td>
</tr>
<tr>
<td>2</td>
<td>H$_2$ + e$^-$ $\rightarrow$ H$_2^+$ + 2e$^-$</td>
<td>$^{from}$cross section</td>
<td>[96]</td>
</tr>
<tr>
<td>3</td>
<td>N + e$^-$ $\rightarrow$ N$^+$ + 2e$^-$</td>
<td>$^{from}$cross section</td>
<td>[97]</td>
</tr>
<tr>
<td>4</td>
<td>N$_2$ + e$^-$ $\rightarrow$ N$_2^+$ + 2e$^-$</td>
<td>$^{from}$cross section</td>
<td>[97]</td>
</tr>
<tr>
<td>5</td>
<td>N$_2^+$($A^3\Sigma$) + e$^-$ $\rightarrow$ N$_2^+$ + 2e$^-$</td>
<td>$^{from}$cross section</td>
<td>[98]</td>
</tr>
<tr>
<td>6</td>
<td>N$_2^+$($A^3\Sigma$) + e$^-$ $\rightarrow$ N$_2^+$ + 2e$^-$</td>
<td>$^{from}$cross section</td>
<td>[57]</td>
</tr>
<tr>
<td>7</td>
<td>N$_2$ + e$^-$ $\rightarrow$ N$^+$ + N + 2e$^-$</td>
<td>$^{from}$cross section</td>
<td>[99]</td>
</tr>
<tr>
<td>8</td>
<td>H$_2$ + e$^-$ $\rightarrow$ H$^+$ + H + 2e$^-$</td>
<td>$^{from}$cross section</td>
<td>[100]</td>
</tr>
<tr>
<td>9</td>
<td>H$_2$ + e$^-$ $\rightarrow$ H$_2$ (v=4) + e$^-$</td>
<td>$^{from}$cross section</td>
<td>[66]</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>$^{Reference}$</th>
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References:


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</thead>
<tbody>
<tr>
<td>10</td>
<td>$NH + e^- \rightarrow NH^+ + 2e^-$</td>
</tr>
<tr>
<td>11</td>
<td>$NH + e^- \rightarrow N^+ + H + 2e^-$</td>
</tr>
<tr>
<td>12</td>
<td>$NH_2 + e^- \rightarrow NH_2^+ + 2e^-$</td>
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<tr>
<td>13</td>
<td>$NH_3 + e^- \rightarrow NH_3^+ + H + 2e^-$</td>
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<tr>
<td>14</td>
<td>$NH_4^+ + e^- \rightarrow NH_4^+ + 2e^-$</td>
</tr>
<tr>
<td>15</td>
<td>$NH_2 + e^- \rightarrow NH_2^+ + H + 2e^-$</td>
</tr>
<tr>
<td>16</td>
<td>$NH_3 + e^- \rightarrow NH_3^+ + H + H + 2e^-$</td>
</tr>
<tr>
<td>17</td>
<td>$NH_4^+ + e^- \rightarrow N^+ + H + H + 2e^-$</td>
</tr>
<tr>
<td>18</td>
<td>$NH_2 + e^- \rightarrow H^+ + NH + 2e^-$</td>
</tr>
<tr>
<td>19</td>
<td>$H_2^0 + e^- \rightarrow H + H + 2e^-$</td>
</tr>
<tr>
<td>20</td>
<td>$H^+_2 + e^- \rightarrow H_2^0 + e^-$</td>
</tr>
<tr>
<td>21</td>
<td>$H^+_3 + e^- \rightarrow H + H + H + e^-$</td>
</tr>
<tr>
<td>22</td>
<td>$N_2^+ + e^- \rightarrow N + N + e^-$</td>
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<tr>
<td>23</td>
<td>$NH^+ + e^- \rightarrow H + H + e^-$</td>
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<tr>
<td>24</td>
<td>$NH_2^+ + e^- \rightarrow NH + H + e^-$</td>
</tr>
<tr>
<td>25</td>
<td>$NH_3^+ + e^- \rightarrow NH_3 + H + e^-$</td>
</tr>
<tr>
<td>26</td>
<td>$NH_4^+ + e^- \rightarrow NH_4^0 + e^-$</td>
</tr>
<tr>
<td>27</td>
<td>$NH_3 + H \rightarrow NH_2 + H_2$</td>
</tr>
<tr>
<td>28</td>
<td>$NH_4^+ + H \rightarrow NH_3 + H$</td>
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<tr>
<td>29</td>
<td>$NH + H \rightarrow NH + H + e^-$</td>
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<tr>
<td>30</td>
<td>$N_2H^+ + e^- \rightarrow N_2 + H + e^-$</td>
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<tr>
<td>31</td>
<td>$N_2H^+ + e^- \rightarrow NH + H + e^-$</td>
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<tr>
<td>32</td>
<td>$N_2 + e^- \rightarrow N + N + e^-$</td>
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<tr>
<td>33</td>
<td>$H_2^0 + e^- \rightarrow H + H + e^-$</td>
</tr>
<tr>
<td>34</td>
<td>$NH + e^- \rightarrow N + H + e^-$</td>
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<td>35</td>
<td>$NH_2 + e^- \rightarrow NH_2 + e^-$</td>
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<td>36</td>
<td>$NH_3 + e^- \rightarrow NH_3 + H + e^-$</td>
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<tr>
<td>37</td>
<td>$NH_4^+ + e^- \rightarrow NH_4^0 + e^-$</td>
</tr>
<tr>
<td>38</td>
<td>$NH_3 + e^- \rightarrow NH_2 + H + e^-$</td>
</tr>
<tr>
<td>39</td>
<td>$NH_4^+ + e^- \rightarrow NH_3 + H + e^-$</td>
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<td>40</td>
<td>$NH_2 + e^- \rightarrow NH_2 + 2H$</td>
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<td>41</td>
<td>$NH_3 + e^- \rightarrow NH_2 + H + e^-$</td>
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<td>42</td>
<td>$NH_4^+ + e^- \rightarrow NH_3 + H$</td>
</tr>
<tr>
<td>43</td>
<td>$NH_2 + e^- \rightarrow NH_2 + 2H$</td>
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<tr>
<td>44</td>
<td>$NH_3 + e^- \rightarrow NH_2 + H + e^-$</td>
</tr>
<tr>
<td>45</td>
<td>$NH_4^+ + e^- \rightarrow NH_3 + H$</td>
</tr>
<tr>
<td>46</td>
<td>$NH_2 + e^- \rightarrow NH_2 + H + e^-$</td>
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<tr>
<td>47</td>
<td>$NH_3 + e^- \rightarrow NH_2 + H + e^-$</td>
</tr>
<tr>
<td>48</td>
<td>$NH_4^+ + e^- \rightarrow NH_3 + H + e^-$</td>
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<td>49</td>
<td>$NH_2 + e^- \rightarrow NH_2 + 2H$</td>
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<td>$NH_2 + e^- \rightarrow NH_2 + H + e^-$</td>
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<td>56</td>
<td>$NH_3 + e^- \rightarrow NH_2 + H + e^-$</td>
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<td>57</td>
<td>$NH_4^+ + e^- \rightarrow NH_3 + H$</td>
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<td>$NH_2 + e^- \rightarrow NH_2 + H + e^-$</td>
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<td>59</td>
<td>$NH_3 + e^- \rightarrow NH_2 + H + e^-$</td>
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<td>$NH_4^+ + e^- \rightarrow NH_3 + H + e^-$</td>
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<td>$NH_3 + e^- \rightarrow NH_2 + H + e^-$</td>
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<td>$NH_4^+ + e^- \rightarrow NH_3 + H$</td>
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<tr>
<td>64</td>
<td>$NH_2 + e^- \rightarrow NH_2 + H + e^-$</td>
</tr>
<tr>
<td>65</td>
<td>$NH_3 + e^- \rightarrow NH_2 + H + e^-$</td>
</tr>
<tr>
<td>66</td>
<td>$NH_4^+ + e^- \rightarrow NH_3 + H$</td>
</tr>
<tr>
<td>67</td>
<td>$NH_2 + e^- \rightarrow NH_2 + H + e^-$</td>
</tr>
</tbody>
</table>

*Notes:*

- $T_{\text{eq}}$ is the equilibrium temperature.
- $T_{\text{eq}}$ is taken as $300$ K for most reactions.
- Values in parentheses are computed from Table 9.
- Values in italics are computed from Table 10.

Values for $T_{\text{eq}}$ are:

- $T_{\text{eq}} = 300$ K (unless otherwise specified).

**References:**

- [10] 
- [11] 
- [12] 
- [13] 
- [14] 
- [15] 
- [16] 
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- [49] 
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- [52] 
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- [54] 
- [55] 
- [56] 
- [57] 
- [58] 
- [59] 
- [60] 
- [61] 
- [62] 
- [63] 
- [64] 
- [65] 
- [66] 
- [67]
Table 2. Plasma chemical reactions included in the model

<table>
<thead>
<tr>
<th>Reaction</th>
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<tbody>
<tr>
<td>$H_2^+ + N \rightarrow N^+ + H_2$</td>
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<tr>
<td>$H_2^+ + NH \rightarrow NH^+ + H_2$</td>
</tr>
<tr>
<td>$H_2^+ + NH_2 \rightarrow NH_2^+ + H_2$</td>
</tr>
<tr>
<td>$H_2^+ + NH \rightarrow NH_2^+ + H$</td>
</tr>
<tr>
<td>$H_2^+ + N \rightarrow NH^+ + H_2$</td>
</tr>
<tr>
<td>$H_2^+ + NH_3 \rightarrow NH_2^+ + H$</td>
</tr>
<tr>
<td>$H_2^+ + H_2 \rightarrow H_2^+ + H$</td>
</tr>
<tr>
<td>$H_2^+ + N \rightarrow NH^+ + H_2$</td>
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<tr>
<td>$H_2^+ + N \rightarrow NH^+ + H$</td>
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<td>$H_2^+ + NH_3 \rightarrow NH_2^+ + H_2$</td>
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<td>$H_2^+ + N \rightarrow NH^+ + H_2$</td>
</tr>
<tr>
<td>$H_2^+ + NH \rightarrow NH_2^+ + H_2$</td>
</tr>
<tr>
<td>$H_2^+ + N_2 \rightarrow N_2H^+ + H_2$</td>
</tr>
<tr>
<td>$N_2^+(A^3\Sigma) + H \rightarrow NH + N$</td>
</tr>
<tr>
<td>$NH^+ + H_2 \rightarrow NH_2^+ + H$</td>
</tr>
<tr>
<td>$NH^+ + N \rightarrow N_2^+ + H$</td>
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<td>$NH^+ + N \rightarrow N_2^+ + H$</td>
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<td>$NH^+ + NH \rightarrow NH_2^+ + N$</td>
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<td>$NH_2^+ + NH_3 \rightarrow NH_2^+ + NH_2$</td>
</tr>
<tr>
<td>$N_2^+ + N \rightarrow N_2 + NH^+$</td>
</tr>
<tr>
<td>$H_2 + e^- \rightarrow H_2 + e^-$</td>
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<td>$H + e^- \rightarrow H + e^-$</td>
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<tr>
<td>$N_2 + e^- \rightarrow N_2 + e^-$</td>
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<tr>
<td>$N + e^- \rightarrow N + e^-$</td>
</tr>
<tr>
<td>$NH_3 + e^- \rightarrow NH_3 + e^-$</td>
</tr>
</tbody>
</table>

4.1.2 Definition of the environment

H₂–N₂ plasmas have been widely studied in the last few decades e.g. [123, 124]. The aim mostly concerned the role of plasma for the catalytic synthesis of NH₃. The parameters of those plasmas, though, are orders of magnitude far from the high-density plasmas ($n_e>10^{19} m^{-3}$) produced in linear machines and divertors. We are hereby interested in investigating the recombination mechanisms of H⁺ induced by the presence of nitrogen in the volume phase. Considering the values of $n_e$ and $T_e$ in a semi-detached plasma beam in linear machines, two different cases of study have been taken into account, namely in the centre and at the edges of the plasma beam. For both cases, a 5% N₂ content has been studied. In figure 1 a typical semi-detached Magnum-PSI $T_e$ and $n_e$ profile is shown, with values from ≈ 1.5 eV to ≈ 0.35 eV for $T_e$ and from ≈ 2*10¹⁰ m⁻³ to 2.5*10¹⁹ m⁻³ for $n_e$. 

43
4.1.3 Global model results: N-MAR as a new recombination path

For the simulation of the centre of the plasma beam, plasma parameters (provided as output by the code) are $T_e = 1.2$ eV and $n_e = 2.6 \times 10^{20}$ m$^{-3}$. The initial densities are $1.0 \times 10^{21}$ m$^{-3}$ for molecular hydrogen and $5.0 \times 10^{19}$ m$^{-3}$ for N$_2$. The input power density adopted was set at 2500 J/m$^3$. The most relevant H$^+$ recombination processes highlighted in in the model are reported in Figure 2.

The sinks reactions for H$^+$ highlighted by the model are ion conversion with H$_2^+$ and with NH (reactions 62 and 64), producing H$_2$ and NH$^+$. The first branch is the well-established hydrogenic MAR[125], while the second involves nitrogen monohydride and will be referred to as N-MAR. The main loss route of H$^+$ is indicated to be N-MAR with a contribution of $\approx 70\%$ for the N$_2$ content examined in this case of study. Sources for the NH molecule are via electron-impact direct dissociation of NH$_x$ species, dissociative recombination of NH$_x^+$ ions and by neutral-neutral atomic transfer.

About 85% of H$_2^+$ is lost by dissociative recombination (reaction 19) and, to a minor extent by reacting with N-species, namely $\approx 10\%$ is consumed by proton transfer with N$_2$ (reaction 66) and $\approx 5\%$ by ion conversion with ammonia (reaction 65) gaining N$_2$H$^+$ and NH$_3^+$ respectively. NH$^+$ sink paths, depicted...
in figure 3, is by dissociative recombination (= 90%), and for less than 10% by atom transfer with N, producing \( \text{N}_2^+ \) and H (reaction 83).

\[
\text{NH}^+ \xrightarrow{\text{Atom transfer}} \text{N}_2^+ + \text{H} \quad (10\%)
\]

\[
\text{NH}^+ \xrightarrow{\text{Dissociative recombination}} \text{N} + \text{H} \quad (90\%)
\]

Figure 3. relative contribution of NH\(^+\) sinks in the beam centre.

Ammonia and its derivate ion NH\(^+\) are not significantly produced in the volume phase. The precursors of those species are rapidly consumed by, ion conversion, dissociation and recombination mechanisms. In divertor-like experimental conditions NH\(_3\) is produced via of Eley-Rideal and Langmuir-Hinshelwood processes, involving both volume-surface and surface-surface interactions on a (cold) metal wall\([126]\). NH\(_3\) is then released in the volume phase. Assuming an influx of NH\(_3\) from the target and/or from the reactor walls towards the plasma beam, ammonia undergoes ion conversion with H\(^+\) with a contribution of 42\%, dissociation by electron impact for 25\% and via H atom transfer for the remaining 33\%. NH\(_3^+\) is calculated to be entirely consumed by two dissociative recombination producing H\(_2\) + NH and NH\(_2\) + H.

In the plasma edge \(T_e\) is about 0.8 eV and \(n_e\) is \(\sim 5 \times 10^{19} \text{m}^{-3}\). The most important reaction paths started by H\(^+\) are shown in figure 4.

Differently from the centre of the beam, where H\(^+\) undergoes two separate ion conversions, the principal sink route of H\(^+\) in this case is via ion conversion with H\(_2\)(v). H\(_2^+\) is consumed by dissociative recombination and proton transfer with N\(_2\), gaining 2 H and N\(_2^+\), with a relative contribution of 60\% and 40\% respectively. N\(_2^+\) is then consumed by dissociative recombination producing NH and N\(_3\). This additional reaction path involving N\(_2\) as proton acceptor will be referred to as another N-MAR process.

Differently from the conditions in the plasma centre, where ion conversion is promptly followed by dissociative recombination, in the milder plasma edge conditions, a further molecular-induced step occurs indicating N\(_2^+\) as ionic mediator. The reduced reaction scheme obtained from the full model is:
elastic collisions are also

The two N-MAR mechanisms, together with the most important hydrogen reactions and electron-induced processes, have been inserted in the model. Rate coefficients are the same as in the full version. Electron-induced ionization, vibrational excitation, dissociation and elastic collisions are also taken into account. For completeness, the most relevant neutral-neutral process has been implemented in the reduced version as well, namely \( H_2 + N \rightarrow NH + H \). That is in fact the most important process in such environment that relates two neutral key-species i.e. molecular hydrogen and atomic nitrogen. Such chemistry has been implemented in Eunomia. Those simulation results will be discussed in chapter 5.

### 4.1.4 Comparison between the full and the reduced global models

To verify the reliability of the reaction scheme derived from the fully extended Plasimo global model, comparisons between the full and the reduced model have been done. The aim is to implement the highlighted relevant processes in spatially-resolved codes. The chemical species implemented in the new global model, together with their steady-state densities are reported in table 4.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>( H + e^- \rightarrow H^+ + 2e^- )</td>
<td>Ionization</td>
</tr>
<tr>
<td>( H_2 + e^- \rightarrow H^+_2 + 2e^- )</td>
<td>Ionization</td>
</tr>
<tr>
<td>( N_2 + e^- \rightarrow N + N + e^- )</td>
<td>Dissociation</td>
</tr>
<tr>
<td>( H_2 + e^- \rightarrow H_2v + e^- )</td>
<td>Vibrational excitation</td>
</tr>
<tr>
<td>( H^+_2 + e^- \rightarrow H + H )</td>
<td>Dissociative recombination</td>
</tr>
<tr>
<td>( H_2 + N \rightarrow NH + H )</td>
<td>Atom transfer</td>
</tr>
<tr>
<td>( N_2H^+ + e^- \rightarrow N_2 + H )</td>
<td>Dissociative recombination</td>
</tr>
<tr>
<td>( NH + H^+ \rightarrow NH^+ + H )</td>
<td>Ion conversion</td>
</tr>
<tr>
<td>( NH^+ + e^- \rightarrow NH + N )</td>
<td>Dissociative recombination</td>
</tr>
<tr>
<td>( H + e^- \rightarrow H + e^- )</td>
<td>Elastic</td>
</tr>
<tr>
<td>( H_2 + e^- \rightarrow H_2 + e^- )</td>
<td>Elastic</td>
</tr>
<tr>
<td>( N + e^- \rightarrow N + e^- )</td>
<td>Elastic</td>
</tr>
<tr>
<td>( N_2 + e^- \rightarrow N_2 + e^- )</td>
<td>Elastic</td>
</tr>
</tbody>
</table>

| Table 3. Reduced reaction scheme obtained |

The initial densities have been kept the same in both cases of study i.e. \( 1*10^{21}\text{m}^{-3} \) for \( H_2 \) and \( 5*10^{19}\text{m}^{-3} \) for \( N_2 \). The achieved \( T_e \) is 1.2 eV in the full model and 1.16 eV in the reduced one. The electron densities gained in the simulations are almost identical, which is a strict requirement in order to deal with the same plasma environment. To compensate the absence of the main NH sources i.e. electron-impact dissociation of NH, species and dissociative recombination of their ionic derivatives, an extra source of NH has been added together with an identical sink of N and H \( (8*10^{20}\text{m}^{-3}\text{s}^{-1}) \); in this way, the system is closed and the particle balance is conserved. The total amount of NH particles added in the simulation corresponds to 7% conversion of nitrogen to ammonia, which is in line with literature studies [89, 127], [128].
The obtained densities are shown in *figure 5*. The densities of the hydrogenic species are in very good agreement. This confirms the importance of the reactions producing H, which are the ion conversion of H⁺ with H₂(v=4) and with NH, and the dissociative recombination of H₂⁺ and NH⁺.

H⁺ is the main ionic species in the system and is consumed via ion conversions. According to the models, N₂ sinks are electron-induced dissociation and proton transfer with H₂⁺, the latter being highlighted as second branch of the N-MAR processes. N main sources are via *reaction 51* and *reaction 23*, which is the final step of the first N-MAR path.

The final densities of NH are in good agreement. The difference is due to the absence in the reduced version of the electronically excited species N₂(A^3Σ⁺) and its efficient atomic transfer with H (*reaction 81*), which acts as a source for NH. Such discrepancy suggests the small importance of other NH sink mechanisms among the plasma parameters examined here. In both extended and reduced models, the main source of NH⁺ is the ion conversion between NH and H⁺. N₂H⁺, pointed out to be an important ion mediator in N-MAR(2), is verified to be produced via proton transfer and consumed by dissociative recombination i.e. *reaction 30* and 31.

To benchmark the reduced model among a wider range of plasma parameters, a comparison between the extended and the reduced model has been carried out for other two different scenarios i.e. beam-edge conditions with \( T_e = 0.8 \text{ eV} \) and \( n_e = 6 \times 10^{19} \text{m}^{-3} \) (*figure 5b*) and a high-density higher-temperature case with \( n_e = 3.4 \times 10^{20} \text{m}^{-3} \) and \( T_e = 1.8 \text{ eV} \) (*figure 5c*). Results are shown in *figure 5*. The densities of the underlined relevant species are again in very good agreement. We hereby prove the validity of the reduced set of chemical equations for parameters \( 5 \times 10^{19} < n_e < 3.5 \times 10^{20} \text{m}^{-3} \) and \( 0.8 < T_e < 2 \text{ eV} \). For scenarios with \( n_e < 10^{19} \text{m}^{-3} \), a different reduced set of reactions would be needed. In such plasma environment, in fact, molecular ions become the major ion species, being proton transfer the dominant ion-neutral inelastic mechanism. Insights on the most important plasma chemistry regarding such environment is discussed in the next section.
The most effective relations, named N-MAR and stated in figure 2 and 4, have been confirmed to be the most relevant. The balance between the different species densities set by the chemical equations and validated here, has to be considered true only for divertor-relevant (high-density low-temperature) hydrogen plasma in the presence of nitrogen.

4.1.5 H\textsubscript{2}/N\textsubscript{2} plasma chemistry for different plasma parameters

To investigate a wider range of plasma scenarios i.e. less ITER-relevant but yet interesting in a perspective of complex plasma chemistry in, for instance, several linear devices, an electron density scan has been carried out for values from 6.8\times10^{17} \text{ m}^{-3} to 1.2\times10^{19} \text{ m}^{-3}. The electron temperature is kept at 2.5 eV. Attention is given to the density evolution of molecular ions, being the charged species populating this type of relatively low-density plasmas [129]. Results are show in figure 6 and figure 7.
At high-density low-temperature plasma, NH\textsubscript{x+x} species (with 0<x<5) are predominantly produced via ion conversion with H\textsuperscript{+} and are efficiently depleted by means of dissociative recombination processes, basically N-MAR, as follows:

1) H\textsuperscript{+} + NH\textsubscript{x} \rightarrow NH\textsubscript{x+1} + H \hspace{1cm} \text{Ion conversion}
2) NH\textsubscript{x+1} + e\textsuperscript{-} \rightarrow NH\textsubscript{x} + H \hspace{1cm} \text{Dissociative recombination}

At lower n\textsubscript{e}, other processes become dominant and are governed by the presence of protonated molecules. At n\textsubscript{e} = 1.2*10\textsuperscript{19} m\textsuperscript{-3}, the densities of NH\textsubscript{x} species follow inversely the amount of H atoms bound to N (figure 4). In this regime, in fact, dissociative recombination de-populates first the highly hydrogenated molecular ions. A population inversion occurs when moving towards lower electron densities i.e. ~ 3*10\textsuperscript{18} m\textsuperscript{-3}, with NH\textsubscript{4} the most abundant ion. This is due to the following atomic transfer reactions:

3) NH\textsuperscript{+} + H\textsubscript{2} \rightarrow NH\textsubscript{2+} + H \hspace{1cm} \text{Reaction 82}
4) NH\textsubscript{2+} + H\textsubscript{2} \rightarrow NH\textsubscript{3+} + H \hspace{1cm} \text{Reaction 94}
5) NH\textsubscript{3+} + H\textsubscript{2} \rightarrow NH\textsubscript{4+} + H \hspace{1cm} \text{Reaction 97}

Moreover, NH\textsubscript{4} is also produced via a so-called proton transfer chain, which is initiated by H\textsubscript{3} and molecular nitrogen. This path is characterised by the following reactions:

6) H\textsubscript{3} + N\textsubscript{2} \rightarrow N\textsubscript{2}H\textsuperscript{+} + H\textsubscript{2} \hspace{1cm} \text{Reaction 80}
7) N\textsubscript{2}H\textsuperscript{+} + NH\textsubscript{3} \rightarrow NH\textsubscript{4} + N\textsubscript{2} \hspace{1cm} \text{Reaction 98}

This mechanism occurs at n\textsubscript{e} < 4*10\textsuperscript{18} m\textsuperscript{-3} (figure 5), when the density of H\textsubscript{3} and N\textsubscript{2}H\textsuperscript{+} decrease steeply and NH\textsubscript{4} increases. At density ~ 8*10\textsuperscript{17} m\textsuperscript{-3}, N\textsubscript{2}H\textsuperscript{+} and NH\textsubscript{4} are almost equally populated.

The effect of electron temperature on H\textsubscript{2}/N\textsubscript{2} plasma chemistry with densities in the order of ~ 10\textsuperscript{16} m\textsuperscript{-3} has been extensively studied in the last years [130], [131] given the importance it has in the field of plasma processing. For what concerns divertor-relevant electron densities i.e. n\textsubscript{e} > 5*10\textsuperscript{19} m\textsuperscript{-3} with electron temperatures above 3 eV, electron-induced mechanisms are expected to play a major role.

4.1.6 The role of molecular ion H\textsubscript{3}\textsuperscript{+}

About H\textsubscript{3}\textsuperscript{+} ion, there is still debate in the field of divertor plasma physics whether it has to be included or not in numerical codes. To study that, a parallel work has been done focusing on the plasma conditions where such species has to be considered relevant and where it hasn’t.
The first successful studies on the production of such ion date back to the first half of the last century[132]. \( \mathrm{H}_3^+ \) is gained by means of a proton transfer reaction:

\[ \mathrm{H}_2^+ + \mathrm{H}_2 \rightarrow \mathrm{H}_3^+ + \mathrm{H} \]

with a rate constant of \( k = 2 \times 10^{-9} \, \text{cm}^3\,\text{s}^{-1} \) [117]. This process competes with dissociative recombination of \( \mathrm{H}_2^+ \):

\[ \mathrm{H}_2^+ + e^- \rightarrow \mathrm{H} + \mathrm{H} \]. \( \mathrm{H}_3^+ \) is efficiently consumed in low temperature plasmas (\( T_e < 3-4 \, \text{eV} \)) by two dissociative recombination reactions whose rate coefficients are plotted in figure 8. The density evolution of \( \mathrm{H}_3^+ \) over time is calculated by the code as:

\[
\frac{d[\mathrm{H}_3^+]}{dt} = \left( k_{(74)} \times [\mathrm{H}_2^+] \times [\mathrm{H}_2] \right)_{\text{production}} - \left( k_{(20)} \times n_e \times [\mathrm{H}_3^+] \right)_{\text{consumption}} - \left( k_{(21)} \times n_e \times [\mathrm{H}_3^+] \right)_{\text{consumption}} \tag{4.1}
\]

It is dependent on the electron density. In the model, \( T_e \) is 1.5 eV while the electron density has been changed by tuning the input power density. The density evolution of \( \mathrm{H}^+ \) and \( \mathrm{H}_3^+ \) as a function of \( n_e \) is reported in figure 9.

A population inversion occurs at \( n_e \approx 7 \times 10^{18} \, \text{m}^{-3} \), i.e. two orders of magnitude lower than the electron density expected in ITER divertor i.e. \( 10^{20}-10^{21} \, \text{m}^{-3} \) [133]. The high electron density characterizing divertor and Magnum-PSI plasmas leads to a very efficient recombination of \( \mathrm{H}_3^+ \) and its precursor \( \mathrm{H}_2^+ \). In the SOL upstream region in tokamaks, \( T_e \approx 100 \, \text{eV} \) [73], therefore, \( \mathrm{H}_2 \) is fully dissociated and ionized, making \( \mathrm{H}^+ \) the sole hydrogenic species flowing to the divertor plate. Hence, we can deduce that the role \( \mathrm{H}_3^+ \) is negligible in Magnum-PSI and ITER-relevant divertor \( \mathrm{H}_2^+ \) plasma. Similar conclusion has been obtained in [77], where simulations of ITER-like and DIII-D-like divertor plasmas have been done. This is different from what has been observed in PISES-A[33], where \( \mathrm{H}_2^+ \) was detected in significant amount by mass spectrometry. Electron density in that study is between \( 10^{17} \) and \( 10^{18} \, \text{m}^{-3} \) [134]. Recent experiments in GAMMA10/PDX regarding the role of MAR [135], stated the possibility of \( \mathrm{H}_3^+ \) formation in those plasma conditions and with a V-shaped target (electron density around \( 1 \times 10^{17} \, \text{m}^{-3} \)). Finally, more studies would be needed to fully understand the role of \( \mathrm{H}_3^+ \) in closed divertor configurations, where the recycled incoming flux of neutral \( \mathrm{H}_2(\nu) \) from the target is enhanced, compared to more common geometries adopted in tokamaks and linear machines.

### 4.2 Global modelling of a \( \mathrm{H}_2 – \mathrm{He} \) plasma

Regarding the \( \mathrm{H}_2/\mathrm{He} \) seeding case, the reader is referred to figure 5 in chapter 3 where a negative influence on detachment led by the injection of \( \mathrm{H}_2/\mathrm{He} \) mixture compared to only \( \mathrm{H}_2 \) is reported. An increase of roughly 10\% of the heat load on the target with increasing the content of \( \mathrm{He} \) in the puffed gases was observed. Such trend is believed to be indicative of less recombination, due to dilution of molecular hydrogen. A global model of that scenario has been set up and the plasma chemical
reactions adopted are reported in Table 1. Given that the aim of this study is to understand the influence of different impurities on plasma recombination and detachment, particular attention has been given to the recombination paths of \( H^+ \) and \( H_2^+ \) in the presence of He.

In the simulations, one vibrationally excited species for molecular hydrogen, namely \( v=4 \), and one electronically excited state for atomic helium (\( \text{He}^*2^3\Sigma \)) have been included. They are important for ion conversion (reaction 7) and two-step ionization (reactions 10 and 12).

<table>
<thead>
<tr>
<th>N</th>
<th>Reaction</th>
<th>Rate ((\text{m}^3\text{s}^{-1}))</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( H_2 + e^- \rightarrow H + H + e^- )</td>
<td>from cross section</td>
<td>[100]</td>
</tr>
<tr>
<td>2</td>
<td>( H_2 + e^- \rightarrow H_2(v = 4) + e^- )</td>
<td>from cross section</td>
<td>[66]</td>
</tr>
<tr>
<td>3</td>
<td>( H_2 + e^- \rightarrow H^+ + H + 2e^- )</td>
<td>(9.4 \times 10^{-16} \times T_e^{0.45} \times \exp \left( - \frac{29.94}{T_e} \right))</td>
<td>[136]</td>
</tr>
<tr>
<td>4</td>
<td>( H + e^- \rightarrow H^+ + 2e^- )</td>
<td>from cross section</td>
<td>[137]</td>
</tr>
<tr>
<td>5</td>
<td>( H_2 + e^- \rightarrow H_2^+ + 2e^- )</td>
<td>from cross section</td>
<td>[138]</td>
</tr>
<tr>
<td>6</td>
<td>( H_2^+ + H_2 \rightarrow H_2^3 + H )</td>
<td>(2 \times 10^{-15})</td>
<td>[117]</td>
</tr>
<tr>
<td>7</td>
<td>( H_2(v = 4) + H^+ \rightarrow H_2^+ + H )</td>
<td>(2.5 \times 10^{-15})</td>
<td>[36]</td>
</tr>
<tr>
<td>8</td>
<td>( H_2^+ + e^- \rightarrow H + H )</td>
<td>(1.6 \times 10^{-14} \times T_e^{-0.43})</td>
<td>[103]</td>
</tr>
<tr>
<td>9</td>
<td>( H_2^+ + e^- \rightarrow H_2 + H )</td>
<td>(4.36 \times 10^{-14} \times T_e^{-0.52})</td>
<td>[104]</td>
</tr>
<tr>
<td>10</td>
<td>( He + e^- \rightarrow He^*(2^3S) + e^- )</td>
<td>(5.05 \times 10^{-14} \times \exp \left( - \frac{22.5}{T_e} \right))</td>
<td>[139]</td>
</tr>
<tr>
<td>11</td>
<td>( He^*(2^3S) \rightarrow He + hv )</td>
<td>(6.72 \times 10^{11})</td>
<td>[139]</td>
</tr>
<tr>
<td>12</td>
<td>( He^*(2^3S) + e^- \rightarrow He^+ + 2e^- )</td>
<td>(1.28 \times 10^{-13} \times T_e^{0.6} \times \exp \left( - \frac{4.78}{T_e} \right))</td>
<td>[139]</td>
</tr>
<tr>
<td>13</td>
<td>( He + e^- \rightarrow He^+ + 2e^- )</td>
<td>(1.5 \times 10^{-15} \times T_e^{0.68} \times \exp \left( - \frac{24.6}{T_e} \right))</td>
<td>[139]</td>
</tr>
<tr>
<td>14</td>
<td>( HeH^+ + e^- \rightarrow He + H )</td>
<td>(1.0 \times 10^{-14} \times T_e^{-0.6})</td>
<td>[103]</td>
</tr>
<tr>
<td>15</td>
<td>( H_2^+ + He \rightarrow HeH^+ + H )</td>
<td>(1.3 \times 10^{-16})</td>
<td>[117]</td>
</tr>
<tr>
<td>16</td>
<td>( He^+ + H_2 \rightarrow He + H_2^+ )</td>
<td>(1.7 \times 10^{-21})</td>
<td>[117]</td>
</tr>
<tr>
<td>17</td>
<td>( HeH^+ + H \rightarrow He + H_2^+ )</td>
<td>(9.1 \times 10^{-16})</td>
<td>[117]</td>
</tr>
<tr>
<td>18</td>
<td>( HeH^+ + H_2 \rightarrow He + H_3^+ )</td>
<td>(1.8 \times 10^{-15})</td>
<td>[117]</td>
</tr>
<tr>
<td>19</td>
<td>( He + e^- \rightarrow He + e^- )</td>
<td>from cross section</td>
<td>[57]</td>
</tr>
</tbody>
</table>

Table 5. Helium-driven plasma chemical reactions adopted in the \( \text{H}_2/\text{He} \) global model.

No mechanisms involving directly \( H^+ \) and He have been found in the literature. Nevertheless, the proton transfer reaction (reaction 15) between \( H_2^+ \) and He, followed by dissociative recombination i.e. \( \text{HeH}^+ + e^- \rightarrow \text{He} + \text{H} \) (reaction 14) constitutes a further neutralization path with \( \text{He}^+ \) as ionic mediator. Results indicate that, for electron density of \( n_e = 1 \times 10^{19} \text{ m}^{-3} \) the main molecule-driven route for \( H_2^+ \) consumption is with \( H_2 \) leading to the production of \( \text{H}_3^+ \). The proton transfer reaction with He constitutes only the 5% of the total sinks of \( \text{H}_2^+ \). With \( n_e = 1 \times 10^{20} \text{ m}^{-3} \) the main sink is entirely via dissociative recombination (reaction 8). The electron temperature for those simulations was 1.5 eV. A schematic representation of these results is presented in figure 10.
Figure 10. Global model output of H$_2^+$ sink reaction paths in a H$_2$/He plasma for two electron density scenarios. $T_e$ was 1.5 eV in both cases.

The density distribution of molecular ions in a H$_2$+He plasma calculated with the global model are plotted in figure 11 as a function of electron density, with values from $6*10^{18}$ to $1*10^{20}$ m$^{-3}$. With $n_e$ below $10^{19}$ m$^{-3}$, the dominant species is H$_3^+$, which is produced via proton transfer between H$_2^+$ and H$_2$. HeH$^+$ has a peak at $n_e \sim 2*10^{19}$ m$^{-3}$, which also corresponds to the point where H$^+$ becomes as populated as H$_3^+$. When moving towards higher $n_e$, dissociative recombination of H$_2^+$ becomes dominant, hence a depopulation of molecular ions occurs. As a result, for divertor-relevant and Magnum-PSI typical plasmas, no additional recombination effects are driven by the presence of He. Although no beneficial effects for detachment come along the presence of He, as it is shown experimentally and confirmed hereby by the global model, a spatially-resolved code is mandatory to exclude/include any further mechanism that could influence plasma parameters in a detached-like scenario, such as elastic processes leading to momentum loss and/or influences on the radial transport. These simulations will be presented in chapter 5.

Figure 11. Density of molecular ions as a function of $n_e$ calculated with PLASIMO. No significant density is achieved in the case of HeH$^+$ for divertor and Magnum-PSI-relevant electron densities.
### 4.3 Global modelling of a H$_2$–Ar plasma

Similarly to H$_2$/He seeding, argon shows a negative impact on plasma detachment in terms of both plasma pressure and heat load increase (figure 4 and 5 in chapter 3), while increasing the content of the noble gas in the injected mixture with H$_2$. The power load increases by ≈ 10% between the 0% Ar and the 20% Ar. This phenomenon is, again, appointed to be again due to dilution of hydrogen molecule, reflecting in less volume recombination of the plasma. In order to closely look into volume processes occurring in a hydrogen plasma with H$_2$/Ar seeding, another global plasma model has been created. An electronically-excited state of Ar, i.e. Ar$^*_{4p}$, has been added being an important intermediate state for multi-step ionization. Reactions are reported in table 6.

<table>
<thead>
<tr>
<th>N</th>
<th>Reaction</th>
<th>Rate (m$^{-3}$s$^{-1}$)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H$_2$ + e$^-$ → H + H + e$^-$</td>
<td>from cross section</td>
<td>[100]</td>
</tr>
<tr>
<td>2</td>
<td>H$_2$ + e$^-$ → H$_2$(v = 4) + e$^-$</td>
<td>from cross section</td>
<td>[66]</td>
</tr>
<tr>
<td>3</td>
<td>H$_2$ + e$^-$ → H$^+$ + H + 2e$^-$</td>
<td>9.4 x 10$^{-16}$ x T$^{-0.45}_e$ x exp(−29.94/T$_e$)</td>
<td>[136]</td>
</tr>
<tr>
<td>4</td>
<td>H + e$^-$ → H$^+$ + 2e$^-$</td>
<td>from cross section</td>
<td>[137]</td>
</tr>
<tr>
<td>5</td>
<td>H$_2$ + e$^-$ → H$_2$ + 2e$^-$</td>
<td>from cross section</td>
<td>[138]</td>
</tr>
<tr>
<td>6</td>
<td>H$_3^+$ + H$_2$ → H$_2$ + H$^+$</td>
<td>2 x 10$^{-15}$</td>
<td>[117]</td>
</tr>
<tr>
<td>7</td>
<td>H$_2$ + H$_2$ → H$_2$ + H</td>
<td>2.5 x 10$^{-15}$</td>
<td>[121]</td>
</tr>
<tr>
<td>8</td>
<td>H$_3^+$ + e$^-$ → H + H</td>
<td>1.6 x 10$^{-14}$ x T$^{-0.43}_e$</td>
<td>[103]</td>
</tr>
<tr>
<td>9</td>
<td>H$_3$ + e$^-$ → H$_2$ + H</td>
<td>4.36 x 10$^{-14}$ x T$^{-0.52}_e$</td>
<td>[104]</td>
</tr>
<tr>
<td>10</td>
<td>Ar + e$^-$ → Ar$^+$ + 2e$^-$</td>
<td>2.39 x 10$^{-14}$ x T$^{-0.57}_e$ x exp(−17.43/T$_e$)</td>
<td>[140]</td>
</tr>
<tr>
<td>11</td>
<td>Ar$^*$(4p) + e$^-$ → Ar$^+$ + 2e$^-$</td>
<td>1.23 x 10$^{-12}$ x T$^{-0.25}_e$ x exp(−3.71/T$_e$)</td>
<td>[140]</td>
</tr>
<tr>
<td>12</td>
<td>Ar$^+$ + H$_2$ → Ar + H$_2$</td>
<td>2 x 10$^{-17}$</td>
<td>[117]</td>
</tr>
<tr>
<td>13</td>
<td>Ar$^+$ + H$_2$ → ArH$^+$ + H</td>
<td>6.7 x 10$^{-16}$</td>
<td>[117]</td>
</tr>
<tr>
<td>14</td>
<td>Ar + H$_3^+$ → ArH$^+$ + H$_2$</td>
<td>3.7 x 10$^{-16}$</td>
<td>[117]</td>
</tr>
<tr>
<td>15</td>
<td>Ar + H$_2$ → Ar$^+$ + H</td>
<td>2 x 10$^{-16}$</td>
<td>[117]</td>
</tr>
<tr>
<td>16</td>
<td>Ar + H$_2$ → ArH$^+$ + H</td>
<td>2.1 x 10$^{-15}$</td>
<td>[117]</td>
</tr>
<tr>
<td>17</td>
<td>ArH$^+$ + H$_2$ → H$_3$ + Ar</td>
<td>6.3 x 10$^{-16}$</td>
<td>[117]</td>
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<tr>
<td>18</td>
<td>ArH$^+$ + e$^-$ → Ar + H</td>
<td>1 x 10$^{-15}$</td>
<td>[141]</td>
</tr>
<tr>
<td>19</td>
<td>Ar + e$^-$ → Ar + e$^-$</td>
<td>from cross section</td>
<td>[57]</td>
</tr>
</tbody>
</table>

Table 6. Argon-driven plasma chemical reactions adopted in the H$_2$/Ar global model. Hydrogenic reactions adopted are the ones listed in Table 1.

Concerning H$_3^+$, for low $n_e$, proton transfer with H$_2$ and with Ar are the main sinks and account for 85% and 15% respectively, producing H$_3$ and ArH$^+$. For Magnum-PSI-relevant plasma conditions, where $n_e$ is in the order of 1.5 x 10$^{20}$m$^{-3}$, H$_3^+$ is consumed almost entirely by dissociative recombination, while proton transfer (reaction 16) constitutes only 5% of the total sink processes. For electron densities around 10$^{19}$m$^{-3}$, the sources for H$_3^+$ are proton transfer reactions i.e. reaction 6 and 17. The contributions are about 80% and 20% respectively. Above such density threshold, H$_3^+$ is barely produced due to the very efficient dissociative recombination of its precursor H$_2^+$, as it was showed in section 4.1.6. The main sink for H$_3^+$ is dissociative recombination in both cases. The electron temperature in the simulations is set at 1.5 eV. Argon appears to have a similar behaviour as helium, in this experimental conditions. A visual representation of these plasma chemical paths is reported in figure 12.
Figure 12. Global model output of H$_2^+$ sink reaction paths in a H$_2$/Ar plasma for two electron density scenarios. $T_e$ was 1.5 eV in both cases.

4.4 Conclusions

It has been shown that no ion-recombination paths appear to be relevant in the presence of either Ar and He (injected together with H$_2$), among the parameters range considered in this study. In the case of N$_2$, however, the outcome is different. In fact, N-H induced volume-recombination processes seem to play a crucial role in divertor-relevant detached-like hydrogen plasma. Such insights are in-line with what has been observed experimentally and presented in the previous chapter. To further investigate these findings, Eunomia standalone and B2.5-Eunomia simulations have been carried out, aiming to provide insights into the effect of different impurities on detached-like divertor plasmas and ITER-relevant linear machines.
Chapter 5
Spatially-resolved simulations of a detached-like plasma in the presence of different impurities.

5.1 Numerical simulations for divertor-relevant plasma physical-chemistry
Extrapolating experimental results from linear plasma machines in order to make one-to-one comparison with real divertors would be misleading: they are two substantially different systems. In fact, in a tokamak the electron temperature at the midplane separatrix is around 100 eV, while can go below 1 eV in highly-detached conditions. It is evident that linear machines cannot fully reproduce such scenario, which is typical of the SOL. Moreover, the ion source in a divertor is mostly concentrated in the recycling-region which is located between the X-point and the divertor target plate. Ionization of recycled neutrals occurs due to power coming from upstream via conduction. In Magnum-PSI (and most of the state-of-the-art plasma machines) the the plasma source is decoupled from what occurs in the target chamber, providing a constant plasma influx. Therefore, it simulates the divertor region between the ionization front and the target. Edge-transport code, though, can provide a valuable tool in order to perform code-experiment benchmarking i.e. reproducing trends observed experimentally [142][143][38]. In such way, missing physics and chemistry can be highlighted and, eventually, improved. Another important feature of transport codes used in linear machines is that they can give insights into processes responsible for phenomena observed experimentally i.e. doing the book keeping between different mechanisms: in our case, for instance, on the effect of additional volumetric plasma chemistry on plasma properties. What has been previously shown among the experiments exposed in chapter 3 and the theory developed in chapter 4 i.e. the beneficial effects on detachment led by N2, is now being studied exploiting Monte Carlo code Eunomia. A dedicated study regarding the other two impurities as well i.e. He and Ar has been carried out using Eunomia coupled with the fluid code B2.5, as explained in chapter 2. The scope is to verify the reproducibility of the observed experimental behaviours with a newly-implemented code suit and not to pursue quantitative comparisons between experiments and simulations. Moreover, particular attention is paid on the role of different impurities in the plasma volume.

5.2 Simulating N2 seeding in detached-like conditions in linear plasma machines with Eunomia code
Eunomia runs for H2+N2 seeding have been carried out by using the parameters characterizing a typical semi-detached H2 plasma in Magnum-PSI with $T_e = 1.5$ eV and $n_e = 2.5\times10^{20}m^{-3}$ as peak values. These parameters have a full-width half-maximum (FWHM) of 20 mm and are constant along the beam. The profile is Gaussian. May be worth underlining that in Eunomia standalone a static plasma background is used. In detached scenarios, neutrals play a major role in cooling down the plasma by means of electron-neutral and ion-neutral collisions, and by increasing the molecular-driven recombination frequency[144]. H2+N2 seeding has been modelled and, for these cases of study, the puffing location has been set at the target. The most relevant N-species acting as electron donor highlighted by the global model analysis is NH radical. As was shown in chapter 4, the precursor of such species is by far ammonia. NH3 is almost entirely produced by means of surface processes. Modelling of those wall-induced mechanisms is beyond the scope of this thesis, which is strictly focused on volume processes. NH3 acts as a source for NH through electron impact dissociation processes i.e. $NH_3 + e^- \rightarrow NH + H + H + e^-$ and $NH_3 + e^- \rightarrow NH + H_2 + e^-$. Ion conversion of ammonia ($H^+ + NH_3 \rightarrow NH_3^+ + H$) is very efficient in this plasma environment, with $k_61 = 1.33\times10^9$ cm$^3$s$^{-1}$ for a gas temperature of 0.2 eV. NH$_3^+$ dissociatively recombines efficiently leading NH and 2H. A further source of NH is the amino radical NH$_2$. This species contributes to the production of NH via electron-impact dissociation. Its ion
derivative i.e. \( \text{NH}_2^+ \) contributes again to the production of \( \text{NH} \) via dissociative recombination. To take these processes into account in Eunomia runs while avoiding the inclusion of a too large plasma chemistry set of species and processes, a source of \( \text{NH} \) from the target has been added, corresponding to 5% of the total nitrogen injected. Such value is in-line with nitrogen conversion to ammonia reported in various experiments in both tomakas[127],[89] and linear machines[145]. The volume sources of \( \text{NH} \) included in Eunomia are atom transfer and dissociative recombination of \( \text{N}_2\text{H}^+ \), as can be recalled in table 3 in chapter 4. To provide the full picture of the highlighted volume mechanisms and how they compare with the hydrogenic MAR, the rate coefficients are plotted as a function of electron temperature in figure 1, with \( n_e = 1 \times 10^{20}\text{m}^{-3} \).

When looking at the reaction rate of hydrogen MAR compared to N-MAR, one can promptly see that \( \text{N}_2 \)-related process are more effective than the only-\( \text{H}_2 \) mechanisms. It appears to be clear that nitrogen-related species play a role in the conversion of ions to neutrals. This is also in accordance with the high proton affinity of \( \text{NH}_3 \) i.e. 854 kJ/mol [146].

In Eunomia, the gas temperature is provided as an output, and is calculated to be 0.21 eV. Such molecular temperature is considered to be due to the efficient ion-neutral elastic collision which acts as heating mechanism for heavy particles. Atomic and molecular nitrogen temperatures are in the same range i.e. between 0.15 and 0.24 eV. The temperature of atomic hydrogen given by the code goes up to \( \sim 0.45 \) eV. We address this to be caused by the resonant charge exchange process i.e. \( \text{H}^+ + \text{H} \rightarrow \text{H}^+ + \text{H} \), a well-known cooling mechanism for hydrogen ion[147].

In figure 2 the density distribution of \( \text{NH} \) for a 5% nitrogen seeding case is showed. Such species decreases moving away from the target along the plasma beam due to the effective N-MAR. Elastic collisions of \( \text{NH} \) with \( \text{N}_2 \) and \( \text{H}_2 \) may also play a role enhancing the perpendicular diffusion of the species in respect to the plasma beam. The density increases outside the beam, where the concentrations of \( \text{H}_2 \) and \( \text{N} \) are high, leading an efficient atom transfer process.

In figure 3 the spatially-resolved collision frequency of the first N-MAR is shown. The test-particle collisional events are peaked in the centre of the beam in the vicinity of the plate. This is in line with the density distribution of figure 2, given that in such region \( \text{NH} \) is efficiently consumed via N-MAR.

Figure 1. Reaction rates of the most important molecule-driven processes in a detached hydrogen plasma with nitrogen seeding. Solid lines correspond to ion conversion (IC), dotted are dissociation (DISS), dashed are dissociative recombination(DR) and dot-dashed is the hydrogenic MAR. The reaction rate of ion conversion of \( \text{H}^+ \) with \( \text{NH}_x \) molecules is higher than the hydrogenic MAR.
Such mechanism is addressed to further contribute to the conversion of incoming atomic hydrogen ions to neutrals, reducing the incoming flux towards the target.

To quantify the influence of the N-MAR process on the overall recombination efficiency, four different cases of studies, characterized by different puffing scenarios at a background neutral pressure of 2 Pa, have been set up as follows:

\[
\frac{[N_2]}{[H_2] + [N_2]} = 0, 5, 10, 20 \%
\]

While keeping fixed the amount of molecules injected in the system from the target i.e. \(2.1 \times 10^{20} \text{ m}^{-3} \text{s}^{-1}\), four different nitrogen contents have been examined. The aim is to compare the recombination efficiency by tracing the density of atomic hydrogen, which is eventually the end product of any recombination process in this specific high-density low-temperature H\(_2\) plasma environment. MARs and N-MARs convert ion-electron pairs to neutral atoms, yielding an increased production of H and consuming electrons. Radial profiles from the model results are taken at 3 cm in front of the target and are shown in figure 4.
The density of H increases from \( \approx 1 \times 10^{19} \text{m}^{-3} \) to \( \approx 3.5 \times 10^{19} \text{m}^{-3} \) between the 0% and 20% \( \text{N}_2 \) seeding scenarios, respectively. Both those parameters have a Gaussian profile. The only difference between the 0% \( \text{N}_2 \) case and the ones with \( \text{N}_2 \) is the addition of new plasma chemical reactions paths extracted from the full global model and explained in chapter 4 i.e. elastic collisions between \( \text{N}_2, \text{H}_2 \) and related species, the above-mentioned N-MAR and the proton transfer from \( \text{H}_2^+ \) and \( \text{N}_2 \), yielding \( \text{N}_2\text{H}^+ \) and followed by dissociative recombination i.e. N-MAR(2), as follows:

\[
\text{H}_2^+ + \text{N}_2 \rightarrow \text{N}_2\text{H}^+ + \text{H} \quad \text{Proton transfer}
\]

\[
\text{N}_2\text{H}^+ + e^- \rightarrow \text{NH} + \text{N} \quad \text{Dissociative recombination}
\]

\[
\rightarrow \text{N}_2 + \text{H} \quad \text{Dissociative recombination}
\]

This process is found by numerical simulations to be relevant from the edges of the plasma beam outwards, where \( n_e \) goes below \( \approx 5 \times 10^{19} \text{m}^{-3} \) and the \( \text{H}_2^+ \) sink mechanism producing \( \text{N}_2\text{H}^+ \) is favorable compared to the dissociative recombination (DR) channel, according to the relation:

\[
\frac{d[H^+_2]}{dt} = (k_{IC} \ast [H^+] \ast [H_2v])_{source} - (n_e \ast [H^+_2] \ast k_{DR})_{sink} - (([N_2] \ast [H^+_2] \ast k_{N-MAR(2)})_{sink} (5.1)
\]

With \( k_{IC} \), \( k_{DR} \) and \( k_{N-MAR(2)} \) being the rate coefficients for ion conversion, dissociative recombination of \( \text{H}_2^+ \) and N-MAR(2). Moving radially towards the centre of the beam, electron density increases, hence \( \text{H}_2^+ \) is predominantly lost via DR. These processes, in particular N-MAR(1), seem to further contribute to enhance the recombination efficiency in respect to only-\( \text{H}_2 \) seeding. Such influence is due to the role played by \( \text{NH}_x \) molecules and \( \text{NH} \) radical, being the final product of IC-DR cycles of \( \text{NH}_x \) with \( 1 < x \leq 3 \). It is important to state here that for plasma scenarios where the electron density goes below \( 10^{18} \text{m}^{-3} \), other molecular ions such as \( \text{NH}_4^+ \) and related processes, should be included in the simulation. To further investigate the role of N-MAR in Magnum-relevant parameters range, Eunomia simulations have been carried out with and without N-MAR. The content of seeded \( \text{N}_2 \) together with the plasma parameters, have been kept identical in both cases. The obtained radial H density profiles are shown in figure 5.
The density of H with N-MAR is calculated to be higher by a factor - 2.5, showing the importance of such process on the neutralization of H\(^+\) in the volume phase. This further indicates that the presence of N\(_2\) and, subsequently of NH, contributes to further enhance recombination processes in the centre of the beam via N-MAR(1) mechanisms.

Although no direct evidence on the contribution of N\(_2\)H\(^+\) increasing recombination frequency can be directly provided with this code, its importance is not to be considered only of a phenomenological nature. In fact, N\(_2\)H\(^+\) acts as source for NH, which has been proved to constitute the most important N-related species in the conversion of ions to neutrals. Further studies on the reaction paths leading to N\(_2\)H\(^\), moreover, can contribute to the overall comprehension of the plasma chemical effects caused by the presence of nitrogen in a low-temperature hydrogen plasma.

Although the limitations posed by the absence of plasma simulations i.e. with a fixed plasma background, the above-mentioned exercise provides further insights into the effect of N\(_2\) seeding in detached-like plasmas in linear machines. In particular, the spatially-resolved collision frequency over the entire volume, the density distribution of NH and the yield of H with and without N-MAR, are all clear indicators that what has been previously observed experimentally may be qualitatively explained by means of newly-addressed plasma chemical reaction paths. Simulations of Eunomia coupled with the fluid code B2.5 are presented in the next section, concerning N\(_2\), He and Ar seeding.
5.3 B.2.5-Eunomia simulations of plasma detachment in Magnum-PSI with different impurities

The baseline scenario, i.e. attached plasma conditions, have been set up without any external neutral source (gas puffing) and the achieved background neutral pressure in the target chamber corresponds to ≈ 0.3 Pa. As can be seen in figure 6(a), the plasma beam is conserved throughout its whole path in the target chamber. In particular, we can observe a peak in the electron density in the vicinity of the target. This is due to ion recycling at the wall, which leads to desorption of neutrals that are promptly ionized. In attached plasma conditions, the plasma environment near the wall is in the so-called high recycling regime. Similar findings have been described in [84], where simulations with SOLEDGE2D-EIRENE[40] suite have been carried out for linear plasma device Pilot-PSI.

Figure 6. Comparison between attached (a) and detached (b) plasma scenarios. On the left, the highlighted region (in blue) corresponds to the volume between the skimmer and the target. The red circle is the puffing location in the simulations. Plot (c) shows the radial electron density, taken at 3 cm in front of the target, for both the attached and detached cases.

In figure 6(b), a detached plasma scenario has been obtained by actively puffing H$_2$ in the target chamber. The background neutral pressure resulting is ≈ 2 Pa. The seeding location is depicted by the red circle in figure 6. The “gaseous chamber” concept, which has been experimentally studied by means of several linear machines as described in [33], has been successfully replicated in this simulation. As can be observed, $n_e$ quickly drops once the beam enters the target chamber, passing from ≈ 5E19 m$^{-3}$ to ≈ 1E19 m$^{-3}$. Figure 6(c) shows the radial profile of electron density taken at 3 cm in front of the target. The notable difference indicates higher recombination taking place in the detached case. Similarly to what has been observed experimentally, recombination acts as electron sink and, therefore, less ion eventually reach the surface of the target. A characteristic feature of detachment, compared to attached case, is the plasma pressure drop led by momentum loss and volume recombination processes.

Dedicated code-experiments have been carried out in order to study the influence of different impurities on plasma parameters. In principle, we replicated the experiments presented in chapter 3. The novelty of this exercise lays in the fact that new plasma chemical processes have been included in a kinetic-fluid coupled code. The aim is to highlight possible different volume-driven effects on plasma detachment. In particular, the role of reactive N$_2$-related NH radical and N-MARs is of great interest, given that NH$_x$ molecules are surely produced in the divertor. The particle source for NH has been set
assuming a conversion efficiency of nitrogen to ammonia (molecular precursor for NH radical) of 7%, which is in line with previous studies[127][128]. While N₂ is injected in the location depicted in figure 6, the source for NH has been set at the target plate. Simulations about puffing of H₂+He and H₂+Ar have been carried out. The modelled total plasma pressure i.e. \(2k\eta_neT_e\) is calculated at 3 cm in front of the target for a 2 Pa-like neutral background pressure scenario. Results of the simulations are reported in figure 7.

![Figure 7](image)

Figure 7. Modelled total plasma pressure measured at 3 cm in front of the target for three impurity species. Similar to experimental observations, the presence of nitrogen leads to a plasma pressure drop, while helium and argon give an opposite effect i.e. deteriorating the detachment performance.

The presence of nitrogen seeding in combination with H₂ has led to a net decrease of the plasma pressure by roughly 35%. This value may be overestimated due to the fact that NH (electron donor responsible for the first step of N-MAR) is injected entirely from the surface of the target. Regarding H₂ + Ar and H₂ + He puffing scenarios, a reversed effect is achieved. In fact, plasma pressure increases by \(\approx 20\%\) in both cases, reducing the effectiveness of detachment. No significant differences are recorded between He and Ar scans, indicating that the absence of impurity-induced volume recombination processes might lead to a dilution effect of H₂ in the plasma parameters range adopted in the simulations. The heat flux, calculated at the sheath edge with no pre-sheath or sheath effects taken into account, provided the same trend. Worth to be underlined that a full description of the sheath physics is beyond the capabilities of B2.5, as it was explained in section 2.2.3 of chapter 2.

To address the contribution of N-MAR and MAR respectively in a nitrogen seeding case, the collision frequency of these recombination processes has been monitored and is shown in figure 8.

![Figure 8](image)

Figure 8. N-MAR (left) and MAR (right) collision frequency. In the vicinity of the target, N-MAR appears to be dominant compared to the hydrogenic MAR.

The N-MAR process occurs extensively in the vicinity of the target (axially) and radially along the whole beam, while it becomes negligible when moving far away from the plate at about 5 cm. The spatial distribution of such process indicates an enhanced recombination of incoming hydrogen ions before
they reach the target. N-MAR, therefore, might be responsible for the results achieved both experimentally and with the numerical codes. The main constrain in these simulations lays in the fact that the source of NH is set only at the target, while in actual experiments NH$_{10}$ molecules are formed on the surface of the vessel (in this case, the walls of the target chamber). To provide a full 2-dimensional description of the dynamics leading to N-induced plasma detachment and to accurately define the NH$_{10}$ sources, further studies concerning the gas-wall interactions would be needed.

Regarding the purely hydrogenic process, hardly any MAR events appear to be occurring in the simulation. The vibrational excited states of H$_2$, which are needed for the first ion conversion step of MAR, are simulated in the code. Nevertheless, the contribution of this two-step reaction doesn't seem relevant in the condition hereby examined. That might be due to the low $T_e$ ($< 1$eV), which is given by the code as an output. Moreover, it is worth to be underlined that the three-body recombination reaction i.e. $H^+ + e^- + e^- \rightarrow H^* + e^-$, where $H^*$ is an electronically excited state, is not implemented in the code.

These results confirm what has been observed experimentally in Magnum-PSI and GAMMA10/PDX i.e. that adding inert species in the puffed mixture does not have beneficial effects for detachment. An increase in plasma pressure leads to an enhanced particle flux, hence to a higher heat flux to the target. Although a quantitative comparison between experiments and simulations is beyond the scope of this work, the same trend is obtained when comparing Magnum-PSI experimental results with the model. In both scenarios, the addition of H$_2$ + N$_2$ leads to a synergetic effect that leads to plasma pressure reduction in front of the target.

5.4 Conclusions

In the framework of divertor simulator and linear plasma machines, spatially-resolved codes constitute an important tool to investigate the physics and the chemistry occurring during experimental campaigns. This thesis focuses on the role of the plasma chemistry led by the presence of such species and their effect on plasma recombination i.e. a key-feature to achieve plasma detachment. Eunomia, a Monte Carlo code suited for the transport of neutrals in “generic” linear plasma devices, has been implemented with the most relevant plasma chemical reactions characterising a H$_2$-N$_2$ plasma environment. To evaluate the effectiveness of ion recombination, the density of atomic hydrogen has been monitored. Worth underlining that H is the eventual product of any recombination process in a hydrogen plasma. In Eunomia standalone a static plasma background is used. Interestingly, the density of H observed in front of the target increases with increasing the content of N$_2$ in the injected gas mixture. Moreover, switching off the N-MAR process led to a lower H density, therefore indicating that less recombination is taking place.

Subsequently, Eunomia has been coupled with the fluid code B2.5. Detachment-like experiments with three different impurities i.e. N$_2$, He and Ar have been pursued, similarly to the experiments carried out in Magnum-PSI and presented in chapter 3. The total plasma pressure, calculated again at 3 cm in front of the target, qualitatively reproduces the trends observed experimentally: while N$_2$ leads to beneficial effects for the detached plasma i.e. plasma pressure further drops compared to the only-H$_2$ seeding case, both He and Ar led to an opposite trend. Plasma pressure increases while adding either of these two species in the puffed mixture.

To carry out quantitative comparison between experiments and simulations, dedicated studies on the “free parameters” currently assumed in the code e.g. cross-field transport coefficients, potential boundary and plasma flow from the source should be carried out. Moreover, the model assumes an axisymmetric environment, which is not the case in real Magnum-PSI environment.
Chapter 6
Conclusions and Outlook

In the frame of this study, dedicated experiments on plasma detachment and impurity seeding in the linear machine Magnum-PSI have been carried out. Neutral background pressure scans have been performed in the presence of different seeded gas mixtures, namely H₂, N₂ + H₂, He + H₂ and Ar + H₂, resulting in highly different effects on the detached-like hydrogen plasma parameters. An extensive set of diagnostics has been utilized, looking at plasma density and temperature, radiated power, heat loads onto the target and presence of molecular species by means of both mass spectrometry and optical-emission spectroscopy. To provide a theoretical basis for the experimental results, numerical simulations have been implemented and a two-step approach has been followed: at first, extended plasma chemical models have been set up aiming to achieve reduced sets of chemical equations for each different seeding scenarios. Secondly, the reduced reaction schemes have been implemented into spatially-resolved codes suited for linear plasma devices i.e. Eunomia standalone for the transport of neutrals and B2.5-Eunomia, a coupled code where plasma equations are also solved. In this way, a broader description of the plasma chemistry and physics can be provided. This thesis sheds light on the chemistry-driven volumetric processes occurring in the recombination zone of a ITER-relevant detached-like hydrogen plasma. Answers to the research questions posed in chapter 1 are given hereafter.

What is the influence of nitrogen-driven plasma chemistry on plasma detachment?

Nitrogen is the leading candidate for impurity seeding in ITER. Therefore, it is one of the most important species that has to be studied in detail in order to predict its influence on plasma parameters in the vicinity of the target i.e. between the ionization front and the divertor plate. Besides its radiative capabilities along the SOL, where temperatures can be up to ≈ 100 eV, molecule-driven plasma chemical processes are expected to influence the rate of ion recombination in the divertor, where temperatures are expected to be < 5 eV. This is a key feature that characterizes plasma detachment, neutralizing incoming ions before they reach the target.

Nitrogen seeding experiments carried out in ITER-relevant divertor plasma scenarios by means of Magnum-PSI reveal a beneficial effect of N₂+H₂ mixtures on detachment parameters. In fact, a drop in the electron density has been diagnosed with Thomson Scattering and, interestingly, electron temperature does not seem to be affected. This finding indicates an enhancement of recombination, being a sink for ions and, therefore, electrons. Another insight concerning the influence of H₂+N₂ puffing is the heat load collected at the target. This has been measured with calorimetry. We observe that by enhancing the content of N₂ among the seeded mixture, the heat load decreases significantly for all the background neutral pressures examined. Again, this finding indicates that such puffed mixture leads to an improvement of detachment, resulting in heat loads more tolerable for the material. Furthermore, radiated power from the plasma in the target chamber has been monitored with a bolometry system. No substantial effect is observed among the whole scan. This implies that both the heat load reduction and the plasma pressure drop, while increasing the content of injected N₂, is due to volumetric recombination.

It is well established that in divertor-relevant environment, when nitrogen is puffed, ammonia is formed. The mechanisms for NH₃ formation are related to surface-surface and surface-volume processes and have been extensively studied in the last few decades. Formation mechanisms of NH₃
are not studied in details here, given that the scope of this work is to understand the implications of the presence of $N_2$ and $NH_x$ molecules (and derived ions) in the volume phase of an ITER divertor-relevant hydrogen plasma. Global modelling simulations highlighted a new recombination path, named here as N-MAR(1) (Nitrogen-Molecular Assisted Recombination), that involves $H^+$ neutralization via the following two-step process: ion conversion $H^+ + NH \rightarrow H + NH^+$ followed by dissociative recombination $NH^+ + e^- \rightarrow N + H$. This process effectively converts hydrogen ions to neutrals. Moreover, at lower electron densities e.g. $n_e < 10^{19} \text{m}^{-3}$ (such as at the periphery of the plasma beam), another reaction path is found to be important i.e. N-MAR(2): $H_2 + N_2 \rightarrow N_2H^+ + H$, followed by $N_2H^+ + e^- \rightarrow N_2 + H$ or $NH + N$. These processes, together with other fundamental ones, have been subsequently implemented in the Eunomia code and B2.5-Eunomia. Simulations of both codes qualitatively confirmed what has been previously observed experimentally: the seeding of $N_2 + H_2$ leads to an enhanced ion recombination in the volume phase, resulting in an improvement on plasma detachment.

Similar experiments have been carried out in the linear device GAMMA10/PDX, located at the University of Tsukuba, and capable to operate plasmas with temperatures one order of magnitude higher than Magnum-PSI. Electron density was in the order of $10^{17} \text{m}^{-3}$. Combining experimental results from these two machines provides further understanding of the behavior of different impurities on plasma detachment for a larger parameters range. Interestingly, the synergetic effect led by $H_2+N_2$ seeding has been observed as well, again barely influencing $T_e$ while significantly reducing $n_e$ and ion flux to the target. Moreover, as it has been diagnosed in Magnum-PSI, the $NH^+$ emission band observed with optical-emission-spectroscopy increases while increasing the content of $N_2$ in the seeded mixture, indicating the strong presence of such species, which acts as electron donor in the first-step of N-MAR(1).

Conclusions

It has been shown that nitrogen seeding, together with hydrogen, has a synergetic effect in increasing the recombination of incoming ions in a divertor-like detached hydrogen plasma. Ammonia-related species are found to be mainly responsible for a newly-proposed recombination path i.e. N-MAR. Experimental trends have been reproduced qualitatively with two different codes implemented with the most relevant plasma chemistry obtained by global simulations. Results from GAMMA10/PDX showed a very similar behavior, with $N_2+H_2$ being the most beneficial injected mixture for the detached plasma. We can conclude that the plasma chemistry governing a detached hydrogen plasma, in the presence of nitrogen, is important and should be included in the state-of-the-art codes for divertor tokamaks, according to what has been shown in this thesis both experimentally (with two different linear machines) and confirmed with modelling.

What is the influence of other impurities i.e. argon and helium on plasma detachment?

The influence on plasma detachment led by other impurities besides $N_2$ has been studied with both experiments in Magnum-PSI and numerical simulations. A parallel experimental study at GAMMA10/PDX has been done, similarly to the $N_2$ case. Two poorly-reactive species i.e. argon and helium have been used. This choice has been taken for the following purposes:

- Argon can be puffed in the plasma edge due to its radiative properties along the SOL, cooling down $T_e$. This species, though, has been poorly studied in divertor-relevant plasmas so far. Hence, a dedicated study on its effects on the detached plasma region is needed. Similarly,
although a by-product of the fusion reaction, there are very few studies dealing with helium seeding in the plasma region during detachment within ITER-like plasma parameters.

- To exclude a priori any synergetic effect induced by the presence of $\text{H}_2$ together with other species, as it has been shown for the $\text{N}_2$ case, given that both Ar and He are inert. In this way, we may de-couple the influence of N-MAR with other well-known recombination processes.
- Evaluate the consequence of the hydrogen dilution effect in the seeded gas mixture i.e. comparing the efficiency of recombination led by molecular hydrogen alone with $\text{H}_2 +$ impurity mixtures.

By maintaining the same background neutral pressure, different mixtures have been puffed with different impurity content. Plasma parameters have been diagnosed with Thomson Scattering and the heat load at the target with calorimetry. When compared to the $\text{H}_2+\text{N}_2$ scenario, an opposite trend has been achieved with $\text{H}_2+\text{Ar}$ and $\text{H}_2+\text{He}$. The plasma pressure measured close to the target increases notably while increasing the presence of either He or Ar in the injected mixture. This implies a lower “degree” of detachment. When looking at the heat loads, a significant increase with both He and Ar is achieved. This means that the more impurity is mixed in with $\text{H}_2$, the more power is delivered to the target, hence, plasma detachment is deteriorated. Such negative effect might be due to the lower amount of hydrogen molecules available for volume recombination processes.

Dedicated global model simulations have been set up for both $\text{H}_2 + \text{He}$ and $\text{H}_2 + \text{Ar}$ seeding scenarios. No impurity-driven recombination paths seem to be present in these environments at divertor-relevant electron densities. It appears clear that the presence of these inert species in a detached scenario does not imply any beneficial consequence on plasma extinction before reaching the target. On the contrary, a dilution effect of molecular hydrogen occurs, lowering the amount of possible neutralization channels for $\text{H}^+$. Numerical simulations with B2.5-Eunomia, whose chemistry has been improved to include Ar and He, qualitatively confirm what has been observed experimentally i.e. plasma pressure and heat load increase while increasing the impurity content.

Experiments in the GAMMA10/PDX linear device have been carried out using $\text{H}_2+\text{Ar}$ seeding in detached-like conditions. When looking at the ion flux to the target for different cases, interesting outcomes occur. Argon seeding does not affect the incoming flux, while $\text{H}_2+\text{Ar}$ and only $\text{H}_2$ lead both to a significant reduction. Worth to be stressed that $\text{H}_2+\text{N}_2$ seeding led to a flux reduction which is twice the one with Ar. These data further demonstrate the absence of any synergetic effect with $\text{H}_2+\text{Ar}$ puffed mixtures, which is in line with what has been observed in Magnum-PSI and calculated with the simulations of two different codes.

Conclusions

Experimental campaigns in Magnum-PSI have been done regarding Ar and He seeding in the target chamber together with hydrogen in detached-like plasma scenarios. The influence on plasma pressure and heat flux, and therefore the extent of volume recombination, have been evaluated. No synergy for either $\text{H}_2+\text{He}$ and $\text{H}_2+\text{Ar}$ has been found to be present. In fact, both pressure and heat flux increase while increasing the content of the impurity in the injected mixture, leading to negative effects on detachment. This behavior is opposite to what has been previously shown for the case of $\text{H}_2+\text{N}_2$. To investigate the plasma chemistry led by the presence of He and Ar in a hydrogen plasma, global models have been set up. The most relevant processes have been then included in the coupled code B2.5-Eunomia. No significant recombination path for $\text{H}^+$ due to the presence of such impurities emerged by the global simulations. Furthermore, B2.5-Eunomia qualitatively reproduced the trends observed experimentally. Results from GAMMA10/PDX confirmed the inert behavior on plasma parameters when the impurity is puffed alone and exclude any synergy when they are injected with hydrogen.
Is it possible to reproduce experimental results in Magnum-PSI with dedicated codes?

To further understand the experimental results observed in Magnum-PSI, numerical simulations are needed. Detachment-like experiments have been carried out and indicate a synergy with H\textsubscript{2}+N\textsubscript{2} seeding leading to heat flux reduction and drop in plasma pressure. Opposite trends have been achieved with both H\textsubscript{2}+He and H\textsubscript{2}+Ar, showing higher heat loads collected at the target. This indicates a decrease in volume recombination of H\textsuperscript{+}. To confirm that this effect is mostly due to plasma chemical processes occurring in the detached-like region in the target chamber, spatially-resolved simulations have been carried out. At first, the Eunomia standalone code has been used. Eunomia is a Monte Carlo code suitable for simulating the transport of neutrals in linear plasma machines. Although such models are characterized by a static plasma background i.e. n\textsubscript{e} and T\textsubscript{e} profiles are re-stored in the simulation after every cycle, important information can be extracted regarding, for instance, spatial distributions of atoms/molecules and H\textsuperscript{+} volumetric sinks. Nitrogen seeding experiments have been reproduce in a newly-updated version of Eunomia. This variant of the code is implemented with the plasma chemistry highlighted in this work i.e. the reduced reactions scheme achieved from global modelling. H\textsubscript{2}+N\textsubscript{2} seeding scans have been simulated for nitrogen content up to 20 percent. The density of atomic hydrogen has been used as indicator for recombination, being the product of any plasma neutralization process in the scenarios considered in this thesis. Hence, radial profiles of the H density have been taken in the vicinity of the target. Interestingly, n\textsubscript{H} increases while increasing the content of N\textsubscript{2} puffed. Moreover, runs have been carried out with and without N-MAR. The latter led to a concentration of H remarkably lower compared to the case when N-MAR are included. These outcomes point to the importance of N\textsubscript{2} and NH-driven mechanisms in enhancing the extinction of incoming hydrogen ions, leading to beneficial effect for plasma detachment. The trends achieved with Eunomia standalone qualitatively reproduce what has been observed experimentally, underlining the relevance of the plasma chemistry highlighted by means of global simulations.

The Eunomia code has subsequently been coupled with B2.5, which solves plasma transport equations. In this case, the Magnum-PSI geometry has been implemented in the code. The most relevant plasma chemistry derived from zero-dimensional simulations for N\textsubscript{2}+H\textsubscript{2}, He+H\textsubscript{2} and Ar+H\textsubscript{2} seeding in hydrogen plasma has been added. Regarding H\textsubscript{2}+N\textsubscript{2} puffing, a reduction in both plasma pressure and heat loads occurred, confirming the synergetic effect observed experimentally in both Magnum-PSI and GAMMA10/PDX. On the other hand, both He and Ar seeding simulations led to an increase in the plasma pressure and heat loads, confirming the negative effect these impurities have on the detached-like plasma.

**Conclusions**

Plasma recombination in the vicinity of the target in a H\textsubscript{2}+N\textsubscript{2} seeding scenario is hereby confirmed to be enhanced due to the presence of N-MAR process. The non-beneficial effect on detachment observed with both Ar and He may be due to the absence of volume recombination paths in the presence of such chemically-inert species. A dilution effect of H\textsubscript{2}, which implies less hydrogen molecule available to undergo MAR, may also be responsible for the results obtained. If on one hand H\textsubscript{2}+N\textsubscript{2} seeding improves plasma detachment making the heat flux more tolerable for the target, H\textsubscript{2}+He and H\textsubscript{2}+Ar showed a reversed effect. What has been achieved experimentally is qualitatively confirmed with global models, Eunomia standalone and B2.5-Eunomia.
Outlook

Experimentally, this thesis presented clear results regarding the effect of different impurities in a detached-like hydrogen plasma in linear machine Magnum-PSI. A parallel set of experiments has been carried out in linear device GAMMA10/PDX. A large set of diagnostics has been used in both cases. Considering the synergetic effect led by N2+H2 seeding and the presence of N-MAR, studying the intensity of Balmer-H lines as a function of the presence of N2 may lead to a further understanding of the interplay/competition between hydrogenic MAR and N-MAR. Thomson Scattering measurements at the source location in Magnum-PSI would also provide a clearer picture on the power conservation along the plasma beam, hence, ultimately exclude/include any power limitation effects that may lead to detachment. A collective Thomson Scattering system is currently being tested in Magnum-PSI, aiming to deliver important information i.e. ion temperatures and plasma parallel velocity. Comparing those data with spatially-resolved codes like e.g. Soledge2D-Eirene[86], B2.5-Eunomia[50] and LINDA[38], would be a useful exercise to underline the possible missing physics (or chemistry) in the current state-of-the-art code packages. Moreover, examining the influence of two or more impurities seeded together, both experimentally and theoretically, may provide deeper insights on the dynamics of detachment formation during D-T campaign in future fusion reactors, where helium, nitrogen and other noble gases will be present in divertor environments.

From the plasma chemistry modelling point of view, a dedicated study on the effect of vibrational excited molecular nitrogen would provide further insights into the dominant processes occurring in both divertor and linear machines. Such implementation would also shed more light on the production mechanisms of ammonia, which is a topic of current interest in the field of divertor plasma physics. To the knowledge of the author, no scaling laws for the rate coefficients of N2(v) in ion conversion, proton transfer and dissociative ionization are currently available in the literature.

The theoretical and experimental findings in this work underline the important role of N2 and NHx molecules in the last part of the divertor plasma in reducing the particle flux to the target plate. An opposite feature has been found concerning helium and argon seeding. This implies that a positive effect in the heat loads mitigation can be gain by seeding nitrogen directly in the divertor region while, in current tokamak scenarios, it is most commonly seeded in the mid-plane region. The main drawback of nitrogen seeding lays in the so-called fuel retention issue, namely, the formation of tritiated ammonia, where nitrogen bonds with tritium hence effectively removing fuel from the system. Although nitrogen is the leading candidate for impurity seeding in ITER’s plasma edge, a solution to this problem still has to be established. The research on catalysis-driven isotope exchange in two-phase systems is widely pursued by several groups around the globe, and is generally carried out within the framework of pharmaceutical chemistry[148][149][150]. To the knowledge of the author, there is no available literature dealing with isotope exchange studies concerning tritiated ammonia. Filling this gap of knowledge by means of a close collaboration between the field of plasma-edge fusion and catalysis is needed in order to provide the knowledge to solve this crucial issue.

In this work, the importance of plasma chemistry and volume recombination in the fundamental understanding of plasma-neutrals interaction in a detached-like hydrogen plasma scenario has been shown. The highlighted divertor-relevant plasma-chemical volume processes should be included in tokamak edge and divertor plasma codes for simulation of impurity seeding and plasma detachment. In such a way, a proper description of the essential volumetric mechanisms occurring in the vicinity of the target can be provided, and subsequently used to make more precise predictions for experiments in current and future generation tokamaks.
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Part B

Publications
Chapter 7

Studying the influence of nitrogen seeding in a detached-like hydrogen plasma by means of numerical simulations


7.1 Abstract

The leading candidate for impurity seeding in ITER is currently nitrogen. To date, there are only a few studies on the plasma chemistry driven by N$_2$/H$_2$ seeding and its effect on the molecular-activated recombination of incoming atomic hydrogen ions in a detached-like scenario. Numerical simulations are needed to provide insights into such mechanisms. The numerous amount of plasma chemical reactions that may occur in such an environment cannot be entirely included in a 2 or 3-dimensional code such as Eirene. A complete global plasma model, implemented with more than 100 plasma chemical equations and 20 species, has been set up on the basis of Plasimo code. This study shows two main nitrogen-included recombination reaction paths resulted to be dominant, i.e. the ion conversion of NH followed by dissociative recombination and a proton transfer between H$_2^+$ and N$_2$, producing N$_2$H$.^+$. These two processes are referred to as N-MAR (nitrogen-molecular activated recombination) and have subsequently been implemented into Eunomia, a spatially-resolved Monte Carlo code, designed to simulate the neutrals inventory in linear plasma machines such as Pilot-PSI and Magnum-PSI. To study the effect of N$_2$ on the overall recombination, three cases of study have been set up: from a defined puffing location with a constant total seeding rate of H$_2$ + N$_2$, three N$_2$ ratios have been simulated, i.e. 0, 5 and 10%. The parameter monitored is the density of atomic hydrogen, being the final hydrogenic product of any recombination mechanism in the scenario considered. The difference in H density between the 0% case and the 10% case is about a factor 3. The importance of NH as electron donor is highlighted and N-MARs confirmed as reaction routes enhancing the conversion of ions to neutrals, making the heat loads to the divertor plate more tolerable. This work is a further step towards the full understanding of the role of N$_2$-H$_2$ molecules in a detached divertor plasma.

7.2 Introduction

Understanding and controlling plasma-surface interaction in the divertor region is one of the most important challenges towards realizing fusion power. Experiments have shown [1][2] that impurity seeding facilitates the achievement of a so-called detached plasma regime. Nitrogen is currently the leading candidate for impurity seeding in ITER [3]. The divertor detached operational regime is characterized by a plasma pressure drop along magnetic field lines towards the target in the Scrape Off Layer (SOL) and a strong reduction of the plasma ion flux onto the target resulting in low power loads [4]. Such pressure drop is due to ion-neutral interactions which give rise to plasma momentum transfer to the walls through the neutral channel, ion removal by means of recombination mechanisms and plasma cooling due to radiation [5].
Molecular-Activated Recombination (referred to as MAR) and electron-ion recombination (EIR) are very efficient processes in Low T (≤ 1.5 eV) [6] and involve molecular hydrogen in vibrational excited states[7]. The rate coefficients for these processes are highlighted in figure 1. The first experimental investigations of MAR have been carried out in linear machines Nagdis-II [8] and ULS[9].

The aim of this work is to investigate the plasma chemistry induced by nitrogen in a detached-like hydrogen plasma, pointing out the most important processes to be added in spatially-resolved codes, where an implementation of the whole plasma chemistry would not be computationally feasible. Little is known on the detailed plasma chemical processes occurring in ITER divertor relevant conditions i.e. high density, low temperature plasmas in the presence of nitrogen. To study this complex scenario, an extensive global plasma model of H₂+N₂ chemistry has been set up on the basis of Plasimo code[10]. The general features of the global model are presented in section 7.3, while the plasma chemistry is described in sections 7.3.2 and 7.3.3. The model is created with the purpose of identifying the dominant plasma-chemical processes occurring in the plasma close to the target when N₂ is added into the system. In order to prove the reliability of the reduced set of chemical equations, a reduced global model has been implemented and the outputs are compared with the full version for three different plasma scenarios. The results are in good agreement in all cases and are shown in section 7.4.6. The reduced set of chemical equations relevant for Magnum-PSI i.e. high-density low-temperature plasma has been subsequently implemented in Eunomia [11], a spatially resolved Monte-Carlo code for the transport of neutrals originally developed for the Magnum-PSI[12] predecessor Pilot-PSI[13]. To study the influence of N₂ and related species on the recombination mechanisms, the density of atomic hydrogen has been traced for three different seeding cases. Conversion of ions to neutrals has been proved to be enhanced by the presence of nitrogen by up to 30 %. The output are shown is section 7.6. Finally, a summary of this work, together with the conclusions, are given in section 7.7.

7.3 Global modelling with Plasimo code

In Global Models spatial averages of the physical parameters are calculated from plasma ignition to the fulfilment of the steady state[14]. The outcomes of the zero-dimensional simulation is collected by solving a system of coupled differential equations i.e. the energy balance, the quasi - neutrality condition and the particle balance, whose solution describes the evolution of ionic and neutral species as a function of time. The electron energy balance is solved simultaneously. The power is assumed to be uniformly distributed and the plasma is spatially homogeneous throughout the whole volume. The input parameters to be defined are input power and density of precursor gases (H₂ and N₂), while nₑ and Tₑ are given as output of the simulation.

The source terms are formulated from the reaction rates, thus every reaction can be initiated by any of the species included in the model. This type of code is computationally less expensive than spatially...
resolved hybrid models, hence we are able to include a detailed and extensive chemistry, without causing any significant increasing of the computational effort [15].

In the model, the electron energy distribution function (EEDF) is assumed to be maxwellian. Despite the limitations imposed by a zero-dimensional simulation, where no transport effects are considered, important outputs can be obtained providing detailed insights into the dominant atomic and molecular-induced processes governing the volume collisions in a detached-like plasma system.

7.3.1 Governing equations

The time-dependent evaluation of number densities of the chemical species is calculated as follows:

\[
\frac{dn_i}{dt} = \sum_r (v_r^p - v_r^d) k_r(t) \prod_i n_i^{v_d} = S_i
\]

where \(v_r^p\) and \(v_r^d\) are the stoichiometric coefficients of the reactants (\(d\)) and the products (\(p\)) of the reaction, \(k_r(t)\) is the rate coefficient and \(n_i\) is the density of species \(i\).

The electron energy balance is defined as:

\[
\frac{d \left( \frac{2}{2} n_e e T_e \right)}{dt} = P_{\text{input}}(t) - Q_{\text{inelas}} - Q_{\text{elas}}
\]

where \(n_e\) and \(T_e\) are the electron density [m\(^3\)] and temperature [eV] respectively, \(e\) the elementary charge, \(P_{\text{input}}\) the input power density, \(Q_{\text{inelas}}\) and \(Q_{\text{elas}}\) the energy losses from inelastic and elastic collisions between electrons and heavy particles.

In inelastic electron-induced collisions with heavy particles, the energy difference between left and right hand side of the reaction is due to energy loss by the electron. Hence, the total inelastic source term is written as:

\[
Q_{\text{inelas}} = \sum_r E_e n_r n_e k_{\text{reac}} = E_e R
\]

With \(E_e\) the electron energy transfer (one per reaction) and \(R\) the triple product of rate times reactants densities.

In this model quasi-neutrality is assumed, thus plasma is neutrally charged. The electron density is therefore calculated from:

\[
n_e = \sum_r \frac{n_i q_i}{e}
\]

Where \(n_i\) is the density of the ionic species \(i\), \(q_i\) its charge and \(e\) the elementary charge.

The totality of the power supplied to the gas is assumed to be consumed by the plasma, thus lost and supplied power must balance. The input power density is then used to create ion - electron pairs by means of inelastic electron - induced processes.

7.3.2 Chemical model

The chemical species simulated in this study are reported in Table 1. The energy of electrons in our case of study is generally not high enough to cause direct dissociation of \(N_2\) \((E_a = 9.79\) eV\). It has been recently reported [16] that the \(A^3\Sigma\) excited molecule can act as intermediate compound for the dissociation of \(N_2\) in low \(T\) plasma predominantly via the reaction \(N_2^*(A^3\Sigma) + H \rightarrow NH + N\) and to a minor extent \((\approx 30\%)\) via \(N_2^*(A^3\Sigma) + e \rightarrow N + N\). These processes, together with ionization of \(N_2\) from the \(A^3\Sigma\) state, have been included. Diazenilium ions \(N_2H^+\) and ammonium \(NH_4^+\) are included in the
simulations. An extensive set including all the NH$_3$ and NH$_3^+$ has been implemented in the code. Although it is now well-established that the hydrogenation of N to produce ammonia occurs mainly on the surface [21], these species have been added due to the role they play in the volume phase such as ion conversion, proton transfer and recombination processes. It’s worth stressing that the aim is to obtain a reduced set of chemical equations and that global modelling allows us to study a large number of different processes among several species. Molecular hydrogen in vibrational excited state (v = 4) has been added in the model, given the important role it plays in the ion conversion with H$^+$, which is the main ion species in our plasma.

A recent work carried out by Body et al. [17] and published in this journal provides a detailed description of plasma-chemical processes leading to the production of ammonia. Particular efforts are thereby spent in the modelling of plasma-wall heterogeneous reactions, given the importance they have in the synthesis of NH$_3$. In the present work, the selection of processes has been done focusing on volume processes relevant in detached-like hydrogen plasma in the presence of nitrogen, in order to evaluate the role of N and N$_2$-H$_2$ species in recombination mechanisms. The list of the plasma-chemical reactions adopted in this study is presented in Table 2 in section 7.3.3.

<table>
<thead>
<tr>
<th>$H_2$ species</th>
<th>$N_2$ species</th>
<th>$H_2$-$N_2$ species</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H, H_2, H^+, H_2^+, H_2N=3, H_3^+$</td>
<td>$N_2, N, N_2(A^3\Sigma), N_2^+, N^+$</td>
<td>$NH, NH_2, NH_3, NH_3^+, NH_2^+, NH^+, N_2H^+, NH_4^+$</td>
</tr>
</tbody>
</table>

Table 1. The chemical species included.

7.3.3 Plasma chemical reactions

The chemical equations incorporated in the model cover a wide range of process types, i.e. ionization, dissociation, dissociative ionization, dissociative recombination, ion-neutral, neutral-neutral and elastic collisions. The set of the chemical equations adopted in this work is listed in table 2. The rate coefficient for ionization and elastic collisions with electrons is gained by averaging the product of cross section and velocity over the EEDF. The relation can be written explicitly[15]:

$$k_i = \int_{E_{th}}^{\infty} \sigma_i(E) v(E) f(E) dE$$

With $E_{th}$ the threshold energy of the collision, $E$ the electron energy, $f(E)$ the electron energy distribution function, $v(E)$ the electron velocity and $\sigma_i$ the cross section of collision $i$. Data concerning the remaining classes of reactions have been taken from the most comprehensive databases available in the literature such as UMIST, LxCat, NIST, Anichich’s review and are referenced in table 2. These rates are expressed in the generalized Arrhenius form[18]:

$$k(T_e) = A \left( \frac{T_e}{1 \text{eV}} \right)^n \exp\left(-\frac{E_a}{T_e}\right)$$

Where $A$ is declared in cm$^3$/s$^1$ and $E_a$, the activation energy of the reaction, together with $T_e$, in eV. The temperature of neutrals in the simulations ($T_N$) has been set at 0.2 eV. Such value has been estimated by numerical simulations in [19] to be in the temperature range of molecules in the Pilot-PSI hydrogen plasma beam, which is characterized by very similar plasma parameters to Magnum-PSI’s, in terms of electron density and temperature.

<table>
<thead>
<tr>
<th>NR.</th>
<th>Reaction</th>
<th>Rate coefficient (cm$^3$/s$^1$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$H + e^- \rightarrow H^+ + 2e^-$</td>
<td>from cross section</td>
<td>[20]</td>
</tr>
<tr>
<td>2</td>
<td>$H_2 + e^- \rightarrow H^+ + 2e^-$</td>
<td>from cross section</td>
<td>[20]</td>
</tr>
<tr>
<td>3</td>
<td>$N + e^- \rightarrow N^+ + 2e^-$</td>
<td>from cross section</td>
<td>[21]</td>
</tr>
<tr>
<td>4</td>
<td>$N_2 + e^- \rightarrow N_2^+ + 2e^-$</td>
<td>from cross section</td>
<td>[21]</td>
</tr>
<tr>
<td>5</td>
<td>$N_2 + e^- \rightarrow N_2(A^3\Sigma) + e^-$</td>
<td>from cross section</td>
<td>[22]</td>
</tr>
<tr>
<td>6</td>
<td>$N_2(A^3\Sigma) + e^- \rightarrow N_2^+ + 2e^-$</td>
<td>from cross section</td>
<td>[23]</td>
</tr>
<tr>
<td>Reaction</td>
<td>ΔG (kJ/mol)</td>
<td>Ref.</td>
<td></td>
</tr>
<tr>
<td>----------</td>
<td>-------------</td>
<td>------</td>
<td></td>
</tr>
<tr>
<td>( N_2 + e^- \rightarrow N^+ + N + 2e^- )</td>
<td>2.9 × 10^{-9} \times \exp(-29.71/T_\text{g})</td>
<td>[24]</td>
<td></td>
</tr>
<tr>
<td>( H_2 + e^- \rightarrow H^+ + H + 2e^- )</td>
<td>9.4 × 10^{-10} \times \exp(-29.94/T_\text{g})</td>
<td>[25]</td>
<td></td>
</tr>
<tr>
<td>( H_2 + e^- \rightarrow H_2e \rightarrow + e^- )</td>
<td>6.7 × 10^{-10} \times \exp(-1.89/T_\text{g})</td>
<td>[26]</td>
<td></td>
</tr>
<tr>
<td>( NH + e^- \rightarrow NH^+ + 2e^- )</td>
<td>2.1 × 10^{-8} \times \exp(-15.49/T_\text{g})</td>
<td>[27]</td>
<td></td>
</tr>
<tr>
<td>( NH + e^- \rightarrow N^+ + H + 2e^- )</td>
<td>7.6 × 10^{-9} \times \exp(-16.82/T_\text{g})</td>
<td>[27]</td>
<td></td>
</tr>
<tr>
<td>( NH + e^- \rightarrow NH^+ + 2e^- )</td>
<td>1.3 × 10^{-9} \times \exp(-12.4/T_\text{g})</td>
<td>[27]</td>
<td></td>
</tr>
<tr>
<td>( NH_3 + e^- \rightarrow NH_2^+ + H + 2e^- )</td>
<td>2.2 × 10^{-8} \times \exp(-17.97/T_\text{g})</td>
<td>[27]</td>
<td></td>
</tr>
<tr>
<td>( NH_3 + e^- \rightarrow NH_2^+ + H + 2e^- )</td>
<td>1.5 × 10^{-8} \times \exp(-13.61/T_\text{g})</td>
<td>[27]</td>
<td></td>
</tr>
<tr>
<td>( NH_3 + e^- \rightarrow NH_2^+ + H + 2e^- )</td>
<td>1.6 × 10^{-8} \times \exp(-15.41/T_\text{g})</td>
<td>[27]</td>
<td></td>
</tr>
<tr>
<td>( NH_3 + e^- \rightarrow NH_2^+ + H + 2e^- )</td>
<td>5.4 × 10^{-10} \times \exp(-26.06/T_\text{g})</td>
<td>[27]</td>
<td></td>
</tr>
<tr>
<td>( NH_3 + e^- \rightarrow N^+ + H_2 + 2e^- )</td>
<td>8.8 × 10^{-11} \times \exp(-29/T_\text{g})</td>
<td>[28]</td>
<td></td>
</tr>
<tr>
<td>( NH_3 + e^- \rightarrow H^+ + NH_2 + 2e^- )</td>
<td>1.3 × 10^{-10} \times \exp(-28.55/T_\text{g})</td>
<td>[28]</td>
<td></td>
</tr>
<tr>
<td>( H_2 + e^- \rightarrow H + H + e^- )</td>
<td>1.6 × 10^{-8} \times (T_\text{f}/0.026)^{-0.83}</td>
<td>[29]</td>
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</tr>
<tr>
<td>( H_2^+ + e^- \rightarrow H_2 + e^- )</td>
<td>2.34 × 10^{-8} \times (T_\text{f}/0.026)^{-0.52}</td>
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<td></td>
</tr>
<tr>
<td>( H_2^+ + e^- \rightarrow N + N + e^- )</td>
<td>4.36 × 10^{-8} \times (T_\text{f}/0.026)^{-0.52}</td>
<td>[30]</td>
<td></td>
</tr>
<tr>
<td>( N^+_2 + e^- \rightarrow N + e^- )</td>
<td>1.7 × 10^{-7} \times (T_\text{f}/0.026)^{-0.3}</td>
<td>[31]</td>
<td></td>
</tr>
<tr>
<td>( NH^+ + e^- \rightarrow N + H + e^- )</td>
<td>8.4 × 10^{-8} \times \exp(-11.18/T_\text{g})</td>
<td>[25]</td>
<td></td>
</tr>
<tr>
<td>( NH + e^- \rightarrow N + H + e^- )</td>
<td>4.7 × 10^{-8} \times \exp(-7.69/T_\text{g})</td>
<td>[35]</td>
<td></td>
</tr>
<tr>
<td>( NH_2 + e^- \rightarrow NH + H + e^- )</td>
<td>4.5 × 10^{-8} \times \exp(-7.61/T_\text{g})</td>
<td>[35]</td>
<td></td>
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<tr>
<td>( NH_2 + e^- \rightarrow N + H + e^- )</td>
<td>1.5 × 10^{-7} \times \exp(-11.44/T_\text{g})</td>
<td>[35]</td>
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<tr>
<td>( NH_3 + e^- \rightarrow NH_2 + H + e^- )</td>
<td>1.3 × 10^{-7} \times \exp(-11.06/T_\text{g})</td>
<td>[35]</td>
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<tr>
<td>( NH_3 + e^- \rightarrow NH_2 + H + e^- )</td>
<td>4.2 × 10^{-8} \times \exp(-7.59/T_\text{g})</td>
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<tr>
<td>( NH_3 + e^- \rightarrow NH + H_2 + e^- )</td>
<td>4.1 × 10^{-8} \times \exp(-4.81/T_\text{g})</td>
<td>[35]</td>
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<tr>
<td>( H_2 + NH \rightarrow NH_2 + H )</td>
<td>5.96 × 10^{-11} \times \exp(-0.67/T_\text{g})</td>
<td>[37]</td>
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</tr>
<tr>
<td>( NH_3 + H \rightarrow NH_2 + H_2 )</td>
<td>8.4 × 10^{-14} \times (T_\text{f}/0.026)^{-0.89} \times \exp(-0.41/T_\text{g})</td>
<td>[38]</td>
<td></td>
</tr>
<tr>
<td>( NH + NH_2 \rightarrow NH_3 + N )</td>
<td>1.66 × 10^{-12}</td>
<td>[38]</td>
<td></td>
</tr>
<tr>
<td>( N + NH_2 \rightarrow N_2 + H_2 )</td>
<td>1.2 × 10^{-10}</td>
<td>[39]</td>
<td></td>
</tr>
<tr>
<td>( NH_2 + H_2 \rightarrow NH_3 + N )</td>
<td>5.4 × 10^{-11} \times \exp(-0.56/T_\text{g})</td>
<td>[40]</td>
<td></td>
</tr>
<tr>
<td>( NH + NH \rightarrow NH_2 + N )</td>
<td>1.7 × 10^{-12} \times (T_\text{f}/0.026)^{12}</td>
<td>[41]</td>
<td></td>
</tr>
<tr>
<td>( NH + NH \rightarrow N_2 + H + H )</td>
<td>0.5 × 10^{-11}</td>
<td>[18]</td>
<td></td>
</tr>
<tr>
<td>( NH_2 + H \rightarrow NH + H_2 )</td>
<td>6.6 × 10^{-11} \times \exp(-0.1586/T_\text{g})</td>
<td>[42]</td>
<td></td>
</tr>
<tr>
<td>( NH + NH \rightarrow N_2 + H )</td>
<td>5 × 10^{-14} \times (T_\text{f}/0.026)</td>
<td>[42]</td>
<td></td>
</tr>
<tr>
<td>( H_2 + N \rightarrow NH + H )</td>
<td>4.65 × 10^{-11} \times \exp(-1.43/T_\text{g})</td>
<td>[37]</td>
<td></td>
</tr>
<tr>
<td>( N + NH \rightarrow N_2 + H )</td>
<td>5 × 10^{-11}</td>
<td>[39]</td>
<td></td>
</tr>
<tr>
<td>( NH + H \rightarrow N + H_2 )</td>
<td>5.4 × 10^{-11} \times \exp(-0.0142/T_\text{g})</td>
<td>[42]</td>
<td></td>
</tr>
<tr>
<td>( N^+ + H_2 \rightarrow NH^+ + H )</td>
<td>5 × 10^{-10}</td>
<td>[43]</td>
<td></td>
</tr>
<tr>
<td>( N^+ + NH \rightarrow NH^+ + N )</td>
<td>1 × 10^{-9}</td>
<td>[44]</td>
<td></td>
</tr>
<tr>
<td>( N^+ + H \rightarrow H^+ + N )</td>
<td>2 × 10^{-10}</td>
<td>[45]</td>
<td></td>
</tr>
<tr>
<td>( N^+ + N \rightarrow N_2 + N )</td>
<td>2 × 10^{-11}</td>
<td>[43]</td>
<td></td>
</tr>
<tr>
<td>( N^+ + NH \rightarrow NH^+ + N )</td>
<td>3.7 × 10^{-10} \times (T_\text{f}/0.026)^{-0.5}</td>
<td>[44]</td>
<td></td>
</tr>
<tr>
<td>( N^+ + H_2 \rightarrow NH + H_2 )</td>
<td>2.1 × 10^{-10}</td>
<td>[43]</td>
<td></td>
</tr>
<tr>
<td>( N^+ + NH \rightarrow N_2 + H )</td>
<td>3.7 × 10^{-10} \times (T_\text{f}/0.026)^{-0.5}</td>
<td>[44]</td>
<td></td>
</tr>
<tr>
<td>( N^+ + NH_2 \rightarrow NH_2^+ + H )</td>
<td>1.7 × 10^{-9}</td>
<td>[43]</td>
<td></td>
</tr>
<tr>
<td>( N^+ + NH_2 \rightarrow NH_2^+ + N )</td>
<td>4.7 × 10^{-10}</td>
<td>[43]</td>
<td></td>
</tr>
<tr>
<td>( H^+ + NH \rightarrow NH^+ + H )</td>
<td>2.1 × 10^{-9} \times (T_\text{f}/0.026)^{-0.5}</td>
<td>[44]</td>
<td></td>
</tr>
<tr>
<td>( H^+ + NH_2 \rightarrow NH_2^+ + H )</td>
<td>2.9 × 10^{-9} \times (T_\text{f}/0.026)^{-0.5}</td>
<td>[44]</td>
<td></td>
</tr>
<tr>
<td>( H^+ + H_2 \rightarrow H + H_2^+ )</td>
<td>2.5 × 10^{-9}</td>
<td>[47]</td>
<td></td>
</tr>
</tbody>
</table>
\[
\begin{array}{lll}
65 & H_2^2 + NH_3 \rightarrow H_2 + NH_2^+ & 5.7 \times 10^{-9} \\
66 & H_2^2 + N \rightarrow N_2H^+ + H & 2 \times 10^{-9} \\
67 & H_2^2 + N \rightarrow N^+ + H_2 & 1.9 \times 10^{-9} \\
68 & H_2^2 + N \rightarrow N_2H^+ + H & 5 \times 10^{-10} \\
69 & H_2^2 + NH \rightarrow NH^+ + H_2 & 7.6 \times 10^{-10} \times (T_{pp} / 0.026)^{-0.5} \\
70 & H_2^2 + NH_2 \rightarrow NH_2^+ + H_2 & 7.6 \times 10^{-10} \times (T_{pp} / 0.026)^{-0.5} \\
71 & H_2^2 + NH \rightarrow NH_2^+ + H & 2.1 \times 10^{-9} \times (T_{pp} / 0.026)^{-0.5} \\
72 & H_2^2 + NH_2 \rightarrow NH_2^+ + H & 5 \times 10^{-11} \\
73 & H_2^2 + NH \rightarrow NH_2^+ + H & 5 \times 10^{-11} \\
74 & H_2^2 + H_2 \rightarrow H_2^+ & 2 \times 10^{-9} \\
75 & H_2^+ + N \rightarrow NH^+ + H_2 & 2.6 \times 10^{-10} \\
76 & H_2^+ + N \rightarrow NH_2^+ + H & 3.9 \times 10^{-10} \\
77 & H_2^2 + NH_3 \rightarrow NH_2^+ + H_2 & 4.4 \times 10^{-9} \times (T_{pp} / 0.026)^{-0.5} \\
78 & H_2^2 + NH_2 \rightarrow NH_2^+ + H_2 & 1.8 \times 10^{-9} \times (T_{pp} / 0.026)^{-0.5} \\
79 & H_2^2 + NH \rightarrow NH_2^+ + H_2 & 1.3 \times 10^{-9} \times (T_{pp} / 0.026)^{-0.5} \\
80 & H_2^2 + N \rightarrow N_2H^+ + H_2 & 1.9 \times 10^{-9} \\
81 & N_2H^+ + N \rightarrow N_2H^+ + N & 2.8 \times 10^{-10} \\
82 & NH^+ + N \rightarrow NH_2^+ + H & 1 \times 10^{-9} \\
83 & NH^+ + N \rightarrow NH_2^+ + H & 1 \times 10^{-9} \\
84 & NH^+ + N \rightarrow NH_2^+ + N & 6.5 \times 10^{-10} \\
85 & NH^+ + NH \rightarrow NH_2^+ + N & 1 \times 10^{-9} \\
86 & NH^+ + N \rightarrow NH_2^+ + N & 1.5 \times 10^{-9} \\
87 & NH^+ + NH_2 \rightarrow NH_2^+ + NH & 1 \times 10^{-9} \\
88 & NH^+ + NH \rightarrow NH_2^+ + NH & 1 \times 10^{-9} \\
89 & NH^+ + NH \rightarrow NH_2^+ + N & 6 \times 10^{-10} \\
90 & NH_2^+ + N \rightarrow NH_2^+ + N & 9.1 \times 10^{-11} \\
91 & NH_2^+ + NH \rightarrow NH_2^+ + N & 7.3 \times 10^{-10} \\
92 & NH_2^+ + NH \rightarrow NH_2^+ + NH & 1.2 \times 10^{-9} \\
93 & NH_2^+ + NH \rightarrow NH_2^+ + NH & 1.2 \times 10^{-9} \\
94 & NH_2^+ + H_2 \rightarrow NH_2^+ + H & 2 \times 10^{-10} \\
95 & NH_2^+ + H_2 \rightarrow NH_2^+ + H & 2.1 \times 10^{-9} \\
96 & NH_2^+ + NH \rightarrow NH_2^+ + N & 7.1 \times 10^{-10} \times (T_{pp} / 0.026)^{-0.5} \\
97 & NH_2^+ + H_2 \rightarrow NH_2^+ + N & 4.4 \times 10^{-13} \\
98 & N_2H^+ + NH \rightarrow NH_2^+ + N & 2.3 \times 10^{-9} \\
99 & N_2H^+ + H \rightarrow NH_2^+ + H & 2 \times 10^{-9} \\
100 & N_2H^+ + NH \rightarrow N_2H^+ + N & 2 \times 10^{-9} \\
101 & N_2H^+ + N \rightarrow N_2H^+ + N & 1 \times 10^{-11} \\
102 & H_2 + e^- \rightarrow H_2 + e^- & \text{from cross section} \\
103 & H + e^- \rightarrow H + e^- & \text{from cross section} \\
104 & N_2 + e^- \rightarrow N_2 + e^- & \text{from cross section} \\
105 & N + e^- \rightarrow N + e^- & \text{from cross section} \\
106 & NH_3 + e^- \rightarrow NH_3 + e^- & \text{from cross section}
\end{array}
\]

Table 2. Reactions included in the global model.

7.4 Global model results

Hydrogen plasmas with nitrogen content have been widely studied in the last few decades [49],[50], [51]. The aim of such studies mostly concerned the role of plasma in lowering the activation energy needed for the catalytic synthesis of ammonia. The parameters of those plasmas were substantially different from the scenario considered in this paper, i.e. far from the high-density low-temperature plasmas produced in linear machines and divertors. The purpose of this study is to characterize the plasma chemistry relevant for N2-seeded divertor hydrogen plasma. In particular, we are interested in investigating the recombination mechanisms of H+ introduced by the presence of nitrogen in the volume phase. Before the implementation in the Eunomia code, the dominant processes have been highlighted by means of a global model and the results are presented hereafter. A verification of the extracted processes will follow and will be presented in section 7.4.6.
7.4.1 Plasimo results: new reaction paths in the presence of nitrogen

Global modelling can provide deep insights into the plasma chemistry occurring in a rather complex environment. Considering the shape of $n_e$ and $T_e$ in a semi-detached plasma beam in linear machines, two different cases of study have been considered. For both cases, a 5% $N_2$ content has been studied. In figure 2 a typical semi-detached Magnum-PSI $T_e$ and $n_e$ profiles are shown.

![Figure 2. Electron temperature and density profiles of a ‘semi-detached’ Magnum-PSI plasma beam diagnosed by means of Thomson Scattering at 3 cm from the target. The two different cases of study are highlighted in blue (peak) and red (edges). The background pressure in the target chamber is set at 2Pa.](image)

TS profiles are peaked in the centre and decrease towards the edge of the beam, with values from $\approx 1.5$ eV to $\approx 0.35$ eV for $T_e$ and from $\approx 2*10^{20}$ m$^{-3}$ to $2.5*10^{19}$ m$^{-3}$ for $n_e$. Clearly, such differences imply different plasma chemical processes to be dominant on a local scale.

7.4.2 Centre of the plasma beam

For the simulation of the centre of the plasma beam, the parameters calculated by the code are $T_e = 1.2$ eV and $n_e = 2.65*10^{20}$ m$^{-3}$. The most relevant processes highlighted in this section are reported in Figure 3. The initial densities are $1*10^{21}$ m$^{-3}$ for molecular hydrogen and $5*10^{19}$ m$^{-3}$ for $N_2$. The input power density adopted to achieve parameters relevant for this study was set at 2500 J/m$^3$. The simulation time is set at 1.3 ms.

![Figure 3. $H^+$ sink routes calculated by the code in the centre of the beam. The first branch, concerning $H_2$ in vibrational excited state, corresponds to the well-established molecular activated recombination. The second one involves NH as electron donor in the ion conversion with $H^+$ and is followed by electron-ion recombination of NH+. This reactions path can be referred to as N-MAR.](image)
The principal sinks reactions for H\(^+\) is ion conversion with molecular hydrogen in vibrational excited state and with NH (reactions 62 and 64), leading \(\text{H}_2^+\) and NH\(^+\) respectively. The first branch is the well-established hydrogenic MAR first step, while the second involves nitrogen monohydride and will be referred to as N-MAR. The main loss route of H\(^+\) is indicated by the code to be reaction 62 with a relative contribution of \(\approx 70\%\). In this model one vibrational excited state of \(\text{H}_2\) i.e. \(v=4\), is taken into account. NH molecule is produced via electron-impact direct dissociation of NH\(_x\) species, dissociative recombination of NH\(_x^+\) ions and by neutral-neutral atomic transfer (reactions 49 and 81).

About 85\% of H\(_2^+\) is lost by dissociative recombination (reaction 19) and, to a minor extent by reacting with N-species, namely \(\approx 10\%\) is consumed by proton transfer with N\(_2\) (reaction 66) and \(\approx 5\%\) by ion conversion with ammonia (reaction 65) gaining N\(_2\)H\(^+\) and NH\(_3^+\) respectively. As can be seen in figure 4, the dominant NH\(^+\) sink path is by dissociative recombination (\(\approx 90\%\)), gaining one atom of nitrogen and one of hydrogen (reaction 21) and for less than 10\% by atom transfer with N, producing N\(_2^+\) and H (reaction 83).

![Figure 4. relative contribution of NH\(^+\) sinks in the beam centre.](image)

No significant amount of ammonia or its derivate ion NH\(_4^+\) is produced in the volume phase. The precursors of those species are rapidly consumed by dissociation and recombination processes. In a real divertor NH\(_3\) is produced by means of Eley-Rideal and Langmuir-Hinshelwood processes, both involving a (cold) metal wall[52]. The molecule is then released in the volume phase. Although this can occur in a detached-like plasma scenario in a linear device, no wall processes have been implemented in this simulation, given the purpose of studying the most important volume-phase plasma chemistry. Assuming an influx of NH\(_3\) from the target and/or from the reactor walls towards the plasma beam, ammonia undergoes ion conversion with H\(^+\) (reaction 61) with a contribution of 42\%, dissociation by electron impact for 25\% (indicated as the sum of relative contributions of reactions 38 and 39) and via H atom transfer (reaction 41) for the remaining 33\%. The product of reaction 61 i.e. NH\(_3^+\) is calculated to be entirely consumed by dissociative recombination i.e. reaction 26 and 27, producing H\(_2\) + NH and NH\(_2^+\) + H, respectively.

### 7.4.3 Divertor-relevant H\(_2\)/N\(_2\) plasma chemistry for different plasma parameters

To investigate the relevant plasma chemistry occurring among a wider range of plasma scenarios, a parameter scan has been carried out i.e. electron densities from \(6.8 \times 10^{17} \text{ m}^{-3}\) to \(1.2 \times 10^{19} \text{ m}^{-3}\) have been studied. The electron temperature for these simulations has been kept at \(\approx 2.5 \text{ eV}\), which is doubled compared to the Magnum-PSI detached-plasma relevant scenario discussed in section 7.4.2. In this sub-section, attention is paid to the density evolution of molecular ions, being the charged species populating this type of low-density plasmas [53]. Results are show in figure 5 and figure 6.
At high-density low-temperature plasma, NH$_x^+$ species (with 0<x<5) are predominantly produced via ion conversion with H$^+$ and are efficiently depleted by means of dissociative recombination processes, as follows:

1) $H^+ + NH_x \rightarrow NH_x^+ + H$  \hspace{1cm} \text{Ion conversion}
2) $NH_x^+ + e^- \rightarrow NH_{x-1} + H$  \hspace{1cm} \text{Dissociative recombination}

At the densities evaluated in figure 5 and 6, other processes become dominant. These are governed by the presence of protonated molecules. In figure 6 one can observe that at $n_e = 1.2 \times 10^{19}$ m$^{-3}$, the densities of NH$_x$ species follow inversely the amount of H atoms bound to N. In such scenario, dissociative recombination is still important, and tends to de-populate first the highly hydrogenated molecular ions. When moving towards lower electron densities i.e. $\sim 3 \times 10^{18}$ m$^{-3}$, a population inversion occurs, leading to an overturn where NH$_4^+$ is the most present ion. This is due to the following atomic transfer reaction paths:

3) $NH^+ + H_2 \rightarrow NH_2^+ + H$  \hspace{1cm} \text{Reaction 82}
4) $NH_2^+ + H_2 \rightarrow NH_3^+ + H$  \hspace{1cm} \text{Reaction 94}
5) $NH_3^+ + H_2 \rightarrow NH_4^+ + H$  \hspace{1cm} \text{Reaction 97}

Moreover, NH$_4^+$ is gained via a so-called proton transfer chain, which is initiated by H$_3^+$ and molecular nitrogen. This path is characterised by the following reactions:

6) $H_3^+ + N_2 \rightarrow N_2H^+ + H_2$  \hspace{1cm} \text{Reaction 80}
7) $N_2H^+ + NH_3 \rightarrow NH_4^+ + N_2$  \hspace{1cm} \text{Reaction 98}

This mechanism starts to occur at $n_e < 4 \times 10^{18}$ m$^{-3}$ (figure 6), when the density of H$_3^+$ and N$_2$H$^+$ decrease steeply and NH$_4^+$ increases. At density $\sim 8 \times 10^{17}$ m$^{-3}$, N$_2$H$^+$ and NH$_4^+$ are almost equally populated. It is worth to underline here that reaction 80 is also a source for H$_2$ which is a reactant participating in the above-mentioned atom transfer chain.

The effect of electron temperature on H$_2$/N$_2$ plasma chemistry with densities in the order of $10^{16}$ m$^{-3}$ has been extensively studied in the last years [54], [55] given the importance it has in the field of plasma processing. For what concerns divertor-relevant electron densities i.e. $n_e > 5 \times 10^{19}$ m$^{-3}$ with electron temperatures above 3 eV, electron-induced mechanisms are expected to play a major role. As can be seen in figure 7, with temperature above $\sim 3$ eV, the electron-impact ionization becomes dominant compared to the ion conversion – dissociative recombination mechanisms described in equations (1) and (2) in this paragraph. Therefore, the effect of enhanced recombination of H$^+$ given by N-MAR, becomes less important.
Figure 7. Reaction rates for NH₄ species occurring in divertor-relevant hydrogen plasma in the presence of nitrogen. Dotted lines are electron-impact dissociation (DISS), dash-dotted are dissociative recombination (DR), straight lines are ion conversion (IC) while dashed ones constitute direct ionization (ION).

7.4.4 The role of molecular ion H₃⁺

A parallel work has been carried out with the purpose of studying the presence of the protonated molecular hydrogen H₃⁺ in divertor-relevant plasmas. The same H₂/N₂ global model described in section 7.3.2 has been used, given that the plasma chemistry conditioning H₃⁺ is fully implemented.

The first successful studies on the production of such ion date back to the first half of the last century[56]. H₃⁺ is gained by means of a proton transfer reaction between molecular hydrogen and its ion (reaction 74): $H₂^+ + H_2 \rightarrow H_3^++ H$ with a rate constant of $k = 2 \times 10^{-9} \text{ cm}^3\text{s}^{-1}$ [43]. This process competes with another sink of H₃⁺ i.e. reaction 19: $H₂^+ + e^- \rightarrow H + H$. H₃⁺ is efficiently consumed in low temperature plasmas ($T_e <$3-4 eV) by two dissociative recombination reactions, namely reactions 20 and 21. The rate coefficients of these process as a function of $T_e$ are plotted in figure 8. The density evolution of H₃⁺ over time is calculated by the code as:

$$\frac{d[H₃^+]}{dt} = (k_{74} \ast [H₂^+][H_2])_{\text{production}} - (k_{20} \ast n_e \ast [H₃^+])_{\text{consumption}} - (k_{21} \ast n_e \ast [H₃^+])_{\text{consumption}}$$

It is dependent on the electron density. In the model, $T_e$ has been kept fixed at ≈ 1.5 eV while the electron density has been changed by tuning the input power density provided into the system. The output of the simulations are reported in figure 9.
The population inversion occurs at \( n_e \approx 7 \times 10^{18} \text{ m}^{-3} \), which is about two orders of magnitude lower than the electron density characterizing the hydrogen plasma in new-generation linear machines as well as the one expected in ITER divertor i.e. \( 10^{20} - 10^{21} \text{ m}^{-3} \) [57]. Worth mentioning the typical “attached” H\(_2\) plasma in Magnum-PSI has \( T_e \leq 5 \text{ eV} \), while for detached-like scenarios \( T_e \) falls below 1.5 eV.

According to figure 8, for electron temperature between 1.5 and 5 eV, the production of H\(_3^+\) is comparable with the destruction mechanisms. The limiting factor in divertor plasmas is the high electron density, leading to a very efficient recombination of H\(_3^+\) and its precursor H\(_2^+\). Moreover in tokamaks, the electron temperature in the SOL is around \( \approx 100 \text{ eV} \) in the upstream region [58]. At such temperatures, hydrogen is fully dissociated and ionized, making H\(^+\) the only hydrogenic species flowing towards the divertor plate. Thus, we can deduce that the role H\(_3^+\) is negligible in Magnum-PSI and ITER-relevant divertor H\(_2\) plasma. The same conclusion has been obtained in [7].

### 7.4.5 Periphery of the plasma beam

In the edge of the plasma beam \( T_e \) is about 0.8 eV and \( n_e \) is \( \approx 5 \times 10^{19} \text{ m}^{-3} \). The most relevant plasma chemical mechanisms leading to the recombination of hydrogen ion and highlighted by the model for such scenario are shown in figure 10.

![Figure 8. Rate coefficients as a function of \( T_e \) for sources and sinks of H\(_3^+\). Blue line corresponds to the source reaction 74, while black and red are sink processes i.e. reactions 20 and 21.](image1)

![Figure 9. H\(^+\) and H\(_3^+\) densities evolution as a function of \( n_e \) calculated with the global model. Population inversion occurs at \( \approx 7 \times 10^{18} \text{ m}^{-3} \). For divertor-relevant electron densities i.e. \( > 10^{20} \text{ m}^{-3} \) the presence of H\(_3^+\) is negligible. Electron temperature was set at 1.5 eV.](image2)

![Figure 10. H\(^+\) sink routes calculated by the code at the edges of the beam. The first step is the ion conversion with a hydrogen molecule in vibrational excited state, gaining H\(_2^+\). This is followed by dissociative recombination (reaction 19) and proton transfer with \( N_2 \) producing \( N_2^+H\(^+\)\) (reaction 66). Such species is then consumed via reactions 30 and 31, producing NH and \( N_2 \).](image3)
Differently from the centre of the beam, where H' undergoes two separate ion conversions, the principal sink route of H' in this case is almost entirely via ion conversion with H₂[v], leading the production of H₃⁺. This product is consumed by both dissociative recombination and proton transfer with N₂, gaining two hydrogen atoms and N₂H⁺ respectively (reactions 19 and 66). The two sink processes of H₃⁺ in figure 10 have a relative contribution of 60% and 40% respectively. N₂H⁺ is then consumed by dissociative recombination (reactions 30, 31) producing NH and N₂. This additional branch involving N₂ as proton acceptor will be referred to as another N-MAR process. Differently from the conditions in the plasma centre, where the ion conversion is promptly followed by dissociative recombination, in the milder plasma edge conditions, a further molecular-induced step occurs indicating N₂H⁺ as ionic mediator.

H₃⁺ is found to be produced in a negligible amount in this case as well. This is different from what has been previously observed in PISCES-A[59], where H₃⁺ was detected in significant amount by mass spectrometry. Electron density in that study was between 10¹⁷ and 10¹⁸ m⁻³[60]. The density characterizing the edges of Magnum-PSI plasma and used in this study is above 10¹⁹ m⁻³, leading to an enhanced recombination frequency of the precursor H₃⁺ and efficient consumption mechanisms of H₃⁺.

7.4.6 Comparison between the full and the reduced global models

To ultimately verify the reaction scheme derived from the fully extended Plasmo global model, a reduced version has been produced. The chemical species implemented in the new global model and their steady-state densities are reported in table 3. All the most relevant hydrogenic species have been added, together with the nitrogen-related ones that were identified to play a major role in the considered plasma chemistry, as shown in the previous sections.

<table>
<thead>
<tr>
<th>nₑ</th>
<th>H</th>
<th>H₂</th>
<th>H₂v</th>
<th>H⁺</th>
<th>H⁺⁺</th>
<th>N₂</th>
<th>N</th>
<th>NH</th>
<th>NH⁺</th>
<th>N₂H⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>EXT</td>
<td>2.65E20</td>
<td>1.74E21</td>
<td>1.52E16</td>
<td>8.96E14</td>
<td>2.65E20</td>
<td>5.87E14</td>
<td>1.39E19</td>
<td>7.25E19</td>
<td>4.06E15</td>
<td>1.29E15</td>
</tr>
<tr>
<td>RED</td>
<td>2.61E20</td>
<td>1.73E21</td>
<td>1.62E16</td>
<td>8.2E14</td>
<td>2.61E20</td>
<td>6.32E14</td>
<td>1.03E19</td>
<td>8.18E19</td>
<td>1.3E15</td>
<td>4.11E15</td>
</tr>
</tbody>
</table>

Table 3. Electron density together with the species included in the reduced model. The densities achieved in both the full and reduced models (for the centre-of-the-beam case of study) are reported.

The initial densities have been kept the same in both cases of study i.e. 1*10²¹ m⁻³ for H₂ and 5*10¹⁹ m⁻³ for N₂. To achieve Tₑ and nₑ as close as possible, the chosen input power density is 2300 J/m³. This value is slightly lower than the one used in the full model simulation (2500 J/m³) due to the lower amount of particle densities populating the reduced model. Given the longer period needed to reach the steady state in this run, the simulation time is set at 5 ms. The achieved Tₑ is 1.2 eV in the full model and 1.16 eV in the reduced one. The electron densities gained in the simulations are almost identical as well. This is very important in order to deal with the same plasma environment. The plasma chemical reactions adopted for the reduced model are listed in table 4. The processes highlighted in figure 3 and figure 10, corresponding to the new N-MAR branches, have been included. Electron-induced ionization, vibrational excitation, dissociation and elastic collisions are also taken into account. For completeness, the most relevant neutral-neutral process has been implemented in the reduced version as well, namely reaction 49. That is in fact the most important process in such environment that relates two neutral key-species i.e. molecular hydrogen and atomic nitrogen. The scope of this work is to maximally reduce the amount of species and plasma chemical reactions occurring in the volume of a detached-like scenario. In such way, the underlined mechanisms can be implemented in a more detailed spatially-resolved code. To compensate the absence of the main NH sources i.e. electron - impact dissociation of NH, species and dissociative recombination of their ionic derivatives, an extra source of NH has been added together with an identical sink of N and H (8*10⁴⁰ m⁻³·s⁻¹); in this way,
particle balance is conserved and the system is closed. The total amount of NH particles added in the simulation corresponds to ≈ 7 % conversion of nitrogen to ammonia, which is in line with literature studies [61], [62], [63].

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H + e^- \rightarrow H^+ + 2e^-$</td>
<td>Ionization</td>
</tr>
<tr>
<td>$H_2 + e^- \rightarrow H^+_2 + 2e^-$</td>
<td>Ionization</td>
</tr>
<tr>
<td>$N_2 + e^- \rightarrow N + N + e^-$</td>
<td>Dissociation</td>
</tr>
<tr>
<td>$H_2 + e^- \rightarrow H_2v + e^-$</td>
<td>Vibrational excitation</td>
</tr>
<tr>
<td>$H_2v + H^+ \rightarrow H_2^+ + H$</td>
<td>Ion conversion</td>
</tr>
<tr>
<td>$H_2^+ + e^- \rightarrow H + H$</td>
<td>Dissociative recombination</td>
</tr>
<tr>
<td>$H_2 + N \rightarrow NH + H$</td>
<td>Atom transfer</td>
</tr>
<tr>
<td>$N_2 + H_2^+ \rightarrow N_2H^+ + N$</td>
<td>Proton transfer</td>
</tr>
<tr>
<td>$N_2H^+ + e^- \rightarrow N_2 + H$</td>
<td>Dissociative recombination</td>
</tr>
<tr>
<td>$N_2H^+ + e^- \rightarrow NH + N$</td>
<td>Dissociative recombination</td>
</tr>
<tr>
<td>$NH + H^+ \rightarrow NH^+ + H$</td>
<td>Ion conversion</td>
</tr>
<tr>
<td>$NH^+ + e^- \rightarrow N + H$</td>
<td>Dissociative recombination</td>
</tr>
<tr>
<td>$H + e^- \rightarrow H + e^-$</td>
<td>Elastic</td>
</tr>
<tr>
<td>$H_2 + e^- \rightarrow H_2 + e^-$</td>
<td>Elastic</td>
</tr>
<tr>
<td>$N + e^- \rightarrow N + e^-$</td>
<td>Elastic</td>
</tr>
<tr>
<td>$N_2 + e^- \rightarrow N_2 + e^-$</td>
<td>Elastic</td>
</tr>
</tbody>
</table>

Table 4. List of the plasma chemical reactions implemented in the reduced model. The two N-MAR mechanisms, together with the most important hydrogen reactions and electron-induced processes, have been inserted in the model. Rate coefficients are the same as in the full version.

The achieved densities are shown in figure 11. The densities of the hydrogenic species are in very good agreement. This confirms the importance of the reactions producing H, which are the ion conversion of H$^+$ with H$_2$($\nu=4$) and with NH, and the dissociative recombination of H$_2^+$ and NH$^+$, gaining 2 H and N + H respectively. H$_2$ is consumed predominantly via electron-impact vibrational excitation and atom transfer with atomic nitrogen with a relative contribution of about 50% for each process.

H$^+$ in both cases is equal to the electron density. In these global models, quasi-neutrality is always maintained. H$^+$ is the main ionic species in the system and is consumed via ion conversions. Worth mentioning here that the so-called three-body recombination reaction i.e. $H^+ + e^- + e^- \rightarrow H^+(n \geq 6) + e^-$, involving two electrons and H$^+$, becomes efficient at temperatures below 0.7 eV with densities above 1*10$^{21}$m$^{-3}$, hence not relevant for the scenario considered here. According to the models, N$_2$ is depleted by means of electron-induced dissociation and proton transfer with H$_2^+$, the latter being highlighted as second branch of the N-MAR processes. N main sources are via reaction 51 and reaction 23, which is the final step of the first N-MAR path (see figure 3).

The final densities of NH are in good agreement. The difference is due to the absence in the reduced version of the electronically excited species N$_2$(A$^3\Sigma^+$) and its efficient atomic transfer with H (reaction 81), which acts as a source for NH. Such discrepancy suggests the small importance of other NH sink mechanisms i.e. electron-impact dissociation (reaction 34) and atom transfer with H (reaction 51).

In both extended and reduced models, the main source of NH$^+$ is the ion conversion between NH and H$^+$, as stated in section 2.2.2. The slight overestimation of this ion is due to either the absence of the following source collision (reaction 67) H$_2^+ + N \rightarrow NH^+ + H$ and the sink processes via proton transfer i.e. reaction 83 and 84. Such reactions have not been included in the reduced model, considering that constitute less than 10% to the overall relative contribution of sources and sinks of NH$^+$. Our aim is, in fact, to underline only the most important mechanisms leading to the conversion
of atomic hydrogen ions to neutrals, addressing the volume processes introduced by nitrogen-containing species.

$N_2H^+$, pointed out to be an important ion mediator in section 7.4.5, is verified to be produced via proton transfer (reaction 66) and consumed by reaction 30 and 31.

To assure the validity of the reduced model among a wider range of plasma parameters, a comparison between the extended and the reduced model has been carried out for other two different scenarios i.e. beam-edge conditions with $T_e = 0.8$ eV and $n_e = 6\times10^{19} m^{-3}$ and a high-density higher-temperature case with $n_e = 3.4\times10^{20} m^{-3}$ and $T_e = 1.8$ eV. Results are shown in figure 11. The densities of the underlined relevant species are again in very good agreement. We hereby prove the validity of the reduced set of chemical equations for parameters $5\times10^{19} < n_e < 3.5\times10^{20} m^{-3}$ and $0.8 < T_e < 2$ eV. For scenarios with $n_e < 10^{19} m^{-3}$, a different reduced set of reactions would be needed, namely the processes reported in section 7.4.3. In such plasma environment, molecular ions become the major ion species, being proton transfer the dominant ion-neutral inelastic mechanism. An implementation of those processes in a spatially-resolved code is beyond the scope of this work, which focuses on Magnum-PSI relevant plasma scenarios.

The work carried out in this section served to validate the derived set of reactions and species from the full model. The most effective relations, named N-MAR and stated in figure 3 and figure 10 have been confirmed by this exercise to be the most relevant. The delicate balance between the different species densities set by the chemical equations and validated here, has to be considered true only for
the scenario considered i.e. divertor-relevant high-density low-temperature hydrogen plasma in the presence of nitrogen. These processes have been included in Eunomia and a description of the implementation will be given hereafter.

7.5 Eunomia code

Eunomia is a spatially resolved Monte-Carlo code created to simulate neutral particles in linear plasma machines, originally suited to model the neutral inventory in Pilot-PSI and Magnum-PSI. The code is conceptually similar to the well-established Monte Carlo code Eirene[64]. The code solves the equilibrium density, flow velocity and temperature of the ground state species and is based on the test-particle approximation method i.e. simulates test particles which represent many real neutral particles. In Eunomia charged particles are not simulated and plasma equations are not solved. The plasma background is given as an input and $T_e$ and $n_e$ have been taken from Thomson Scattering measurements in Magnum-PSI[65]. In the code, test particles never interact with each other; they undergo through test particle-background particle collisions as follows: a charged particle or a neutral particle is drawn from the maxwellian velocity distribution from the background to be collided with the test particle. Information about species densities and velocity distributions subsequent to each collision event are stored by the code over the simulation grid for every cycle. That constitutes the temporary neutral background, that will be substituted by the newly calculated one the next cycle. In Eunomia, such process is called scoring. In order to calculate sources and sinks for the neutral background, many test-particles are simulated. Each time a test particle visits a cell, the code stores its residence time as estimator of relative density. To determine the actual particle density, the number of real particles represented by a test-particle has to be given as input. The input determines also either the number of test particles or the maximum time to be modelled. Once a source is simulated, the number of test particles is known. The actual number of particles is then calculated by the code as:

$$N_{rp} = \Gamma_{rp} \tau_a$$

Where $\Gamma_{rp}$ is the influx of real particles into the system per second and $\tau_a$ is the averaged residence time. Although no direct effects on the plasma can be modelled with Eunomia in the stand-alone version, important insights on the behaviour of neutral atoms and molecules, such as their sources, sinks, spatial distribution and transport, can be studied. Further specifications on the code, such as calculation of velocity distributions and temperatures, can be found in [11].

7.5.1 Eunomia grid and geometry

Figures 12 and 13, taken from [11], show a schematic view of the linear plasma machine Pilot-PSI and the derived cylindrical symmetry adopted in Eunomia. In the code, the simulation is carried out in a 3-dimensional environment and the results are provided in a 2-D grid averaged over the rotation axis, as can be seen in figure 13. Figure 14 shows the triangular grid on which the cell averaging is done in order to define the neutral background. The rate coefficients of each process is calculated at the beginning of each cycle as a function of the local $T_e$ and $n_e$. 
As shown in figure 14, the cells have flexible areas and become larger moving away from the target. For each wall the test-particles can be either reflected or absorbed. For the axis of symmetry the test-particle will always undergo specular reflection. The walls can act as a recombining front of atomic hydrogen with the following mechanism: $H_w + H_w \rightarrow H_2^{\text{bulk}}$, where the product is released from the wall and enters the volume phase. N-related species have been treated differently i.e. the particles impinging on a wall are thermalized and reflected with a cosine distribution. It is worth mentioning that gas-surface heterogeneous phenomena leading to the production of ammonia are beyond the aim of this study, which is entirely focused on volume processes.

The orange segment corresponds to the plasma source, the blue line is the axis of symmetry of the plasma beam and the red one is the target. Green lines are the walls of the vessel. The shaft of the target, indicated also in green, is treated by the code to act as a vessel wall. For the modelling of the pump (magenta segment in figure 14), the simulation of test-particle is stopped once it reaches that region. The grid depicted here and used in this work is a representation of the Pilot-PSI linear device[66].
7.5.2 Implementation of the reduced model into Eunomia

The hydrogen-related collisions used in the code are listed in table 5. The cross sections for neutral-neutral elastic collisions (reactions n. 1, 2, 3, 9 and 10) are based on the Lennard-Jones potential [67] and the BGK approximation method is used [68]. The rates of such processes depend on the iteratively updated background of the ground-state species. The rates for inelastic collisions between neutrals and charged particles (reactions 5, 6, and 7) are imported from the AMJUEL [69] and HYDHEL [26] databases, which are the same used by Eirene code. For electron-induced processes (reactions 4, 6 and 8), the rates are calculated as a function of the local per-cell $T_e$ and $n_e$ at the beginning of each cycle.

<table>
<thead>
<tr>
<th>N#</th>
<th>Reaction</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$H + H \rightarrow H + H$</td>
<td>Elastic</td>
</tr>
<tr>
<td>2</td>
<td>$H + H_2 \rightarrow H + H_2$</td>
<td>Elastic</td>
</tr>
<tr>
<td>3</td>
<td>$H_2 + H_2 \rightarrow H_2 + H_2$</td>
<td>Elastic</td>
</tr>
<tr>
<td>4</td>
<td>$H + e^- \rightarrow H^+ + 2e^-$</td>
<td>Ionization</td>
</tr>
<tr>
<td>5</td>
<td>$H^+ + H \rightarrow H + H^+$</td>
<td>Charge exchange</td>
</tr>
<tr>
<td>6</td>
<td>$H_2 + e^- \rightarrow H + H + e^-$</td>
<td>Dissociation</td>
</tr>
<tr>
<td>7</td>
<td>$H_2 + H^+ \rightarrow H + H^+$</td>
<td>MAR</td>
</tr>
<tr>
<td></td>
<td>$e^- + H_2^+ \rightarrow H + H_n^+$</td>
<td>MAR</td>
</tr>
<tr>
<td>8</td>
<td>$H^+ + H^+ \rightarrow H + H^+$</td>
<td>MAR</td>
</tr>
<tr>
<td></td>
<td>$H^+ + H^+ \rightarrow H + H_{n=2}^+$</td>
<td>MAR</td>
</tr>
<tr>
<td>9</td>
<td>$H + H^+ \rightarrow H + H^+$</td>
<td>Elastic</td>
</tr>
<tr>
<td>10</td>
<td>$H_2 + H^+ \rightarrow H_2 + H^+$</td>
<td>Elastic</td>
</tr>
</tbody>
</table>

Table 5. Hydrogenic reactions included in Eunomia.

The frequency of MAR processes (reactions 7 and 8) is governed by the first step i.e. ion conversion and dissociative attachment, respectively. The reaction intermediates $H^+_n$ and $H^+$ are assumed to instantaneously recombine. The electronically excited states of atomic hydrogen produced in those processes are not simulated. The de-excitation probability of $H^+(n=2)$ gained in reaction 7 is calculated by the ratio between collisional excitation to $n=3$ and spontaneous decay, while for $H^+(n=3)$ of reaction 8, it is assumed to eventually ionize [70].

The additional nitrogen-included plasma chemistry actualized in the code corresponds to the one highlighted with global modelling and verified by the comparison with the full model, as described in section 2.2.5. In this implementation, neutral - neutral elastic collisions have been added for completeness and are listed in table 6. Such collisions can affect the momentum of the test particles, hence they are important when dealing with spatially-resolved transport codes. This is not the case for zero-dimensional-model, such as the global model platform provided by Plasimo. Data regarding potential energy curves and internuclear distances, needed for the BGK approximation, have been taken from [71], [72] and references therein.

<table>
<thead>
<tr>
<th>N#</th>
<th>Reaction</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$NH + H_2 \rightarrow NH + H_2$</td>
<td>Elastic</td>
</tr>
<tr>
<td></td>
<td>$NH + H \rightarrow NH + H$</td>
<td>Elastic</td>
</tr>
<tr>
<td></td>
<td>$NH + N_2 \rightarrow NH + N_2$</td>
<td>Elastic</td>
</tr>
<tr>
<td></td>
<td>$NH + N \rightarrow NH + N$</td>
<td>Elastic</td>
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<tr>
<td></td>
<td>$H_2 + H_2 \rightarrow H_2 + H_2$</td>
<td>Elastic</td>
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<td></td>
<td>$H_2 + N_2 \rightarrow H_2 + N_2$</td>
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<td></td>
<td>$H + N \rightarrow H + N$</td>
<td>Elastic</td>
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<td></td>
<td>$H + H \rightarrow H + H$</td>
<td>Elastic</td>
</tr>
</tbody>
</table>
Table 6. Neutral-neutral elastic collisions implemented in Eunomia.

<table>
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<tr>
<th>Reaction</th>
<th>Collision Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>(N + N \rightarrow N + N)</td>
<td>Elastic</td>
</tr>
<tr>
<td>(N + N_2 \rightarrow N + N_2)</td>
<td>Elastic</td>
</tr>
<tr>
<td>(H_2 + N \rightarrow H_2 + N)</td>
<td>Elastic</td>
</tr>
<tr>
<td>(N_2 + H \rightarrow N_2 + H)</td>
<td>Elastic</td>
</tr>
</tbody>
</table>

N-MAR mechanisms are treated in a similar way as the hydrogenic MARs i.e. reactions 7 and 8 in table 5: the products are assumed to recombine instantaneously, and the rate-determining step is the ion conversion. An update in the code has been made to include the atom transfer reaction i.e. \(H_2 + N \rightarrow NH + H\). This mechanism has been treated in a two-step process: firstly, this reaction acts as a source for NH and H i.e. these products are generated as new test particles based on the rate constant and the reactants background information. The velocities are drawn randomly from maxwellian distributions. Secondly, the particle balance is conserved by adding compensating collision process that terminates the reactant test particles i.e. N and H\(_2\), which follow the usual collision mechanics in the simulation. This collision also uses the same rate constant as the source reaction.

7.6 Eunomia results

Eunomia runs have been carried out by using the parameters that characterize a typical semi-detached hydrogen plasma in Magnum-PSI linear device i.e. \(T_e = 1.5\) eV and \(n_e = 2.5 \times 10^{20} \text{m}^{-3}\). In the code, both these parameters have a full-width half-maximum (FWHM) of 20 mm and are constant along the beam. In linear plasma machines detachment scenarios are achieved by means of gas puffing, causing an increased background neutral pressure. Neutrals play a major role in cooling down the plasma by means of electron - neutral and ion - neutral collisions, and by increasing the molecular-assisted recombination frequency[73]. Gas seeding has been modelled and the injection location has been set at the target. The key feature introduced by nitrogen seeding investigated in this paper is the enhanced frequency of the recombination mechanisms compared to a case where only H\(_2\) is puffed into the system. The most relevant N-species acting as electron donor highlighted in this work is NH. Precursor of such species is mostly ammonia. NH\(_3\) is almost entirely produced by means of surface processes. Although modelling of those wall-induced mechanisms is beyond the scope of this paper, which is strictly focused on volume processes, NH\(_3\) also acts as a source for NH through reactions 37 and 39 with \(k_37 = 1.5 \times 10^{-9} \text{cm}^3\text{s}^{-1}\) and \(k_39 = 9.5 \times 10^{-12} \text{cm}^3\text{s}^{-1}\). Ion conversion of ammonia (reaction 61) leading to NH\(_3^+\) is very efficient in this plasma environment, with \(k_{61} = 1.33 \times 10^{-9} \text{cm}^3\text{s}^{-1}\) for a gas temperature of 0.2 eV. Such temperature has been highlighted by previous studies [11] to be the temperature of neutrals in the plasma beam of Pilot-PSI and Magnum-PSI linear machines. In Eunomia, the gas temperature is provided as an output, and is calculated by the code to be 0.21 eV in the simulations carried out and presented hereafter. Such high molecular temperature is considered by us to be due to the efficient ion-neutral elastic collision leading to momentum transfer, which acts as heating mechanism for heavy particles. Atomic and molecular nitrogen temperatures are in the same range i.e. between 0.15 and 0.24 eV. The temperature of atomic hydrogen given by the code goes up to \(~0.45\) eV. We address this to be caused by the resonant charge exchange process i.e. \(H^+ + H \rightarrow H + H^+\), a well-known cooling mechanism for hydrogen ion (reaction 5 in table 5). NH\(_3^+\) undergoes dissociative recombination with a rate of \(2.04 \times 10^{-8} \text{cm}^3\text{s}^{-1}\) with \(T_e = 1.5\) eV, leading NH and 2H (reaction 26). Another source of NH is the amino radical NH\(_2\). This species contributes to the production of NH via reactions 35 and 47, namely electron-impact dissociation, with \(k_{35} = 2.57 \times 10^{-10} \text{cm}^3\text{s}^{-1}\) and \(k_{47} = 2.98 \times 10^{-11} \text{cm}^3\text{s}^{-1}\) for \(T_e = 1.5\) eV and Tgas = 0.2 eV. Its ion derivative i.e. NH\(_2^+\), which is produced via ion conversion (reaction 63) and proton transfer (reaction 82), contributes efficiently to the production of NH by means of dissociative recombination (reaction 24), with \(k_{47} = 2.01 \times 10^{-8} \text{cm}^3\text{s}^{-1}\). To take these processes into account in Eunomia runs, a source of NH from the target has been added, corresponding
to 5% of the total nitrogen injected. The volume sources of NH included in the model are atom transfer and dissociative recombination of \( \text{N}_2\text{H}^+ \), both listed in table 4.

In figure 15 the density distribution of NH calculated by Eunomia for a 5% nitrogen seeding case is shown. NH decreases moving away from the target along the plasma beam due to the effective N-MAR i.e. reaction 20 in table 4. Elastic collisions of NH with \( \text{N}_2 \) and \( \text{H}_2 \) may also play a role enhancing the perpendicular diffusion of the species in respect to the plasma beam. The density increases outside the beam, where the concentrations of \( \text{H}_2 \) and N are high, leading an efficient atom transfer process.

In figure 16 the spatially-resolved collision frequency of the first N-MAR is shown. The test-particle collisional events are localized in the centre of the beam and in the vicinity of the target. This is in line with the density distribution of figure 16, since in that region NH efficiently undergoes N-MAR. Such mechanism is addressed to further contribute to the conversion of incoming atomic hydrogen ions to neutrals, reducing the incoming flux towards the target and eventually making heat loads more tolerable for the material.

To quantify the influence of the N-MAR process on the overall recombination efficiency, three different cases of studies, characterized by different puffing scenarios, have been set up as follows:

\[
\frac{[N_2]}{[H_2] + [N_2]} = 0.5, 10 \%
\]

While keeping fixed the amount of molecules injected in the system from the target i.e. \( 2.1\times10^{20} \text{ m}^{-3}\text{s}^{-1} \), three different nitrogen contents have been examined. The aim is to compare the recombination efficiency by tracing the density of atomic hydrogen, which is eventually the end product of any recombination process in this specific plasma environment.

In figure 17 the H-density radial profile taken at 3 cm in front of the target is shown. Interestingly, the H density in the plasma beam is higher in the 10% and 5% cases, compared to the only-H\(_2\) case. Values
taken in the centre of the plasma beam are $8.75 \times 10^{18}$, $1.98 \times 10^{19}$ and $2.74 \times 10^{19}$ m$^{-3}$ for 0, 5 and 10% \text{N}_2 content.

This indicates that the presence of \text{N}_2 and, subsequently of \text{NH}, contributes to further enhance recombination processes in the centre of the beam via \text{N}-\text{MAR} mechanisms.

The plasma beam in the simulations has a FWHM of 20 mm. The region between radial position 0.01 and 0.02 m is characterised by strong gradient in terms of $T_e$ and $n_e$ i.e. from $1 \times 10^{20}$ to $5 \times 10^{16}$ m$^{-3}$ and from 0.6 to 0.1 eV for electron density and temperature respectively. Within the plasma beam width, the main source for atomic hydrogen is the static plasma itself i.e. \text{H}^+$. \text{H} is produced by means of recombination processes, specifically \text{MAR} and \text{N-MAR}. The seeding location in the simulations is set to be the target segment, hence, it has a wider surface compared to the beam, with a radius of 35 mm.

The density of \text{H} in the region between 10 and 20 mm radius i.e. outside the plasma beam, at 3 cm in front of the target is then barely influenced by plasma-neutrals inelastic collisions, whose study is the main scope of this work. The closeness to the target and the different \text{H}_2/\text{N}_2 seeding ratios led to a discrepancy in \text{H} density between the three cases of study. This is due to transport phenomena and elastic collisions. More detailed study on the transport of charged particles outward the beam will be carried out with the coupled codes B2.5-Eunomia.

Although no direct evidence on the contribution of \text{N}_2\text{H}^+ increasing recombination frequency can be directly provided with this code, its importance is not to be considered only of a phenomenological nature. In fact, it acts as source for \text{NH}, which has been proved to constitute the most important N-related species in the conversion of ions to neutrals. Further studies on the reaction paths leading to \text{N}_2\text{H}^+, moreover, can contribute to the overall comprehension of the plasma chemical effects caused by the presence of nitrogen in the volume phase of a low-temperature hydrogen plasma.

### 7.7 Summary and conclusions

Volume reactions, such as molecular-assisted recombination, can contribute to reduce the incoming ion flux to the divertor plate. To understand the role of nitrogen in the plasma chemistry of a detached hydrogen plasma, numerical simulations are needed. A comprehensive global model has been set up by means of Plasimo code. Two newly-proposed molecular-assisted recombination processes, called \text{N-MAR}, have been highlighted. These reaction paths are: \text{NH} + \text{H}^+ \rightarrow \text{NH}^+ + \text{H}$ followed by $\text{NH}^+ + e^- \rightarrow \text{N} + \text{H}$ in the centre of the beam (where parameters are very similar to the ones foreseen for ITER divertor) and $\text{H}_2^+ + \text{N}_2 \rightarrow \text{N}_2\text{H}^+ + \text{H}$ with the subsequent dissociative
recombination of diazenilium i.e. $N_2H^+ + e^- \rightarrow NH + N$ or $N_2 + H$ in the periphery of the beam. A reduced global model including N-MARs has been implemented and compared with the full model for three different $T_e$ and $n_e$ scenarios. Despite the lower number of species considered and the strong reduction of chemical reactions, the results match properly and the differences are all widely within the order of magnitude. This indicates the processes to be considered the dominant mechanisms occurring in the scenario examined. N-MARs, together with elastic collisions, electron impact dissociation and atomic transfer, have been implemented in Eunomia, a spatially-resolved Monte Carlo code suited for the transport of neutrals in linear machines. The test-particle collision frequency of the first N-MAR in Eunomia is showed to be centrally localized in the vicinity of the seeding location. The density of atomic hydrogen, which is the end product of recombination, has been monitored to compare the effectiveness of nitrogen-induced conversion of ions to neutrals. Results indicate that the presence of $N_2$ affects the content of H by almost a factor 3 between only $H_2$ and 10% nitrogen seeding cases of study. The newly-updated Eunomia code will be coupled with the fluid code B2.5. This will constitute an important numerical tool to study the effects of impurity seeding on detachment for both divertors and linear machines. The reduced plasma-chemical data set obtained in this work can be used and implemented also in other codes for the transport of neutrals in the divertor, such as EIRENE (embedded in SOLPS-ITER package)[74].

7.8 Acknowledgments
DIFFER is part of the Netherlands Organisation for Scientific Research (NWO). This work has been carried out within the framework of the EUROfusion Consortium and has received funding from both Euratom and NWO. The views and opinions expressed herein do not necessarily reflect those of the European Commission.

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Chapter 8

Experimental evidence of enhanced recombination of a hydrogen plasma induced by nitrogen seeding in linear device Magnum-PSI.


8.1 Abstract

In this work we investigate the effects induced by the presence of nitrogen in a detached-like hydrogen plasmas in linear plasma machine Magnum-PSI. Detachment has been achieved by increasing the background neutral pressure in the target chamber by means of H₂/N₂ puffing and two cases of study have been set up, i.e. at 2 and 4 Pa. Achieved ne are ITER-relevant i.e. above 10²⁰m⁻³ and electron temperatures are in the range 0.8 - 2 eV. A scan among five different N₂/H₂+N₂ flux ratios seeded have been carried out, at values of 0, 5, 10, 15 and 20%. A ne decrease while increasing the fraction of N₂ has been observed for both background pressures, resulting in a plasma pressure drop of ~ 30%. Tₑ remains constant among all scans. The peak intensity of NH⁺(A[^3]Π→X[^2]Σ⁺, Δv = 0) at 336 nm measured with optical emission spectroscopy increases linearly with the N₂ content, together with the NH₃ signal in the RGA. A further dedicated experiment has been carried out by puffing separately H₂/N₂ and H₂/He mixtures, being helium a poorly-reactive atomic species, hence excluding a priori nitrogen-induced molecular assisted recombination. Interestingly, plasma pressure and heat loads to the surface are enhanced when increasing the content of He in the injected gas mixture. In the case of N₂, we observe an opposite behaviour, indicating that N-H species actively contribute to convert ions to neutrals. Recombination is enhanced by the presence of nitrogen. Numerical simulations with two different codes, a global plasma-chemical model and a spatially-resolved Monte Carlo code, address the role of NH₃ species behaving as electron donor in the ion conversion with H⁺ by means of what we define here to be N-MAR i.e. NH₃ + H⁺ → NH₂⁺ + H, followed by NH₂⁺ + e⁻ → NH⁺ + H. Considering the experimental findings and the qualitative results obtained by modelling, N-MAR process is considered to be a possible plasma-chemical mechanism responsible for the observed plasma pressure drop and heat flux reduction. Further studies with a coupled code B2.5-Eunomia are currently ongoing and may provide quantitative insights on the scenarios examined in this paper.

8.2 Introduction

Plasma detachment is characterized by a plasma pressure drop along the magnetic field lines towards the divertor target and by a significant reduction of the ion flux together with lower power loads [1]. Detachment is characterized by a “roll-over” of the ion saturation current measured at the target [2]. Such phenomena is achieved by a synergistic effect of radiative losses, momentum transfer from incoming ions to neutrals and volumetric recombination. Although it has been proposed that molecular-activated recombination (MAR), as well as three-body and radiative recombination, may play an important role for plasma detachment in linear devices [3][4][5], a limited contribution of MAR has been highlighted in tokamak divertor detachment [6][7]. In this paper we focus specifically on the role of nitrogen and hydrogenated nitrogen molecules on the neutralization of atomic hydrogen ions and on the effects over plasma parameters. It has been observed [8][9] that impurity seeding facilitates the realization of a detached plasma regime. Nitrogen is the current leading candidate for impurity seeding in ITER[10]. The atomic and molecular processes led by N₂ injection in a divertor-like hydrogen plasma (nₑ > 10²⁰m⁻³) is yet poorly understood. Linear devices have extensively contributed in
understanding plasma detachment because of the good diagnostic accessibility and the capability of maintaining a detached plasma in a steady-state regime for a long time at a relatively low cost [11]. The heat flux to the target is expressed as: \( q = \Gamma [\gamma T_e + E_i] \), whith \( \Gamma \) the ion flux, \( \gamma \) the sheath heat transmission coefficient, and \( E_i \) the intrinsic ion potential energy (18.08 eV per atomic hydrogen ion). The cooling of plasma is not enough by itself to reduce the heat loads, given the ion’s potential released on the plate due to surface recombination process[12]. Volume recombination is needed to reduce the charged particle flux, converting ions to neutrals [13]. It is worth mentioning that the release of H\(_2\) molecules in vibrational excited state from the target depends on the surface temperature and on the adopted material. Further insights on this phenomenon can be found in [14]and references therein. A newly-addressed aspect relative to plasma detachment is the concept of power limitation [15][16]. In a tokamak, the bulk of the particle source is located in the divertor in the vicinity of the target (the mean free path for neutral ionization is smaller than the typical divertor size). The energy for such ionization needs to be provided by power coming from further upstream. Impurities injection radiate away part of this power, typically further upstream from the recycling region. Hence, less power is available for ionization, causing an upshifting of the recombination front and the rollover of the target particle flux. In Magnum-PSI this is not the case, in fact there is a constant particle and energy flux coming from the source. The magnetically confined plasma goes throughout the source and middle chambers without significant power dissipation (differential pumping is designed to remove neutral particles along the beam path). During normal Magnum-PSI operation, even in attached-like scenarios, \( T_e \) is not sufficiently high to drive a relevant ionization source in the target chamber.

The scope of this work is to study the influence of different nitrogen concentrations on the plasma parameters in a detached plasma scenario in the upgraded linear plasma machine Magnum-PSI[17]. This is done by using Thomson Scattering (TS), Optical Emission Spectroscopy (OES), Residual Gas Analyser (RGA) and calorimetry. Numerical simulations have been used to provide qualitative explanation of the observed nitrogen-driven N-MAR processes. In a tokamak perspective, this paper focuses on highlighting the dominant recombination mechanisms occurring in the vicinity of the divertor target in a N\(_2\)-seeded detached hydrogen plasma.

### 8.3 Experimental set up and diagnostics

Linear machine Magnum-PSI is a unique plasma generator capable of mimic the foreseen plasma conditions of ITER divertor, i.e. \( T_e \leq 5 \) eV, \( n_e \geq 10^{20} \text{m}^{-3} \) and particle flux up to \( 10^{24} \text{m}^{-2} \text{s}^{-1} \), leading to heat loads of about 10 MWm\(^{-2}\)[18]. A detailed description of the design of the machine together with its capabilities can be found here[19]. In short, the machine is characterized by three different chambers, namely source chamber, heating and target chamber[20]. Differential pumping, together with skimmers located at the entrance of each chamber, separate these environments. In this way, plasma pressure is conserved throughout the entire beam, hence exposing the target to ITER-relevant plasma. Plasma is generated by means of a cascaded arc plasma source [21] located in the source chamber and is confined in the \( z \) direction towards the target by a superconducting magnet. The background pressure in the target chamber, during normal “attached” operation is \( \approx 0.3 \) Pa. The target consists of a tungsten (W) plane circular target with a diameter of 3 cm and a thickness of 1 mm. Detached-like conditions are achieved by increasing the total background pressure in the target chamber, as will be explained in section 3. \( T_e \) and \( n_e \) have been diagnosed by means of TS, located at 3 cm in front of the target. A detailed description of the system can be found in [22]. For the analysis of nitrogen key-species in the plasma, a two-channel fiber-optic spectrometer (AvaSpec-ULS2048) with a bandwidth coverage between 299 and 579 nm has been used. Of particular interest for this work is the signal at 336 nm, corresponding to the \( \text{NH}^+ (\text{A}^2\Pi \rightarrow \text{X}^2\Sigma^+) \) transition. The location of OES is the same as TS i.e. 3 cm in front of the target. For the monitoring of ammonia, a residual gas analyser (SRS-RGA) has been
adopted. It consists of an ionizer, a quadrupole mass filter and a detector. Peaks at \( m/q \) 15,16 and 17 amu, corresponding to \( \text{NH} \), \( \text{NH}_2 \) and \( \text{NH}_3 \) species, have been monitored in this study. To measure the heat loads onto the target surface, calorimetry has been used.

### 8.4 Plasma detachment in linear machine Magnum-PSI

Detachment of the plasma beam from the target is achieved by gas seeding in the target chamber hence increasing the overall background neutral pressure. In figure 1 is reported a background pressure scan of a \( \text{H}_2 \) plasma, from 0.3 to 16.5 Pa. Neutral pressure has been enhanced by puffing hydrogen in the target chamber. The dotted line corresponds to TS line of sight, while the straight line represents the target location.

![Figure 1](image1.png)

*Figure 1. Background pressure scan. Images taken with Phantom camera with Balmer-alpha filter. Straight and dotted lines correspond to location of the target and TS line of sight respectively.*

In figure 1(a), where a typical attached plasma is depicted, light emission is observed predominantly in the vicinity of the target. This is interpreted as ion recycling at the target, followed by electron-impact excitation of the neutral particles released from the surface. When increasing the neutral background pressure up to \( \approx 6 \) Pa i.e. 1(b), (c) and (d), we observe a shift of the light emitted from the vicinity of the target to throughout the portion of observed plasma beam. Increasing the pressure further (1 (e) and 1(f)) leads to a visible extinction of the plasma beam before reaching the target. The experimental detached-like scenarios chose for this work correspond to 2 and 4 Pa, where plasma parameters are suitable for recombination i.e. \( T_e < 2 \) eV and \( n_e > 5 \times 10^{19} \) m\(^{-3}\).

![Figure 2](image2.png)

*Figure 2. Left: total static plasma pressure as a function of the vessel background pressure. Right: peaked electron temperature as a function of neutral background pressure in the target chamber.*

In figure 2 total static plasma pressure, calculated as \( P_p = 2kT_e n_e \) (assuming \( T_e = T_i \)) is plotted as a function of the background neutral pressure in the vessel. By increasing the amount of gas in the chamber up to 16 Pa, plasma pressure drops almost to zero. We address such behaviour to be mostly due to volumetric recombination of incoming hydrogen ions. The effect of radiative cooling alone on the plasma pressure drop is excluded to be dominant in Magnum-PSI detached-like scenarios because of the constant power input coming from the plasma source. Moreover, given the plasma pressure conservation along the beam [23], no power starvation phenomena are expected to be dominant in
this environment. Regarding H₂-driven volume recombination, MARs are initiated by hydrogen molecules in vibrational excited states and constitute of two different two-step reaction paths, i.e.:

1) \( \text{H}_2(v) + \text{H}^+ \rightarrow \text{H}_2^+ + \text{H} \)

\( \text{H}_2^+ + \text{e}^- \rightarrow \text{H}^+ + \text{H} \)

2) \( \text{H}_2(v) + \text{e}^- \rightarrow \text{H}_2^- + \text{H} \)

\( \text{H}^- + \text{H}^+ \rightarrow \text{H}^0 + \text{H} \)

Reaction (1) is initiated by ion conversion and is followed by dissociative recombination, while the first step of reaction (2) is dissociative attachment, which is followed by mutual neutralization. In both cases, \( \text{H}^+ \) is effectively converted to neutral. In the plasma environment of this case of study, molecular ion \( \text{H}_2^+ \) is poorly produced due to very efficient dissociative recombination of its ionic primitive \( \text{H}_2^+ \)[24].

In a nitrogen-seeded environment we expect plasma chemistry to be influenced by the presence of \( \text{N}_2^+ - \text{H}_2 \) species. In the next paragraph, the effect on plasma parameters caused by the addition of different \( \text{H}_2/\text{N}_2 \) ratios puffed in the target chamber is investigated and discussed.

8.5 Nitrogen seeding experiments

Neutral background pressure has been enhanced in the target chamber by means of two remote controlled seeding valves, one for \( \text{H}_2 \) and the other for \( \text{N}_2 \), with a flow rate up to \( 2.4 \times 10^{-4} \text{m}^3 \text{s}^{-1} \). The \( \text{H}_2 \) gas flow through the source is fixed at \( 1.16 \times 10^{-4} \text{m}^3 \text{s}^{-1} \), the current at 120 A and the applied magnetic field is 1.2 T. The target plate is kept perpendicular to the plasma beam. The RGA is placed at the end of the pump tube that connects the target chamber with the roots pump. A baseline scenario has been defined experimentally and it represents the “attached” case. No molecular gas has been introduced in the vessel, with pumping rate at 100 %, resulting in a background pressure of 0.3 Pa. Peaked plasma parameters obtained in that case are \( T_e = 3.48 \text{ eV} \) and \( n_e = 1.3 \times 10^{20} \text{m}^{-3} \). Subsequently, two detached cases of study have been set up: background neutral pressure has been kept fixed at 2 and 4 Pa. For each case, a scan consisting of different nitrogen flux ratios of puffed gas has been carried out for

\[ \frac{[\text{N}_2]}{[\text{H}_2]+[\text{N}_2]} \times 100 = 0, 5, 10, 15, 20 \% \]

In figure 3 electron density and temperature profiles are reported for each seeding ratio at background pressures of 2 and 4 Pa.
The full-width-half-maximum (FWHM, averaged over all H$_2$/N$_2$ seeding shots) is 16.7 mm at 4 Pa and 15 mm at 2 Pa. This discrepancy is due to the higher neutrals content which leads to an enhancement of elastic collisions frequency, thus increasing diffusion perpendicularly to the plasma beam. This effect in linear plasma machines has been recently investigated by means of Soledge2D-Eirene simulations in [18]. The reduction of the parallel transport due to momentum-transfer processes leads to an increased radial diffusion, resulting in a broadening of the beam. When looking at the different H$_2$/N$_2$ puffing ratios, a clear trend is observed in both cases, with n$_e$ decreasing while increasing the content of N$_2$ in the puffed gas mixture. Peak values of electron density decrease from 2.2*10$^{20}$ m$^{-3}$ to 1.3*10$^{20}$ m$^{-3}$ between N$_2$ = 0 % and N$_2$ = 20 % for the 2 Pa case and from 2.1*10$^{20}$ m$^{-3}$ to 1.3*10$^{20}$ m$^{-3}$ for the 4 Pa one. Electron temperatures peak values were $\sim$1.8 eV at 2 Pa and $\sim$ 1 eV at 4 Pa. T$_e$ remains almost constant among all the different seeding scenarios. Given that T$_e$ is almost constant among the impurity content scan, the heat flux is governed by the particle flux. The significant n$_e$ reduction is hypothesized to be caused by additional recombination mechanisms introduced by the presence of nitrogen, which act as electrons sinks.

Recent theoretical work carried out by our group [26] highlighted newly-proposed plasma chemistry recombination paths, named N-MAR, occurring in a detached-like high-density (n$_e$ > 10$^{20}$ m$^{-3}$) low-temperature (T$_e$ < 2.5 eV) hydrogen plasma in the presence of nitrogen. Such mechanisms have been found to be important converting hydrogen ions to neutrals by a two-step process as follows:

3) NH$_x$ + H$^+$ $\rightarrow$ NH$_{x+1}$ + H $\quad$ **Ion conversion**

NH$_x^+$ + e$^-$ $\rightarrow$ NH$_{x-1}$ + H $\quad$ **Dissociative recombination**

They are initiated by ion conversion between NH$_x$ with 1 $\leq$ x $\leq$ 3 and H$^+$. The products NH$_x^+$ promptly undergo dissociative recombination, the ion conversion being the rate determining step of N-MAR. Particular importance is attributed to NH radical, which acts efficiently as electron donor in the ion conversion with H$^+$. Extensive plasma chemistry simulations by using global modelling [27] with Plasimo code [28] have been set up corresponding to the experimental scenarios showed in figure 3.

In global models the power is assumed to be homogeneously distributed and the plasma is uniform among the simulated volume. The outcome is collected by solving a system of coupled differential equations i.e. the quasi – neutrality, the energy balance and the particle balance. Those solutions describe the evolution of charged and neutral species as a function of time. Although limitations posed by a zero-dimensional code, global models allow one to implement large plasma chemical datasets. Specifically, a model including 20 species and 106 processes has been set-up to obtain a reduced set...
of plasma chemical equations to be then implemented in Eunomia i.e. a spatially-resolved Monte Carlo code suited for simulations of linear plasma devices. Interestingly, the molecular-driven recombination paths of H⁺ calculated by the code points out the relevance of NH radical as electron donor in the ion conversion with H⁺ (70%, figure 4). The formation of NH occurs mostly in the plasma volume via electron-impact dissociation of NH₃.

Figure 4. Recombination paths of H⁺. In Magnum-PSI-relevant densities and temperature the ion conversion with NH followed by dissociative recombination constitutes 70% of the total H⁺ sinks.

The rate coefficients for the N-H₂ driven processes together with hydrogenic MAR [24] are plotted as a function of electron temperature with nₑ = 1*10²⁰m⁻³.

Figure 5. Rate coefficients of the most important molecule-driven processes in a detached hydrogen plasma with nitrogen seeding.

When looking at the reaction rate of hydrogen MAR compared to N-MAR, one can promptly see that N₂-related process are more effective than the only-H₂ mechanisms. It appears to be clear that nitrogen-related species play a role in the conversion of ions to neutrals. This is also in accordance with the high proton affinity of NH₃ i.e. 854 kJ/mol [29].

The most relevant H₂-N₂ plasma chemical processes have been selected from the above-mentioned model and, subsequently, implemented in EUNOMIA, a spatially-resolved Monte Carlo code suited for simulating the neutral inventory in linear plasma machines[30]. MAR and N-MAR convert ion-electron pairs to neutral atoms, yielding an increased production of H. Simulations of the 2 Pa case depicted in figure 3 have been carried out and H density has been monitored to evaluate recombination efficiency occurring in each experimental H₂/N₂ seeding case. In Eunomia standalone, a static plasma background is used. Therefore, the energy carried by the plasma is constant among all the simulations i.e. Tₑ and nₑ are restored after every Monte Carlo cycle. This implies that the increase H density is directly due to enhanced recombination of H⁺. Radial profiles from the model results, taken at 3 cm in front of the target, are shown in figure 6.
In such simulations, plasma beam has a FWHM of 20 mm (between -0.01 and 0.01 m), with $T_e$ peak at 1.5 eV and $n_e$ at $2.5 \times 10^{20}$ m$^{-3}$. Both those parameters have a Gaussian profile. The density of H increases from $\approx 1 \times 10^{19}$ m$^{-3}$ to $\approx 3.5 \times 10^{19}$ m$^{-3}$ between the 0% and 20% N$_2$ seeding. The only difference between the 0% N$_2$ case and the ones with N$_2$ is the addition of new reaction paths i.e. N-MAR (reaction 3) and the proton transfer from H$_2^+$ and N$_2$, yielding N$_2$H$^+$ and followed by dissociative recombination:

4) $H_2^+ + N_2 \rightarrow N_2H^+ + H$ \hspace{1cm} Proton transfer

$N_2H^+ + e^- \rightarrow NH + N$ \hspace{1cm} Dissociative recombination

$\rightarrow N_2 + H$ \hspace{1cm} Dissociative recombination

Reaction 4 is found by numerical simulations be relevant from the edges of the plasma beam outwards, where $n_e$ goes below $\sim 5 \times 10^{19}$ m$^{-3}$ and the H$_2^+$ sink mechanism producing N$_2$H$^+$ is favourable compared to the dissociative recombination (DR) channel, according to the relation:

$$\frac{d[H_2^+]}{dt} = (k_{IC} \times [H^+] \times [H_2])_{source} - (n_e \times [H_2^+] \times k_{DR})_{sink} - ([N_2] \times [H_2^+] \times k_{N-MAR(4)})_{sink}$$

With $k_{IC}$, $k_{DR}$ and $k_{N-MAR(4)}$ being the rate coefficients for ion conversion, dissociative recombination of H$_2^+$ and N-MAR(4). Moving radially towards the centre of the beam, electron density increases, hence H$_2^+$ is predominantly lost via DR. These processes, in particular N-MAR (3), seem to further contribute to enhance the recombination efficiency in respect to only-H$_2$ seeding. Such influence is due to the role played by NH$_x$ molecules and NH radical, being the final product of IC-DR cycles of NH, with $1 < x \leq 3$. To further investigate the role of N-MAR, Eunomia simulations have been carried out with and without N-MAR for the same content of seeded N$_2$. The model and the plasma parameters are identical in both cases. The obtained radial H density profiles are shown in figure 7.
The density of H with N-MAR is calculated to be higher by a factor \( \sim 2.5 \), showing the importance of such process on the recombination of H\(^+\).

A scan among five different N\(_2\) concentrations in a fixed overall background neutral pressure in the target chamber has been carried out while monitoring with OES the peak intensity of NH \((A^3\Pi \rightarrow X^3\Sigma^+; \nu' = 0 \rightarrow \nu'' = 0)\) transition band at 336 nm [31], NH\(_x\) content with RGA and the total static plasma pressure, calculated as \( P_p = 2 k_B n_e T_e \) by means of TS. The intensity of the band at 336 nm has been calculated as \( \frac{1}{t_{\text{exposure}}} \int I(\lambda) d\lambda \), integrating the intensity over the width of the line profile. Results are reported in figures 8(a), (b) and (c).

The plasma pressure drops by \( \sim 30\% \) in both cases, passing from 0.12 to 0.08 kPa at 4 Pa and from 0.21 kPa to 0.14 at 2 Pa. This is due to the reduction of electron density while increasing the N\(_2\) content in the seeded gas mixture. We address such behaviour to be due to nitrogen-included molecular-activated recombination (N-MAR). Simulation results shown in figure 6 point to the same conclusion. It is worth underlining that \( T_e \) remains constant among all the different N\(_2\) seeding percentages.

The intensity of the NH\(^+\) \((A^3\Pi \rightarrow X^3\Sigma^+; \nu' = 0 \rightarrow \nu'' = 0)\) band increases linearly with increasing N\(_2\) content in both cases. The spectrometer used to measure the NH\(^+\) emission intensity consists of only a single fibre, which has a chord-integrated view through the centre of the plasma. Therefore, the radial distribution of NH emissions could not be measured. Peake values have been used.
The molecular peak intensity of NH$_x^*$ (RGA) are similar in both background neutral pressure scenarios, even though the overall content of N$_2$ is higher in the 4 Pa environment. The conversion efficiency (in %) has been calculated by taking the peak values of the RGA signal of the different N-included species and is calculated as follows: $\frac{\sum N_{tot}}{\sum NHx_{tot}} \times 100$, obtaining 4.5 % in the 2 Pa case and 2.8 % in the 4 Pa one. Such difference shall explain the values in figures 5(b).

8.6 Helium and nitrogen seeding: a comparative study

A dedicated set of experiments has been carried out with the purpose of highlighting the role molecular-induced processes in an impurity-seeded detachment scenario. N$_2$ and He have been seeded separately, together with hydrogen, from 0 to 20% at background neutral pressure corresponding to 2 and 4 Pa. Helium has been chosen in order to exclude molecular-activated processes. Plasma parameters have been diagnosed with TS, while the heat flux to the W target have been monitored by means of calorimetry and calculated as follows: $P(W) = f low \left(\frac{kg}{s}\right) dT \left(\frac{J}{kg*K}\right)$. The power is then divided by the surface area. The mass flow is equal to 0.4 kg/s, $dT$ is the temperature difference (in K) of the water before and after the heating occurring when flowing through the heated target and 4200 $\frac{J}{kg*K}$ is the specific heat of water. The experimental parameters are the same as in section 4.

When He is injected into the system, no significant variation on the plasma pressure is present in the 2 Pa case, while a net increase of almost 20% is measured in the 4 Pa one. This is in net contrast to what we observed in figure 8a, which is characterised by a clear drop while increasing the content of N$_2$ in the puffed mixture. If in the nitrogen-seeding case, detachment is enhanced by increasing the N$_2$ ratio, in the He one we observe an opposite trend. To provide further insights, calorimetry measurements have been carried out and the derived incoming heat flux to the target is plotted in figure 9.

![Figure 9. Left: heat load as a function of impurity content in the gas mixture for N$_2$ and He at 2 Pa. Right: heat load as a function of impurity content in the gas mixture for N$_2$ and He at 4 Pa.](image_url)

The heat load onto the W target is due to ion recombination at the wall, releasing their potential hence causing heating on the material. The power deposited on the surface with only H$_2$ seeding is 1.33 MW/m$^2$ and 0.74 MW/m$^2$ at background pressures of 2 and 4 Pa. In the N$_2$ puffing cases, a net decreasing in the heat load occurs, leading to -1.2 MW/m$^2$ at 2Pa and 0.63 MW/m$^2$ at 4Pa. The observed behavior seems to be due to the active role of N-MAR, where NH$_x$ molecules act as electron
donor in the ion conversion with H⁺, contributing to the overall heat flux reduction of 12% at 2 Pa and 18% at 4 Pa.

This increased recombination is qualitatively in line with numerical simulations. When looking at the He case, we observe again a reversed behaviour. In fact, the power loads on the target increase linearly with enhancing the amount of He in the injected gas mixture, leading to heat loads raised by 10 and 16% for 2 and 4 Pa. In this case, we exclude a priori any further molecule-induced plasma chemical processes, being N₂ substituted with a poorly-reactive atom i.e. He. It seems clear that the dilution of hydrogen molecules with He implies a lower occurrence of recombination reactions, hence more ions are eventually reaching the target plate. In the N₂ case we see two recombination mechanisms occurring simultaneously i.e. N-MAR and MAR.

The opposite trends between H₂/N₂ and H₂/He seeding observed in both plasma pressure and heat loads, are indications that (i) nitrogen leads to enhanced recombination, (ii) He in the mixture decreases the ion conversion by diluting H₂. This holds for both scenarios examined i.e. at background neutral pressure in the target chamber of 2 and 4 Pa.

N-MAR appears to actively contribute to enhance the recombination of hydrogen ions in the vicinity of the target in a detached-like scenario. This is the first time that this catalytic effect led by N-H molecules is observed in ITER-relevant plasma-surface interaction environment.

8.7 Summary and conclusion

Plasma detachment experiments with impurity seeding have been carried out in linear machine Magnum-PSI, aiming to confirm experimentally the role of N₂ and N-H species in enhancing the recombination of H⁺ in ITER-relevant divertor detached-plasmas. Firstly, two cases of study have been set up i.e. by seeding neutral gas in the target chamber up to 2 and 4 Pa. Per case, a scan among H₂-N₂ ratio with nitrogen from 0 to 20% has been done. By increasing the content of N₂ in the puffed mixture, a ~ 30% reduction of the plasma pressure is observed in both cases. OES and RGA measurements show a linear increase of NHₓ species as a function of N₂ content. In order to investigate the role of N-induced plasma chemistry in a detached hydrogen plasma, the same experiment has been pursued i.e. seeding separately H₂/N₂ and H₂/He mixtures in identical experimental conditions. In such way, nitrogen-molecular-assisted processes are excluded beforehand in the Helium case. The plasma pressure again decreases in the case of nitrogen, while it increases with He. Calorimetry measurements show the same trend, with heat flux decreasing with N₂, and increasing with He. We attribute such observations to be due to N-MAR. This two-step process is initiated by ion conversion, then followed by dissociative recombination i.e. effectively converting ions to neutrals. Numerical simulations point qualitatively to the same conclusion. A quantitative comparison between these experimental results with a couple code (fluid and kinetic) is currently under preparation and will provide more detailed insights in the most relevant processes causing the observed experimental results.

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8.9 Bibliography


Chapter 9

Investigating the effect of different impurities on plasma detachment in linear plasma machine Magnum-PSI

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9.1 Abstract

To achieve a tolerable heat and particle flux to the divertor target of fusion reactors, so-called plasma detachment is essential to be set up and controlled. Impurity seeding facilitates the achievement of such regime, mostly due to the enhanced plasma radiation led by the excitation-relaxation cycle of such species. Little is known on the impurity-induced plasma chemical processes occurring in the divertor region during detachment operation. In this work, the influence of three different impurities i.e. N\textsubscript{2}, Ar and He on detachment performance is studied. To do so, experimental campaigns on the linear plasma machine Magnum-PSI have been carried out. Results highlight the beneficial role of N\textsubscript{2}+H\textsubscript{2} seeding, decreasing the plasma pressure in front of the target, leading to a reduced heat load compared to pure H\textsubscript{2} seeding case. An opposite trend has been found concerning He and Ar puffing. In fact, injection of H\textsubscript{2}+He and H\textsubscript{2}+Ar gas mixtures led to an increased heat flux. To address the importance of different plasma-chemical reaction paths, global plasma models have been used. The resulting reduced reaction schemes for Ar+H\textsubscript{2}, He+H\textsubscript{2} and N\textsubscript{2}+H\textsubscript{2} have been implemented in B2.5-Eunomia, a coupled code consisting of a Monte Carlo code treating the transport of neutrals and a fluid code solving plasma equations. Simulation results qualitatively reproduce the favourable effect of N\textsubscript{2}, while confirming the deteriorating effect of He and Ar on a detached-like hydrogen plasma. We point the synergetic role of H\textsubscript{2}+N\textsubscript{2} to be due to molecular-driven ion recombination i.e. N-MAR. A direct comparison of the collision frequency between N-MAR and MAR is showed, highlighting the crucial importance on the former in reducing the ion flux to the target plate.

9.2 Introduction

Understanding how to limit and control the enormous heat and particle flux foreseen to be deposited on the divertor plates of future nuclear fusion reactors e.g. ITER, is one of the most crucial issues to be solved in order to achieve fusion electricity[1]. The plasma ejected from the core is channeled along the Scrape-Off-Layer (SOL) towards the plasma-facing-components (PFC)[2] located in the divertor region[3]. Divertor plasma parameters in ITER are expected to be n\textsubscript{e} > 10\textsuperscript{20} m\textsuperscript{-3} with T\textsubscript{e} < 5 eV, leading to head loads of about 10 GWm\textsuperscript{-2} for steady state operation and up to few GW/m\textsuperscript{2} during intrinsic instabilities of the core such as edge-localized-modes (ELMs)[4]. Power is conveyed to the PFC via the ion potential energy, kinetic energy of electrons, ions and neutrals and via radiated power[5]. To make such heat flux tolerable, a so-called detached plasma regime has to be achieved[6]. Detachment is characterized by a plasma pressure reduction along magnetic field lines in the direction of the divertor target; such drop is due to momentum transfer by means of electron/ion elastic collisions with neutrals and charge exchange, plasma radiation and volume recombination. The heat flux to the target, q\textsubscript{w}, can be expressed as:

\[
q\textsubscript{w} = \Gamma (\gamma k\textsubscript{B} T\textsubscript{e} + E\textsubscript{i}) [\text{Wm}^{-2}\text{s}^{-1}]
\]

(1)

Where \(\Gamma\) is the particle flux, \(\gamma\) is the sheath heat transmission coefficient, T\textsubscript{e} the electron temperature and E\textsubscript{i} the ion potential[7]. The sole plasma cooling is not enough to minimize the power load to tolerable values, hence reducing the particle flux to the target is necessary. In hydrogen plasma
scenarios, this occurs by means of electron-ion recombination processes (EIR) and molecular-assisted recombination (MAR), both producing electronically excited states whose energy will be released in the form of photons. These processes are:

\[ H^+ + e^- + e^- \rightarrow H^*(n \geq 6) + e^- \]  
\[ H^+ + H_2(v) \rightarrow H_2^+ + H \]  
\[ H_2^+ + e^- \rightarrow H + H^*(n = 2 - 4) \]

In such way, ions are converted to neutrals before reaching the target, thus avoiding the release of the potential and kinetic energy onto the plate[8] and preventing erosion of PFC. In divertor plasma detachment volumetric processes play a key role in extinguishing charged particles, eventually reducing the heat flux[9][10].

Experiments in tokamaks since the mid-90s have demonstrated steady-state detached regimes by puffing neutral gas in the divertor region [11], observing the recombination front moving upwards from the PFC[12]. Furthermore, seeding of so-called impurities in the tokamak mid-plane and/or in the divertor region facilitates the achievement of detachment [13]. Nitrogen is currently the leading candidate for impurity seeding in ITER[14], given its radiative capabilities. Other species, such as argon and helium, have been studied as potential impurities for detachment and plasma cooling purposes[15]. Little is known on the effect on recombination mechanisms and plasma parameters that these species may cause once injected in such high-density low-temperature divertor-relevant hydrogen plasma.

Linear machines, sometimes referred to as divertor simulators, have actively contribute to a deeper understanding of detachment and plasma-edge physics. The great diagnostics accessibility, together with the capability of sustaining a long steady-state pulse and the relatively low cost of operation[16] make linear machines a fruitful tool to study plasma-neutrals interactions occurring during impurity seeding in detail.

In this work we investigate the influence of three different impurities, N_2, He and Ar are seeded together with H_2 in the target chamber of the recently-upgraded linear machine Magnum-PSI. A description of the apparatus and the diagnostics that have been used is presented in the next section. To underline the most relevant plasma chemistry in such scenarios, global plasma models have been set up and will be presented in section 9.6. The most relevant plasma processes highlighted with global modelling have been implemented in a spatially-resolved coupled code i.e. Eunomia, a 3D Monte Carlo code simulating the transport of neutrals in linear machines and B2.5, a spatially-resolved multi-fluid code that solves plasma equations. The aim is to study the behaviour of different species and their influence on plasma detachment with both experimental observations and dedicated numerical simulations. Moreover, the inclusion of the plasma chemistry induced by the presence of impurities in state-of-the-art codes is a necessary step towards a full description and understanding of the physics governing divertor plasmas.

9.3 Experimental set up and diagnostics

Magnum-PSI is a linear plasma generator built to mimic the plasma-surface-interactions (PSI) that will occur in ITER divertor. The machine can achieve plasma parameters of T_e \leq 5 eV, n_e \geq 10^{19} m^{-3} with ion flux up to 10^{25} m^{-2}s^{-1} [17]. Those conditions lead to heat loads to the target of \sim 10 MWm^{-2} i.e. the expected steady-state loads onto the ITER divertor plates [18]. By using a pulsed source, ELMs-like heat loads up to few GWm^{-2} can also be achieved[19]. In this work, only steady-state scenarios have been studied, both experimentally and by modelling. Magnum-PSI is characterized by three differentially pumped chambers i.e. source, middle and target chamber, as can be seen in figure 1.
The plasma is generated by a cascaded arc source [20] and is confined by applying a magnetic field generated by a superconducting magnet. The beam travels through the three chambers and eventually reaches the target plate. Differential pumping between all three chambers is applied in order to minimize the presence of neutrals along the beam path, which would cause a cooling of the plasma and higher recombination, resulting in lower electron density. The target used in the experiments presented in this work consists in a tungsten circular target with a diameter of 3 cm and thickness of 1 mm. A more detailed description of the machine can be found in [21].

Plasma parameters (temperature and density) have been diagnosed using a Thomson Scattering (TS) system [22] measuring at 3 cm in front of the target. A hydrogen plasma beam has been adopted for all the scenarios examined in this paper.

To study plasma radiation during H\textsubscript{2} and N\textsubscript{2} seeding in detachment experiments, a resistive bolometer has been used. More details on this diagnostic can be found in [23]. The gas seeding valve, necessary for plasma detachment studies, is located laterally in the target chamber just behind the target. To measure the background neutral pressure in the chamber, a baratron type MKS 627B is used. It is located further behind the target compared to the seeding valve.

A two-channel fiber optic spectrometer (AvaSpec-ULS2048) has been used during nitrogen seeding experiments to observe the line intensity at 336 nm. Such wavelength correspond to the NH\textsuperscript{*}(A\textsuperscript{3}\Pi -X\textsuperscript{3}\Sigma) electronic transition. That species is of great interest in our work, concerning both experiments and simulations. The OES view is located at the same axial coordinates as TS i.e. 3 cm in front of the target. To study the heat and particle flux deposited to the tungsten target, calorimetry has been used.

### 9.4 Plasma detachment with hydrogen seeding

Plasma detachment has been successfully achieved in Magnum-PSI by increasing the background neutral pressure in the target chamber by actively seeding hydrogen gas. In figure 2, three snapshots taken during a background pressure scan are shown. Hydrogen plasma has been used. Images are taken with a phantom camera V12.1. A balmer-\(\alpha\) filter has been applied. The target is a tungsten disc with 3 cm diameter and 1 mm thick.
Figure 2a shows a typical high-recycling regime, where ions recombine on the target and are re-emitted as ground state molecules in vibrational excitation or atoms. Those particles will be soon excited via electron-impact in the vicinity of the surface, given the short mean-free-path. Plasma parameters in such conditions were \( T_e = 3.94 \text{ eV} \) and \( n_e = 1.11 \times 10^{20} \text{ m}^{-3} \) and the background neutral pressure was 0.3 Pa. A recombining plasma is observed in figure 2b; in such case, plasma parameters were \( T_e = 0.8 \text{ eV} \) and \( n_e = 2.4 \times 10^{20} \text{ m}^{-3} \) with a pressure of 4.4 Pa. In these conditions, recombination of ions occurs extensively (\( T_e < 2 \text{ eV} \) and \( n_e > 10^{20} \text{ m}^{-3} \)). More specifically, MAR and three-body recombination \( H^+ + e^- + e^- \rightarrow H^* (n > 5) + e^- \) are the main processes leading to the observed emission throughout the beam[24] together with the broadening of the emission. To unequivocally define the relative contribution of MAR and EIR on the scenario shown in figure 3b, a dedicated CR model should be set-up. This goes beyond the scope of this paper. Nevertheless, Balmer-\( \alpha \) emission is mostly due to MAR processes, which are initiated by molecular hydrogen in vibrational excited state. In fact, one can observe a hollowness in the emitted light from the plasma beam up to few cm in front of the target. Such effect is due to \( H_2(v>4) \) molecules coming from the side of the plasma beam and eventually undergo through MAR. The brightness in front of the target is due to \( H_2(v>4) \) coming from the wall and undergoing the same process. The mean-free-path of those species is longer compared to figure 2a because of the milder conditions of the plasma (\( T_e < 1 \text{ eV} \)). Figure 2c depicts an almost entirely extinguished plasma: neutral pressure was 16.8 Pa and led to parameters to be \( T_e = 0.16 \text{ eV} \) and \( n_e = 4 \times 10^{19} \text{ m}^{-3} \). It is hereby proved that different degrees of detachment can be achieved by means of Magnum-PSI. To further characterize the above-mentioned three cases of study, total peaked static plasma pressure (dynamic ion pressure is not included) has been calculated assuming a quasi-neutral thermal plasma, i.e. \( P_p = 2kT_e n_e \). Results are shown in figure 3.

![Figure 3. Total plasma pressure as a function of background neutral pressure in the target chamber of Magnum-PSI. At neutral pressure of 0.3 Pa, plasma pressure is about 0.29 kPa (point a). It goes down to 0.12 kPa at 4.4 Pa (point b) and eventually falls to 0.0042 kPa at 16.8 Pa (point c).](image-url)

Points a, b and c in figure 3 correspond to the same ones depicted in figure 2. The total plasma pressure, derived by Thomson scattering measurements, steeply decreases while enhancing the neutral background pressure by \( H_2 \) gas puffing in the target chamber. It goes from \( P_{\text{plasma}} = 0.29 \text{ kPa at } P_{\text{neutrals}} = 0.3 \text{ Pa} \) (point a), to \( P_{\text{plasma}} = 0.12 \text{ kPa at } 4.4 \text{ Pa} \) (point b) and eventually to \( P_{\text{plasma}} = 0.0042 \text{ kPa at } P_{\text{neutrals}} = 16.8 \text{ Pa} \) (point c). At the highest background neutral pressure, plasma is almost entirely recombined before reaching the W target. Steady-state plasma detachment is achieved in Magnum-
PSI by impurity seeding. Experiments regarding how different impurities injected together with H\textsubscript{2} at different mixture ratios, influence plasma detachment in ITER-divertor relevant conditions, are presented and discussed in the next section.

9.5 Plasma detachment with impurities seeding (N\textsubscript{2}, Ar and He)

In this section a comparative study among different impurity species and their effect on plasma detachment has been carried out. Impurities have been seeded, together with H\textsubscript{2}, with different mixing ratios defined by the partial pressure; the background neutral pressure in the target chamber has been kept constant at 2 and 4 Pa, while changing the ratio as:

\[
\frac{[\text{impurity}]}{[\text{H}\textsubscript{2}]+[\text{impurity}]} \times 100 = 0, 5, 10, 15, 20 \%.
\]

Three different gas species have been puffed with hydrogen i.e. nitrogen, helium and argon. The last two species are poorly reactive, while N\textsubscript{2} and related compounds such as NH\textsubscript{3}, NH\textsubscript{2}, NH react with species populating the generated hydrogen plasma e.g. H\textsuperscript{+}, H\textsuperscript{2}\textsuperscript{+}, H, H\textsubscript{2}(v)[25]. In this section we study experimentally the influence of different impurities seeding on plasma parameters by means of the plasma pressure and the heat flux collected at the target. The injected gas mixtures are H\textsubscript{2} + N\textsubscript{2}, H\textsubscript{2} + He and H\textsubscript{2} + Ar, and the plasma pressure, calculated with Thomson scattering, is shown in figure 4. These measurements have been taken in the plasma volume, at 3 cm in front of the tungsten target.

![Figure 4. Total plasma pressure as a function of impurity content for N\textsubscript{2}, He and Ar. The neutral background pressure in the target vessel is constant at 2 Pa (left) and 4 Pa (right).](image)

For the scans of both background pressures, the baseline scenario i.e. with only H\textsubscript{2} puffing, corresponds to the first point i.e. when no impurity was added in the mixture. Although each baseline scenario can be slightly different due to limited reproducibility of the machine, every scan is carried out maintaining the same experimental conditions among each other. At 2 Pa with N\textsubscript{2} seeding up to 20%, we observe a clear decay that leads to a plasma pressure loss of \( \approx 25\% \). In the helium case, a different trend is achieved. Here, the plasma pressure somewhat varies around 0.21 kPa and remains almost constant. Regarding the Ar-seeding case, the behaviour is similar to the helium one: after a small decrease at 5%, \( P_{\text{plasma}} \) increases by about 10\% during the scans at 10, 15 and 20\% of impurity content, hence reducing the effectiveness of detachment. If on one hand the addition of a mixture of H\textsubscript{2}/N\textsubscript{2} is beneficial for plasma detachment compared to H\textsubscript{2} puffing alone, the other two species show an opposite effect, enhancing the plasma pressure in front of the target.

To unequivocally investigate the effect of these impurities on plasma recombination, heat fluxes collected at the target have been diagnosed by means of calorimetry and results are reported in figure
The power deposited to the tungsten disc is calculated as $P(W) = flow \left(\frac{kg}{s}\right) dT(K) 4200 \left(\frac{J}{kg \cdot K}\right)$, with $flow = 0.4 \frac{kg}{s}$ being the amount of cooling water passing through the diagnostic per second, $dT$ the water temperature difference before and after it has been passed through the heated component and 4200 J is the energy needed to heat up 1 liter of water by 1 K. Worth to be stressed that for the calculation of the heat flux no direct measurements of plasma parameters are used; in such way we can straightforwardly measure the actual heat transported by the plasma to the target. The power load at the target is mostly due to surface recombination of incoming hydrogen ions, where they release their potential and (part of their) kinetic energy, which causes heating of the material. In figure 5 (left), the starting value of heat load for the Ar seeding scan i.e. Ar = 0% is lower compared to H$_2$/N$_2$ and H$_2$/He cases by $\approx 0.7$ MW*m$^{-2}$. Although the experimental settings have been kept the same, plasma conditions were not perfectly reproducible. Nevertheless, for the scope of this work, the trend obtained by puffing different ratios of different species is the most relevant feature to be highlighted and studied.

At background neutral pressure of 2 Pa, when H$_2$ is diluted with He, the measured heat load increases by $\approx 11\%$, from the 0% to the 20% of impurity content. Regarding N$_2$, we obtain a net reduction of heat flux of about 12%. Such findings further confirm the beneficial effect for detachment led by the presence of N$_2$ in the seeded gas mixture. Argon puffing experiments are characterised by an enhancement of heat deposited to the surface of $\approx 12\%$, implying a reduced detachment efficiency.

The same experiments have been carried out with a fixed background pressure of 4 Pa and results are plotted in figure 4 (right) and 5 (right). The same behaviour is observed compared to the 2 Pa case; in fact, $P_{\text{plasma}}$ increases by $\approx 15\%$ between 0 and 20% of impurity content, for both He and Ar. H$_2$/N$_2$ puffing led to a plasma pressure reduction of $\approx 28\%$. The heat flux is reduced by the presence of N$_2$ by 18%, while is enhanced by 16% and almost 40% with H$_2$/He and H$_2$/Ar respectively.

According to these results, Ar seems to be the less beneficial species among the impurities exploited in this study. Helium shows a negative impact on plasma detachment as well, while nitrogen led to an improved detached state among both 2 and 4 Pa cases. Three different impurities have been tested in ITER-relevant hydrogen plasma at the same experimental conditions for the first time. The negative outcome on plasma pressure and heat flux of Ar and He seeding may be due to dilution effect i.e. less hydrogen molecules are inserted in the system, therefore less molecule-driven ion recombination occurs in the volume phase. That is not the case for N$_2$, which shows an effective improvement on the detached plasma performance. When mixtures of H$_2$+N$_2$ are injected into the vessel, the heat flux is subjected to a net decrease. This behaviour is appointed by the authors to be due to presence of N$_2$-driven ion recombination processes, as discussed in [26]. The role of NH$_x$ molecules i.e. NH$_3$, NH$_2$ and

![Figure 5. Heat load on the W target for each impurity at different H$_2$/impurity mixing ratios at 2 Pa (left) and 4 Pa (right).](image-url)
NH as electron donors in the reaction with H\(^+\) has been found to be of a great importance in divertor-relevant hydrogen plasma. Specifically, the following two-step process was found by numerical simulations to be relevant:

\[
\begin{align*}
1) \quad & H^+ + NH_x \rightarrow H + NH_x^+ \\
2) \quad & NH_x^+ + e^- \rightarrow NH_{x-1} + H
\end{align*}
\]

Such mechanism is referred to as N-MAR\(^{[27]}\), and is characterised by an ion conversion promptly followed by dissociative recombination. This process effectively converts ion to neutral, thus dissipating energy from the plasma via volumetric recombination. This may results in a reduced heat flux when increasing the H\(_2\)+N\(_2\) puffing ratio. To investigate the presence of N\(_2\)-H\(_2\) species in the plasma, optical-emission-spectroscopy has been adopted and the outcome is shown in \textit{figure 6}.

\textit{Figure 6.} Left: emission spectra for a H\(_2\) plasma with H\(_2\)/N\(_2\) seeding with peak identification. Right: peak intensity of the NH\(^*\) band at 336 nm for a neutral background pressure of 2 Pa.

On the left, the identification of the main peaks diagnosed with OES is shown. Balmer lines, in particular the transitions \(n = 5 \rightarrow n = 2\) (\textit{Balmer y}) and \(n = 6 \rightarrow n = 2\) (\textit{Balmer d}) at 434 nm and 410 nm respectively, are shown. N\(_2\) transition C\(^3\)\(\Pi \rightarrow \text{B}\(^3\)\(\Pi\); \(\Delta v = 0\)) at 338 nm is also present. Of particular interest is the peak at 336 nm, which is due to the NH\(^+\)(A\(^3\)\(\Pi \rightarrow \text{X}\(^3\)\(\Sigma\)) transition, being NH radical the electron donor in the N-MAR first step i.e. ion conversion with H\(^+\) in high density plasmas. On the right, the intensity of the 336 nm band is plotted as a function of N\(_2\) content in the puffed H\(_2\)/N\(_2\) mixture and calculated as \[\int \frac{I(\lambda)}{t(\text{exposure})} d\lambda.\] The achieved trend clearly indicates a relevant presence of such species in the plasma, thus providing a further indication on the enhanced recombination of hydrogen ions led by NH\(_x\) species. To study the radiated power emitted during the seeding scan, a bolometry system has been used. By such diagnostic, we can include/exclude cooling phenomena led by relaxation of electronically excited species. Results are shown in \textit{figure 7}.
The total radiated power, averaged over the 3 viewing channels, is calculated as:

\[ P_{\text{rad}} = \frac{\pi l_{s,ap}^2}{A_s A_{ap}} d_p \Delta z P_s, \]  

(2)

where \( l_{s,ap} \) is the distance between the sensor and the aperture, \( A_s \) the sensor area, \( A_{ap} \) the aperture area, \( d_p \) the plasma diameter taken as the FWHM measured by Thomson scattering, \( \Delta z \) the axial width and \( P_s \) the power received by the sensor of a bolometer channel and is calculated as follows:

\[ P_s(t) = \frac{1}{S} \left( \Delta U(t) + \tau \frac{d\Delta U(t)}{dt} \right), \]

where \( S \) is the sensitivity of the instrument. No substantial trend in plasma radiation is collected while increasing the content of nitrogen in the puffed gas mixture. Therefore, we shall exclude power-limitation effect (often referred to as “power starvation”) that would lead to a drop in plasma pressure, basically shifting the recombination front backward from the target. The fact that no trend is observed with bolometry further suggests that the reduced heat flux and plasma pressure drop shown in figure 4,5, may be due to volume recombination processes occurring before ions reach the target.

Dedicated experiments in linear plasma machines GAMMA10/PDX [29] and PISCES-E [30] showed similar trends to the ones presented here i.e. a synergetic effect of \( \text{H}_2+\text{N}_2 \) seeding in the recombination of hydrogen ions is observed in both cases. Plasma parameters differ substantially, with \( T_e \) around 10 eV and \( n_e \approx 10^{17} \text{m}^{-3} \) in GAMMA10/PDX and \( T_e \) of about 2 eV with \( 4 \times 10^{16} < n_e < 3 \times 10^{17} \text{m}^{-3} \) in PISCES. Nevertheless, combining those works with this one, the effect of impurities over a wide parameters space can be studied.

In order to shed more light into the physics and the chemistry that are governing these scenarios, numerical simulations are needed. To do so, a two-step approach has been followed and details are provided in the following sections. First, volume-averaged plasma models have been set up with the aim of highlighting the most relevant plasma chemical reactions. Subsequently, these processes have been implemented in B2.5-Eunomia coupled code. These methods are described in section 5 and 6.

9.6 Global model

Global models are zero-dimensional simulations that allow one to implement large plasma chemical data sets, given the assumption of a homogeneous distribution of species and plasma parameters throughout a defined volume[31]. The simulations have been set up using the Plasimo code[32]. The code solves a system of coupled differential equations: particle balance, quasi-neutrality and energy
balance. The adopted electron energy distribution function (EEDF) is Maxwellian. The electron energy balance is calculated as:

\[
\frac{d}{dt}\left(\frac{3}{2}n_e e^2 T_e\right) = P_{\text{input}}(t) - Q_{\text{coll}}
\]

(3)

With \(e\) the elementary charge, \(n_e\) and \(T_e\) electron density (m\(^{-3}\)) and temperature (eV), \(P_{\text{input}}\) the input power density and \(Q_{\text{coll}}\) the energy losses via inelastic and elastic collisions. The time-evolution of both plasma and neutral species is calculated as follows:

\[
\frac{dn_i}{dt} = \sum (s^p_i - s^r_i) k(t) \prod n_i^{s^r_i}
\]

(4)

Where \(s^p_i\) and \(s^r_i\) are the stoichiometric coefficients of products and reactants respectively, \(k(t)\) the reaction rate and \(n_i\) the density of the species \(i\). The reaction rate coefficients are written in the generalized Arrhenius form:

\[
k(T_e) = A (\frac{T_e}{1\text{eV}})^n \exp(-\frac{E_a}{T_e})
\]

(5)

Where \(A\) is declared in cm\(^3\)s\(^{-1}\) and \(E_a\), the activation energy of the reaction, together with \(T_e\), in eV. This type of codes are computationally cheaper than spatially-resolved hybrid models, hence, we can implement extensive chemistry without implying a significant increasing in the computational effort [33]. A wide and detailed global model for \(N_2+H_2\) divertor relevant plasmas, together with a full description of the code, can be found in [27]. Global models have been therefore used in this study for 1. providing theoretical insights into the results achieved during detachment experiments and 2. to highlight the most relevant volume processes to be implemented into a spatially-resolved couple codes.

Regarding the \(H_2+\text{He}\) seeding case, in figure 5 we observe an increase of roughly 10% of the power load with increasing the content of \(\text{He}\) in the puffed gases. Such trend is believed to be indicative of less recombination, due to dilution of molecular hydrogen. The reactions involving helium and included in the model are listed in table 1. Given that the aim of this study is to understand the influence of different impurities on plasma recombination and detachment, particular attention has been given to the recombination paths of \(H^+\) and \(H_2^+\) in the presence of \(\text{He}\). The rate for some of the electron-induced reactions is calculated by the code by integrating the cross section over a maxwellian electron energy distribution function (EEDF), as follows:

\[
k_r = \int_{E_t}^{\infty} \sigma_r(E) v(E) f(E) d(E)
\]

(6)

Where \(E_t\) is the threshold energy of the collision, \(E\) the electron energy, \(f(E)\) the EEDF, \(v(E)\) the electron thermal velocity and \(\sigma_r\) the cross section of collision \(r\). In the simulations, one vibrationally excited species for molecular hydrogen, namely \(v=4\), and one electronically excited state for atomic helium (\(\text{He}^2\text{S}\)) have been included. They are important for ion conversion (reaction 7) and two-step ionization (reactions 10 and 12), respectively.

<table>
<thead>
<tr>
<th>(N)</th>
<th>Reaction</th>
<th>Rate (m(^3)s(^{-1}))</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(H_2 + e^- \rightarrow H + H + e^-)</td>
<td>from cross section</td>
<td>[34]</td>
</tr>
<tr>
<td>2</td>
<td>(H_2 + e^- \rightarrow H_2 (v = 4) + e^-)</td>
<td>from cross section</td>
<td>[35]</td>
</tr>
<tr>
<td>3</td>
<td>(H_2 + e^- \rightarrow H^+ + H + 2e^-)</td>
<td>9.4 \times 10^{-16} \times T_e^{0.45} \times \exp\left(-\frac{29.94}{T_e}\right)</td>
<td>[36]</td>
</tr>
<tr>
<td>4</td>
<td>(H + e^- \rightarrow H^+ + 2e^-)</td>
<td>from cross section</td>
<td>[37]</td>
</tr>
</tbody>
</table>
No mechanisms involving directly H\(^+\) and He have been found in the literature. Nevertheless, the proton transfer reaction (reaction 15) between H\(^+\) and He, followed by dissociative recombination i.e. HeH\(^+\) + e\(^-\) → He + H (reaction 14) constitutes a further neutralization path. Numerical results indicate that, for electron density of \(n_e = 1 \times 10^{19}\) m\(^{-3}\) the main molecule-driven route for H\(^+\) consumption is with H\(_2\), leading to the production of H\(^+\). Reaction 15 is responsible for only 5% of the total sinks of H\(^+\). With \(n_e = 1 \times 10^{20}\) m\(^{-3}\) the main sink is entirely via dissociative recombination (reaction 8). The electron temperature for those simulations was 1.5 eV. A schematic representation of these results is presented in figure 8.

\[
\begin{align*}
5 & \quad H_2 + e^- \rightarrow H_2^+ + 2e^- & \text{from cross section} & \text{[38]} \\
6 & \quad H_2^+ + H_2 \rightarrow H_2^+ + H & \quad 2 \times 10^{-15} & \text{[39]} \\
7 & \quad H_2(v = 4) + H^+ \rightarrow H_2^+ + H & \quad 2.5 \times 10^{-15} & \text{[40]} \\
8 & \quad H_2^+ + e^- \rightarrow H + H & \quad 1.6 \times 10^{-14} \times T_e^{-0.43} & \text{[41]} \\
9 & \quad H_2^+ + e^- \rightarrow H_2 + H & \quad 4.36 \times 10^{-14} \times T_e^{-0.52} & \text{[42]} \\
10 & \quad He + e^- \rightarrow He^\ast(2^3S) + e^- & \quad 5.05 \times 10^{-14} \times \exp \left( \frac{22.5}{T_e} \right) & \text{[43]} \\
11 & \quad He^\ast(2^3S) \rightarrow He + hv & \quad 6.72 \times 10^{11} & \text{[43]} \\
12 & \quad He^\ast(2^3S) + e^- \rightarrow He^\ast + 2e^- & \quad 1.28 \times 10^{-13} \times T_e^{0.6} \times \exp \left( \frac{-4.78}{T_e} \right) & \text{[43]} \\
13 & \quad He + e^- \rightarrow He^\ast + 2e^- & \quad 1.5 \times 10^{-15} \times T_e^{0.68} \times \exp \left( \frac{-24.6}{T_e} \right) & \text{[43]} \\
14 & \quad HeH^\ast + e^- \rightarrow He + H & \quad 1.0 \times 10^{-14} \times T_e^{-0.6} & \text{[41]} \\
15 & \quad H_2^+ + He \rightarrow HeH^\ast + H & \quad 1.3 \times 10^{-16} & \text{[39]} \\
16 & \quad He^\ast + H_2 \rightarrow He + H_2^+ & \quad 1.7 \times 10^{-21} & \text{[39]} \\
17 & \quad HeH^\ast + H \rightarrow He + H_2^+ & \quad 9.1 \times 10^{-16} & \text{[39]} \\
18 & \quad HeH^\ast + H_2 \rightarrow He + H_2^+ & \quad 1.8 \times 10^{-15} & \text{[39]} \\
19 & \quad He + e^- \rightarrow He + e^- & \quad \text{from cross section} & \text{[44]}
\end{align*}
\]

Table 1. Helium-driven plasma chemical reactions adopted in the H\(_2\)/He global model.

The density distribution of molecular ions in a H\(_2\)+He plasma calculated with the global model are plotted in figure 9. In the simulation, the initial densities of H\(_2\) and He correspond to a 5% impurity seeding case i.e. \(n_{H_2} = 1 \times 10^{21}\) m\(^{-3}\) and \(n_{He} = 5 \times 10^{19}\) m\(^{-3}\). The parameter that mostly influences the population of ions in such low temperature – high density plasmas is the electron density. In figure 9 the amount of ions (m\(^{-3}\)) has been calculated for \(n_e\) between \(6 \times 10^{18}\) to \(1 \times 10^{20}\) m\(^{-3}\). With \(n_e\) below \(10^{19}\)
m⁻³, the dominant species is H₃⁺, which is produced via reaction 6. HeH⁺ has a peak at nₑ⁻²*10¹⁸ m⁻³, which also corresponds to the electron density where H⁺ becomes basically as populated as H₃⁺. When moving towards higher nₑ, dissociative recombination of H₂⁺ becomes very efficient, hence a depopulation of such molecule occurs (H₂⁺ is the precursor of H₃⁺). As a result, for divertor-relevant and Magnum-PSI typical plasmas, no additional recombination effects are driven by the presence of He.

Although no beneficial effects for detachment come along the presence of He, as it is shown experimentally and confirmed hereby by the global model, a spatially-resolved code is mandatory to exclude/include any further mechanism that could influence plasma parameters in a detached-like scenario, such as elastic processes leading to momentum loss and/or influences on the radial transport. These simulations will be presented in the next section.

Concerning the Ar seeding cases depicted in figure 4, a similar behaviour as the ones with H₂/He puffing is measured. In fact, the more argon is injected into the system, the more heat is deposited on the W target. The power load increases by ≈ 10% between the 0% Ar and the 20% Ar in the seeded mixture. This phenomenon is appointed to be again due to dilution of hydrogen molecule, reflecting in less volume recombination of the plasma, hence lowering the dissipation of ion potential before reaching the plate. In order to closely look into volume processes occurring in a hydrogen plasma with H₂+Ar seeding, another global plasma model has been created. Hydrogen-related processes are identical to the ones in table 1. An electronically-excited state of Ar, i.e. Ar⁺4p, has been added being an important intermediate state for multi-step ionization. Reactions are reported in table 2.

<table>
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<td>[35]</td>
</tr>
<tr>
<td>3</td>
<td>H₂ + e⁻ → H⁺ + H + 2e⁻</td>
<td>9.4 x 10⁻¹⁶ x Tₑ⁻⁰.⁴⁵ x exp (−29.94/Tₑ)</td>
<td>[36]</td>
</tr>
<tr>
<td>4</td>
<td>H + e⁻ → H⁺ + 2e⁻</td>
<td>from cross section</td>
<td>[37]</td>
</tr>
<tr>
<td>5</td>
<td>H₂ + e⁻ → H₂⁺ + 2e⁻</td>
<td>from cross section</td>
<td>[38]</td>
</tr>
<tr>
<td>6</td>
<td>H⁺ + H₂ → H₃⁺ + H</td>
<td>2 x 10⁻¹⁵</td>
<td>[39]</td>
</tr>
<tr>
<td>7</td>
<td>H₂(v = 4) + H⁺ → H₂⁺ + H</td>
<td>2.5 x 10⁻¹⁵</td>
<td>[40]</td>
</tr>
<tr>
<td>8</td>
<td>H₂⁺ + e⁻ → H + H + H</td>
<td>1.6 x 10⁻¹⁴ x Tₑ⁻⁰.⁴³</td>
<td>[41]</td>
</tr>
<tr>
<td>9</td>
<td>H₃⁺ + e⁻ → H₂ + H</td>
<td>4.36 x 10⁻¹⁴ x Tₑ⁻⁰.⁵²</td>
<td>[42]</td>
</tr>
<tr>
<td>10</td>
<td>Ar + e⁻ → Ar⁺ + 2e⁻</td>
<td>2.39 x 10⁻¹⁴ x Tₑ⁻⁰.⁵⁷ x exp (−17.43/Tₑ)</td>
<td>[45]</td>
</tr>
</tbody>
</table>
Concerning \( \text{H}_2^+ \), for low \( n_e \), proton transfer with \( \text{H}_2 \) and with \( \text{Ar} \) are the main sinks and account for 85% and 15% respectively, producing \( \text{H}_3^+ \) and \( \text{ArH}^+ \). For Magnum-PSI-relevant plasma conditions, where \( n_e \) is in the order of \( 1-5 \times 10^{19} \text{m}^{-3} \), \( \text{H}_2^+ \) is consumed almost entirely by dissociative recombination, while proton transfer (reaction 16) constitutes only 5% of the total sink processes. For electron densities \( \approx 1 \times 10^{19} \text{m}^{-3} \), the sources for \( \text{H}_3^+ \) are proton transfer reactions i.e. reaction 6 and 17. The contributions are about 80% and 20% respectively. Above such density threshold, \( \text{H}_3^+ \) is barely produced due to the very efficient dissociative recombination of its precursor \( \text{H}_2^+ \) (reaction 8). The main sink for \( \text{H}_3^+ \) is reaction 9 in both cases. The electron temperature is set at 1.5 eV. Argon appears to have a similar behaviour as helium, in this experimental conditions. A visual representation of these plasma chemical path is reported in figure 10.

![Figure 10](image)

**Figure 10.** Global model output of \( \text{H}_2^+ \) sink reaction paths in a \( \text{H}_2/\text{Ar} \) plasma for two electron density scenarios. \( T_e \) was 1.5 eV in both cases.

It has been shown that no ion-recombination paths appear to be relevant in the presence of either \( \text{Ar} \) and \( \text{He} \) among the parameters range considered in this study. In the case of \( \text{N}_2 \), however, the outcome is different. In fact, N-H induced volume-recombination processes seem to play a crucial role in divertor-relevant detached-like hydrogen plasma. To further study those findings, B2.5-Eunomia simulations have been carried out, aiming to provide insights into the effect of two different impurities i.e. \( \text{He} \) and \( \text{N}_2 \) on plasma detachment in Magnum-PSI.
9.7 EUNOMIA code

Eunomia is a 3D Monte Carlo code developed to model the neutral transport in linear plasma machines[47]. It is conceptually very similar to the well-established code EIRENE[48]. The code has been originally created to study neutrals in Pilot-PSI [49], the predecessor of Magnum-PSI. For this work, a new grid with Magnum-PSI geometry has been created and will be shown in section 3.3. In the code, so-called test particles are traced: they are representative of many neutral particles. Such way of treating species is called test particle approximation method. In Eunomia standalone, the plasma equations are not solved; the plasma background is assumed to be constant and has to be provided as input. When a test particle collides with a charged or neutral particle from the background, the information regarding the obtained products and velocity distribution are stored by the code for every cycle. The new background is then updated at the beginning of the next cycle. The number of particles per cell is calculated by the code as:

\[ N_p = \Gamma_p T_a \]  

(7)

With \( \Gamma_p \) the influx of particles into the system (s\(^{-1}\)) and \( T_a \) the residence time (averaged). The Boltzmann transport equation, which describes the statistical behaviour of a gas or fluid, is solved by Eunomia as:

\[ \mathbf{v} \cdot \nabla f(\mathbf{r}, \mathbf{v}, i) = \sum C(\mathbf{r}, \mathbf{v}, i, j) + S(\mathbf{r}, \mathbf{v}, i) \]  

(8)

Where the left-hand side is the velocity vector times the probability density function \((f)\) of species \(i\) in position \(\mathbf{r}\) and velocity \(\mathbf{v}\), \(\sum C(\mathbf{r}, \mathbf{v}, i, j)\) is the collision term of inelastic and elastic collisions between neutrals and plasma particles and \(S(\mathbf{r}, \mathbf{v}, i)\) is the source term. Eunomia incorporates particles sources and sinks i.e. absorption due to pumping, conversion of ions to neutrals, recycling and gas puffing. For a more detailed overview on the theoretical background of Eunomia, the reader is referred to [50]. The implementation of the plasma chemistry of \(\text{H}_2 + \text{N}_2\), \(\text{H}_2 + \text{He}\), \(\text{H}_2 + \text{Ar}\) plasmas, necessary for this study, is described in section 3.3. The hydrogenic plasma chemistry contained in Eunomia is shown in table 3.

<table>
<thead>
<tr>
<th>N.</th>
<th>Reaction</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(\text{H} + \text{H} \rightarrow \text{H} + \text{H})</td>
<td>Elastic collision</td>
</tr>
<tr>
<td>2</td>
<td>(\text{H} + \text{H}_2 \rightarrow \text{H} + \text{H}_2)</td>
<td>Elastic collision</td>
</tr>
<tr>
<td>3</td>
<td>(\text{H}_2 + \text{H}_2 \rightarrow \text{H}_2 + \text{H}_2)</td>
<td>Elastic collision</td>
</tr>
<tr>
<td>4</td>
<td>(\text{H} + e^- \rightarrow \text{H}^+ + 2e^-)</td>
<td>Ionization</td>
</tr>
<tr>
<td>5</td>
<td>(\text{H}^+ + \text{H} \rightarrow \text{H} + \text{H}^+)</td>
<td>Charge exchange</td>
</tr>
<tr>
<td>6</td>
<td>(\text{H}_2 + e^- \rightarrow \text{H} + \text{H} + e^-)</td>
<td>Dissociation</td>
</tr>
<tr>
<td>7</td>
<td>(\text{H}_2(v) + e^- \rightarrow \text{H}_2(v \pm 1) + e^-)</td>
<td>Vibrational (de-)excitation</td>
</tr>
<tr>
<td>8</td>
<td>(\text{H}_2(v) + \text{H}^+ \rightarrow \text{H} + \text{H}_2^+)</td>
<td>Ion conversion</td>
</tr>
<tr>
<td></td>
<td>(\text{e}^- + \text{H}_2^+ \rightarrow \text{H} + \text{H}_n = 2)</td>
<td>Dissociative recombination</td>
</tr>
<tr>
<td></td>
<td>(MAR)</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>(\text{H}_2 + e^- \rightarrow \text{H}^+ + \text{H}^-)</td>
<td>Ion conversion</td>
</tr>
<tr>
<td></td>
<td>(\text{H}^+ + \text{H}^- \rightarrow \text{H} + \text{H}_n = 3)</td>
<td>Dissociative recombination</td>
</tr>
<tr>
<td></td>
<td>(MAR)</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>(\text{H} + \text{H}^+ \rightarrow \text{H} + \text{H}^+)</td>
<td>Ion-neutral elastic collision</td>
</tr>
<tr>
<td>11</td>
<td>(\text{H}_2 + \text{H}^+ \rightarrow \text{H}_2 + \text{H}^+)</td>
<td>Ion-neutral elastic collision</td>
</tr>
</tbody>
</table>

Table 3. Hydrogen plasma chemistry included in Eunomia and suited for studying standard \(\text{H}_2\) plasma operations.
9.8 Coupling B2.5-EUNOMIA

The scope of this paper is to study the effect on plasma detachment led by puffing different gas species, namely H₂+N₂ and H₂+He, in the target chamber. New plasma chemistry has been implemented in the code, in order to study the differences between seeding a highly-reactive species (nitrogen and ammonia-related compounds) with a poorly-reactive one (helium).

To provide a full description of the Magnum-PSI scenario during detachment experimental campaigns, the spatially-resolved kinetic Monte Carlo code Eunomia has been coupled with the multi-fluid code B2.5[50]. A detailed description of the code can be found in [51]. The equations solved by the program are based on the Braginskii equations, that are fully explained in [52]. In brief, the code solves the continuity equation for ion \( i \) which is:

\[
\frac{dn_i}{dt} + \nabla \cdot (n_i v_i) = S_{n_i} \tag{9}
\]

With the parallel momentum equation being:

\[
\frac{d}{dt}(m_i n_i v_{||}) + \nabla \cdot (m_i n_i v_i v_{||}) = -\nabla_{||} p_i - (\nabla_{||} n_i) + Z_i e n_i \nabla \Phi + F_k + R_{i||} + S_{m_i v_{||}} \tag{10}
\]

Where \(-\nabla_{||} p_i\) is the ion pressure gradient, \(F_k\) the Coriolis force, \(\nabla_{||} n\) the viscosity tensor, \(Z_i e n_i \nabla \Phi\) the electric force, \(R_{i||}\) the ion-electron friction and \(S_{m_i v_{||}}\) the ion-neutral friction. The parallel momentum balance for electrons is expressed as:

\[
\mathbf{j}_{||} = \sigma_{||} \left( \frac{1}{en} \nabla_{||} n T_e + \frac{0.71}{e} \nabla_{||} T_e - \nabla_{||} \Phi \right) \tag{11}
\]

With \(\sigma_{||}\) the parallel conductivity, \(\frac{1}{en} \nabla_{||} n T_e\) the pressure gradient, \(\frac{0.71}{e} \nabla_{||} T_e\) the temperature gradient and \(\nabla_{||} \Phi\) the electric field. The definitions of radial and perpendicular current are from the sum of (ion and electron) momentum balance equations. The total energy for ions is calculated as:

\[
\frac{d}{dt} \left( \frac{3}{2} n_i T_i + \frac{m_i}{2} v_i^2 \right) + \nabla \cdot \left[ \left( \frac{5}{2} n_i T_i + \frac{m_i}{2} v_i^2 \right) \mathbf{v}_i + \Pi_i \mathbf{v}_i + \mathbf{q}_i \right] = (Z_i e n_i \mathbf{E} - \mathbf{R}_i) \cdot \mathbf{v}_i - Q_{ei} + S_{Ei} \tag{12}
\]

While the electron energy conservation is given as:

\[
\frac{d}{dt} \left( \frac{3}{2} n_e T_e \right) + \nabla \cdot \left( \frac{5}{2} n_e T_e \mathbf{v}_e + \mathbf{q}_e \right) = -e n_e \mathbf{E} \cdot \mathbf{v}_e + \mathbf{R}_i \cdot \mathbf{v}_i + Q_{ei} + S_{Ee} \tag{13}
\]

In the equations, \(\mathbf{q}_e\) and \(\mathbf{q}_i\) are the electron and ion energy fluxes, \(Q_{ei}\) represents the coupling between electrons and ions i.e. the collisional equilibration term, while the terms \(S_{n_i}, S_{m_i v_{||}}\) and \(S_{Ei}\) are sources for particles, momentum and energy due to neutral and are calculated by the Monte Carlo code.

B2.5 is self-consistently coupled with Eunomia, implying that the static plasma background characterising Eunomia standalone is now calculated and updated by B2.5 for every cycle, while Eunomia provides sources and sinks for ion and electron energy, particle density and momentum. A graphical representation is shown in figure 11.
In this work, a new grid representing the upgraded linear machine Magnum-PSI has been used and can be seen in Figure 12. All walls are reflecting walls for the test particle, and the velocity of the reflected particle follows a cosine distribution. Moreover, the outer walls thermalize the reflected particle, therefore, the velocity is rescaled to the wall temperature. The skimmers do not thermalize the particle. Differential pumping is treated in the code as follows: a certain probability rate describes whether the test particle is terminated when crossing this boundary is specified. If that would not be the case, it gets reflected. The probability rate is updated each cycle according to the specified pressure in a specified location within the domain. To achieve the differential pumping, we have different pumps in different locations for each of the pumps.

Figure 11. Graphical representation of the iteration scheme between the two codes, reciprocally providing informations on the plasma itself (B2.5 for Eunomia) and sources and sinks for particles, momentum and energy (Eunomia for B2.5).

Figure 12. right: drawing of Magnum-PSI, where 1. is the plasma source 2. the skimmers 3. the plasma beam and 4. the target. On the left, the geometry used in the simulations of the couple codes is shown.
9.9 Implementation of the codes

The implemented processes regarding N₂-H₂ are listed in table 4. To get to such a reduced scheme, an extensive global plasma model has been firstly made. An internal validation of the code, implying a quantitative comparison of the species densities between the fully-extended model with the reduced one has been carried out for three different cases of study. Plasma scenarios were set at \( T_e(1) = 0.8 \text{ eV} \) and \( n_e(1) = 6 \times 10^{19} \text{m}^{-3} \), \( T_e(2) = 1.2 \text{ eV} \) and \( n_e(2) = 2.6 \times 10^{20} \text{m}^{-3} \), \( T_e(3) = 1.8 \text{ eV} \) and \( n_e(3) = 3.5 \times 10^{20} \text{m}^{-3} \) respectively. Results clearly showed consistency between the two sets. More details on such procedure can be found in [53]. Worth mentioning that the plasma chemical tables presented hereafter have been implemented keeping the ones in table 3 fully activated.

<table>
<thead>
<tr>
<th>N.</th>
<th>Reaction</th>
<th>Type</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>( N_2 + e^- \rightarrow N + N + e^- )</td>
<td>Dissociation</td>
<td>[54]</td>
</tr>
<tr>
<td>13</td>
<td>( H_2 + N \rightarrow NH + H )</td>
<td>Atomic transfer</td>
<td>[55]</td>
</tr>
<tr>
<td>14</td>
<td>( N_2 + H_2^+ \rightarrow N_2H^+ + N )</td>
<td>Proton transfer</td>
<td>[39]</td>
</tr>
<tr>
<td>15</td>
<td>( N_2H^+ + e^- \rightarrow N_2 + H )</td>
<td>Dissociative recombination</td>
<td>[56]</td>
</tr>
<tr>
<td>16</td>
<td>( N_2H^+ + e^- \rightarrow NH + N )</td>
<td>Dissociative recombination</td>
<td>[56]</td>
</tr>
<tr>
<td>17</td>
<td>( N + e^- \rightarrow N^+ + 2e^- )</td>
<td>Ionization</td>
<td>[57]</td>
</tr>
<tr>
<td>18</td>
<td>( NH + H^+ \rightarrow NH^+ + H )</td>
<td>Ion conversion</td>
<td>[58]</td>
</tr>
<tr>
<td>19</td>
<td>( NH^+ + e^- \rightarrow N + H )</td>
<td>Dissociative recombination (N-MAR)</td>
<td>[41]</td>
</tr>
<tr>
<td>20</td>
<td>( N + e^- \rightarrow N + e^- )</td>
<td>Elastic collision</td>
<td>BGK</td>
</tr>
<tr>
<td>21</td>
<td>( N_2 + e^- \rightarrow N_2 + e^- )</td>
<td>Elastic collision</td>
<td>BGK</td>
</tr>
<tr>
<td>22</td>
<td>( NH + H \rightarrow NH + H )</td>
<td>Elastic collision</td>
<td>BGK</td>
</tr>
<tr>
<td>23</td>
<td>( NH + N_2 \rightarrow NH + N_2 )</td>
<td>Elastic collision</td>
<td>BGK</td>
</tr>
<tr>
<td>24</td>
<td>( NH + N \rightarrow NH + N )</td>
<td>Elastic collision</td>
<td>BGK</td>
</tr>
<tr>
<td>25</td>
<td>( H_2 + H \rightarrow H_2 + H_2 )</td>
<td>Elastic collision</td>
<td>BGK</td>
</tr>
<tr>
<td>26</td>
<td>( H_2 + N_2 \rightarrow H_2 + N_2 )</td>
<td>Elastic collision</td>
<td>BGK</td>
</tr>
<tr>
<td>27</td>
<td>( N_2 + N_2 \rightarrow N_2 + N_2 )</td>
<td>Elastic collision</td>
<td>BGK</td>
</tr>
<tr>
<td>28</td>
<td>( H + N \rightarrow H + N )</td>
<td>Elastic collision</td>
<td>BGK</td>
</tr>
<tr>
<td>29</td>
<td>( H + H \rightarrow H + H )</td>
<td>Elastic collision</td>
<td>BGK</td>
</tr>
<tr>
<td>30</td>
<td>( N + N \rightarrow N + N )</td>
<td>Elastic collision</td>
<td>BGK</td>
</tr>
<tr>
<td>31</td>
<td>( N + N_2 \rightarrow N + N_2 )</td>
<td>Elastic collision</td>
<td>BGK</td>
</tr>
<tr>
<td>32</td>
<td>( H_2 + N \rightarrow H_2 + N )</td>
<td>Elastic collision</td>
<td>BGK</td>
</tr>
<tr>
<td>33</td>
<td>( N_2 + H \rightarrow N_2 + H )</td>
<td>Elastic collision</td>
<td>BGK</td>
</tr>
</tbody>
</table>

Table 4. processes included in B2.5-Eunomia to study nitrogen-seeding hydrogen plasma detachment scenarios.

For what concerns simulations regarding He/H₂ puffing in the target chamber, other processes have been added in the code. These are listed in table 5.

<table>
<thead>
<tr>
<th>N.</th>
<th>Reaction</th>
<th>Type</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>34</td>
<td>( He + e^- \rightarrow He^+ (2^3S) + e^- )</td>
<td>Excitation</td>
<td>[59]</td>
</tr>
<tr>
<td>35</td>
<td>( He^+ (2^3S) \rightarrow He + hv )</td>
<td>Radiative relaxation</td>
<td>[59]</td>
</tr>
<tr>
<td>36</td>
<td>( He^+ (2^3S) + e^- \rightarrow He^+ + 2e^- )</td>
<td>Ionization</td>
<td>[59]</td>
</tr>
<tr>
<td>37</td>
<td>( He + e^- \rightarrow He^+ + 2e^- )</td>
<td>Ionization</td>
<td>[59]</td>
</tr>
<tr>
<td>38</td>
<td>( He^+ + e^- \rightarrow He )</td>
<td>Recombination</td>
<td>[57]</td>
</tr>
<tr>
<td>39</td>
<td>( He + e^- \rightarrow He + e^- )</td>
<td>Elastic collision</td>
<td>BGK</td>
</tr>
<tr>
<td>40</td>
<td>( He + H_2 \rightarrow He + H_2 )</td>
<td>Elastic collision</td>
<td>BGK</td>
</tr>
<tr>
<td>41</td>
<td>( He + H \rightarrow He + H )</td>
<td>Elastic collision</td>
<td>BGK</td>
</tr>
<tr>
<td>42</td>
<td>( He + H^+ \rightarrow He + H^+ )</td>
<td>Elastic collision</td>
<td>BGK</td>
</tr>
</tbody>
</table>

Table 5. processes included in B2.5-Eunomia to study helium-seeding hydrogen plasma detachment scenarios.
Finally, the reactions implemented for the H$_2$/Ar seeding case are reported in table 6.

<table>
<thead>
<tr>
<th>N.</th>
<th>Reaction</th>
<th>Type</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>43</td>
<td>Ar + e$^-$ → Ar$^+$ + 2e$^-$</td>
<td>Excitation</td>
<td>[57]</td>
</tr>
<tr>
<td>44</td>
<td>Ar$^+$ + e$^-$ → Ar</td>
<td>Recombination</td>
<td>[57]</td>
</tr>
<tr>
<td>45</td>
<td>Ar + Ar → Ar + Ar</td>
<td>Elastic collision</td>
<td>BGK</td>
</tr>
<tr>
<td>46</td>
<td>Ar + H → Ar + H</td>
<td>Elastic collision</td>
<td>BGK</td>
</tr>
<tr>
<td>47</td>
<td>Ar + H$_2$ → Ar + H$_2$</td>
<td>Elastic collision</td>
<td>BGK</td>
</tr>
<tr>
<td>48</td>
<td>Ar + H$^+$ → Ar + H$^+$</td>
<td>Elastic collision</td>
<td>BGK</td>
</tr>
</tbody>
</table>

Table 6. processes included in B2.5-Eunomia to study Argon-seeding hydrogen plasma detachment scenarios.

In B2.5-Eunomia, the rate for hydrogenic collisions have been taken from AMJUEL[57] and HYDEL databases, which are the ones also used by default in the Eirene code. For the newly-added reactions, the reference for the rate is listed. The cross section for neutral-neutral elastic collisions are calculated by using the BGK approximation method[60] and is based on the Lennard-Jones potential. For electron-driven processes, the rate is calculated by the code as a function of the local (per-cell) electron temperature and density. Molecule-assisted-recombination mechanisms i.e. reactions 8,9 and 17 are treated in such a way that the rate-determining step is the ion conversion. The products of that process are assumed to instantaneously recombine with an electron.

9.10 Simulating plasma detachment in Magnum-PSI by means of B2.5-Eunomia codes.

In this section we present numerical simulations concerning the modelling of the full geometry of linear machine Magnum-PSI. For the first time, couple codes B2.5 and Eunomia have been used to specifically study detached-like experimental scenarios with newly-implemented plasma chemistry. The scope of this exercise is to gain more knowledge on the physics and chemistry occurring during experiments. The authors would like to underline that these simulations have to be considered as code experiments rather than predictive models to be quantitatively benchmarked with experimental data.

9.10.1 Modelling results

The baseline scenario, i.e. attached plasma conditions, have been set up without any external neutral source (gas puffing) and the achieved background neutral pressure in the target chamber corresponds to ≈ 0.3 Pa. As can be seen in figure 13(a), the plasma beam is conserved throughout its whole path in the target chamber. In particular, we can observe a peak in the electron density in the vicinity of the target. This is due to ion recycling at the wall, which leads to desorption of neutrals that are promptly ionized. In attached plasma conditions, the plasma environment near the wall is in the so-called high recycling regime. Similar findings have been described in [61], where simulations with SOLEDGE2D-EIRENE[62] suite have been carried out for linear plasma device Pilot-PSI.
In figure 13(b), a detached plasma scenario has been obtained by actively puffing H$_2$ in the target chamber. The background neutral pressure resulting is ≈ 2 Pa. The seeding location is depicted by the red circle in figure 13. The “gaseous chamber” concept, which has been experimentally studied with several linear machines, as described in [16], has been successfully replicated in this simulation. As can be observed, $n_e$ quickly drops once the beam enters the target chamber, passing from ≈ 5E19 m$^{-3}$ to ≈ 1E19 m$^{-3}$. A further characteristic feature of detachment, compared to attached case, is the plasma pressure drop led by momentum loss and volume recombination processes.

Dedicated code-experiments have been carried out in order to study the difference between He, Ar and N$_2$ puffing, together with H$_2$, at different mixing ratios. In principle, we replicated the experiments presented in section 4.1. The novelty of this exercise lays in the fact that new plasma chemical processes have been included in a kinetic-fluid coupled code. The aim is to highlight possible different volume-driven effects on plasma detachment. In particular, the role of reactive N$_2$-related NH radical and N-MARs is of great interest, given that NH$_x$ molecules are surely produced in the divertor. The particle source for NH has been set assuming a conversion efficiency of nitrogen to ammonia (molecular precursor for NH radical) of 7%, which is in line with previous studies [63][64]. NH$_x$ particles are formed via surface process; while N$_2$ is injected in the location depicted in figure 13, the source for NH has been set at the target plate.

The total plasma pressure modelled at 3 cm in front of the target, together with the heat flux (at the sheath entrance) calculated as in equation 1, are reported in figure 14.
Plasma parameters achieved with the simulations are about in the order of \( n_e \approx 10^{19} \text{m}^{-3} \) with electron temperatures below 1 eV. Although a quantitative comparison between experiments and simulations is beyond the scope of this work, the same trend is obtained when comparing Magnum-PSI results with the model.

The presence of nitrogen seeding in combination with H\(_2\) leads to a net decrease of the plasma pressure by roughly 35%. This value may be overestimated due to the fact that NH (electron donor responsible for the first step of N-MAR) is injected entirely from the surface of the target. Regarding H\(_2\) + Ar and H\(_2\) + He puffing scenarios, a reversed effect is achieved. In fact, plasma pressure increases by \( \approx 20\% \) in both cases, reducing the effectiveness of detachment. No significant differences are recorded between He and Ar scans, indicating that the absence of impurity-induced volume recombination processes might lead to a dilution effect of H\(_2\) in the plasma parameters range characterising these simulations. The heat flux, calculated at the sheath edge with no pre-sheath or sheath effects taken into account, provided the same trend. Worth to underline that a full description of the sheath physics is beyond the capabilities of B2.5. No significant plasma radial transport occurs along the different scans for He, Ar and N\(_2\) cases of study.

These results confirm that adding inert species in the puffed mixture does not have beneficial effects for detachment in the vicinity of the target. An increase in plasma pressure leads to an enhanced particle flux, hence to a higher heat flux to the target.

To address the contribution of N-MAR and MAR respectively, the collision frequency of these recombination processes for a 10% N\(_2\) seeding case has been monitored and is shown in figure 15.

![Figure 15. N-MAR (left) and MAR (right) collision frequency.](image)

The N-MAR process occurs extensively in the vicinity of the target (axially) and radially along the whole beam, while it becomes negligible when moving far away from the plate at about 5 cm. The spatial distribution of such process represents a clear indication of the enhanced recombination of incoming hydrogen ions before they reach the target.

Regarding the purely hydrogenic process, hardly any MAR events appear to be occurring in the simulation. The vibrational excited states of H\(_2\), which are needed for the first ion conversion step of MAR, are simulated in the code. Nevertheless, the contribution of this two-step reaction doesn’t seem relevant in the condition hereby examined. That might be due to the low T\(_e\) (<1 eV), which is given by the code as an output.

The main lack of this model and, to the knowledge of the authors, of any other H\(_2\) - N\(_2\) plasma code, is the absence of a scaling law for the following process:

\[ \text{H}^+ + \text{N}_2(v) \rightarrow \text{H} + \text{N}_2^+, \]

which is a further recombination path for H\(^+\). It is fair to assume that a large fraction of injected N\(_2\) molecules undergo electron-impact vibrational excitation (threshold energy for N\(_2\)(v=0 -> v=1) is 0.29 eV). To provide a description of the entire plasma chemistry going on in a detached-like hydrogen plasma with N\(_2\) seeding, and therefore to make quantitative predictions, a dedicated study on the role of N\(_2\)(v) would be needed.

Moreover, to carry out quantitative comparison between experiments and simulations with B2.5-Eunomia, dedicated studies on the “free parameters” currently assumed in the code e.g. cross-field transport coefficients, potential boundary and plasma flow from the source should be carried out. Nevertheless, the newly-implemented plasma chemistry is responsible for the achieved trends,
indicating that the presence (or the absence) of further ion-recombination paths, that differ from the pure hydrogenic ones, may have positive influence in reducing the particle flux during detachment. Specifically, the role of N-MAR is hereby highlighted experimentally and confirmed with numerical simulations. Therefore, that process should be included in the state-of-the-art divertor-relevant plasma physics codes.

9.11 Conclusion

The effect of different impurities on plasma detachment has been studied by means of both experiments and numerical simulations. Experiments highlighted the beneficial role of N2, seeded together with H2 in the target chamber, compared to He+H2 and Ar+H2, which showed an opposite trend. In the N2-seeding case a plasma pressure decrease and a reduced heat load collected at the target plate is observed, while in the remaining two cases i.e. Ar and He, detachment performance is lowered. The plasma chemistry occurring in divertor-relevant plasma detached scenarios has been studied by means of global plasma modelling and the subsequent reduced set of chemical equations have been implemented in the couple code B2.5-Eunomia. Simulation results qualitatively reproduce the experimental findings, confirming the relevance of N-induced volume recombination processes (N-MAR). Moreover, a comparison between the well-known hydrogenic MAR and N-MAR has been performed, pointing out the significance of the latter in converting hydrogen ion to neutrals via molecule-assisted process. Nitrogen-related volume processes should thus be included in divertor and plasma-edge codes, as N-MAR is such an efficient route for the neutralization of hydrogen ion.

9.12 Acknowledgment

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9.13 Bibliography


Summary

Plasma chemistry in divertor relevant plasmas

One of the crucial issues to produce energy by nuclear fusion is the power exhaust problem. A significant fraction of the power generated in the plasma core is channeled through the scrape-off-layer and is delivered to the plasma-facing-components in the so-called divertor region. Divertor targets, which will be actively-cooled tungsten monoblocks in ITER, are nominally subjected to extremely high heat and particle loads, but can only tolerate up to 10 MW/m² from a technological point of view. To achieve acceptable heat and particle flux onto the divertor targets, so-called plasma detachment is essential to be set up and controlled. Detachment is an operational regime where particular plasma conditions lead to ion recombination in the volume phase, resulting in lower particle flux, and is characterized by a plasma pressure drop along the magnetic field lines towards the target. It has been extensively proven, both theoretically and experimentally, that impurity seeding facilitates achieving detachment. However, little is known on the impurity-induced plasma chemical processes occurring in the divertor region during detachment operation. To address that, dedicated experiments in the linear plasma device Magnum-PSI have been carried out. Linear plasma machines, often referred to as divertor simulators, allow the generation of steady-state divertor-relevant plasma scenarios with great diagnostic accessibility.

Plasma detachment has been firstly achieved by H₂ gas injection in the target chamber, with neutral background pressure ranging from 0.3 to 16 Pa. In this work, the influence of three different impurities i.e. N₂, Ar and He on detachment performance of a hydrogen plasma is evaluated. Those species have been actively puffed in the target chamber, together with H₂, at flux ratios of 0, 5, 10, 15 and 20 %. The background neutral pressures were kept fixed at 2 and 4 Pa i.e. divertor-relevant conditions. Results highlight the beneficial role of N₂+H₂ seeding, decreasing the plasma pressure in front of the target and reducing the heat flux delivered to it. Interestingly, when looking at plasma density and temperature profiles, we observe that electron temperature remains constant among the scans while the electron density decreases with increasing the content of N₂ in the seeded mixture. This is a further indication of enhanced recombination taking place, where ions are converted to neutrals in the plasma volume phase. An opposite trend is found concerning He and Ar. In fact, injection of H₂+He and H₂+Ar gas mixtures led to an increased heat flux in both cases compared to only H₂. A Residual-Gas-Analyzer (RGA) has been used to study the conversion efficiency of N₂ to ammonia, showing conversions between 3 and 5 %. The molecular emission band at 336 nm, corresponding to the electronic transition of NH*(A³Π→X³Σ, Δv = 0), has been observed with optical emission spectroscopy and its intensity increases linearly with the flux ratio of N₂ in the seeded mixture. Moreover, plasma radiation has been monitored by using a bolometry system. No significant trends as a function of injected nitrogen have been observed, hence excluding any power limitation effects.

Similar experiments have been carried out with GAMMA10/PDX, a linear plasma machine located at the University of Tsukuba. The uniqueness of that machine lays in the capability of achieving high electron temperatures, albeit electron densities lower by two orders of magnitude compared to Magnum-PSI. Those experiments allowed us to investigate the effect of impurities on detached-like plasmas in a wider range of parameters. Results are in line with what has been achieved in Magnum-PSI, highlighting H₂+N₂ gas as the most favorable mixture to reduce the particle flux to the target. Numerical simulations are needed to provide a comprehensive understanding of the fundamental atomic and molecular processes occurring in divertor-like environment. A three-step approach has been adopted as follows: at first, global plasma models have been set-up on the basis of Plasimo code.
Global models are spatially-averaged simulations allowing one to implement a large set of plasma chemical equations and to highlight the most relevant processes among them. Extended models have been built up for N$_2$-H$_2$, Ar-H$_2$ and He-H$_2$ plasma scenarios. This study shows two main nitrogen-included recombination reaction paths resulted to be dominant, i.e. the ion conversion of NH followed by dissociative recombination and a proton transfer between H$_2^+$ and N$_2$, producing N$_2$H$^+$. These two processes are referred to as N-MAR (nitrogen-molecular activated recombination). Concerning the remaining two cases, no significant ion recombination process seems to be driven by the presence of either Ar and He. The resulting reduced scheme for H$_2$-N$_2$ chemistry has been implemented in Eunomia, a spatially-resolved Monte Carlo code suited for the transport of neutrals in linear plasma devices. Finally, Eunomia has been coupled with B2.5, a fluid code solving plasma equations. Simulation results of all the three cases of study (H$_2$-He, H$_2$-N$_2$, H$_2$-Ar) qualitatively reproduce the favorable effect of N$_2$, while confirming the deteriorating effect of He and Ar on detachment performance. The importance of NH as electron donor is highlighted and N-MAR confirmed as reaction route enhancing the conversion of ions to neutrals, making the heat loads to the divertor plate more tolerable. This work represents a further step towards the full understanding of the role of plasma chemical volume processes in a detached divertor plasma.
Sommario

Chimica del plasma rilevante per il plasma del divertore

Una delle questioni cruciali per la produzione di energia mediante fusione nucleare è il problema del *power exhaust*. Difatti, una frazione significativa della potenza generata nel nucleo del plasma viene canalizzata attraverso lo *scrape-off-layer* (la regione più esterna al nucleo centrale) e viene erogata ai componenti rivolti al plasma (denominati anche *targets*) nella cosiddetta regione del divertore. In ITER, le componenti del divertore saranno monoblocchi di tungsteno di tungsteno raffreddati attivamente, e saranno sottoposte a carichi di calore e particelle estremamente elevati. Il limite tecnologico per la “sopravvivenza” quest’ultime è di 10 MW/m^2_. Per ottenere un flusso di calore e di particelle accettabile sui *targets* dei divertori, è necessario impostare e controllare il cosiddetto “distacco del plasma”, chiamato anche *plasma detachment*. Questo è un regime operativo in cui particolari condizioni del plasma portano alla neutralizzazione degli ioni in fase volumetrica, con conseguente inferiore flusso di ioni, ed è caratterizzato da una diminuzione di pressione del plasma lungo le linee del campo magnetico in direzione del *target*. È stato ampiamente dimostrato, sia teoricamente che sperimentalmente, che l’addizione di cosidette “impurità” facilita il raggiungimento di tale regime operativo. Tuttavia, si sa poco sui processi chimici del plasma, che si verificano nella regione del divertore durante l’operazione di *detachment*, indotti da queste impurità. A tale proposito, sono stati condotti esperimenti nel dispositivo lineare al plasma ‘Magnum-PSI’. I dispositivi lineari, spesso denominati simulatori di divertore, consentono la generazione di scenari di plasma rilevanti per i divertori, allo stato stazionario, con grande accessibilità diagnostica.

Il *detachment* del plasma è stato inizialmente ottenuto mediante iniezione di gas H\(_2\) nella camera di Magnum-PSI denominata *target*, con una pressione che varia da 0,3 a 16 Pa. In questo lavoro viene valutata l’influenza di tre diverse impurità, ovvero azoto (N\(_2\)), argon (Ar) ed elio (He), sulle prestazioni di *detachment* di un plasma a idrogeno. Quelle specie sono state attivamente inserite nella camera *target*, insieme ad idrogeno allo stato gassoso, con rapporti di flusso di 0, 5, 10, 15 e 20%. Le pressioni sono state mantenute fisse a 2 e 4 Pa, ovvero in condizioni rilevanti per il divertore. I risultati evidenziano il ruolo benefico dell’introduzione di N\(_2\)+H\(_2\), che agisce riducendo il flusso di calore depositato sul *target*. È interessante notare che, osservando i profili di densità e di temperatura del plasma, si evince che la temperatura elettronica rimane costante mentre la densità elettronica diminuisce con l’aumentare del contenuto di N\(_2\) nella miscela inserita. Questa è un’ulteriore indicazione del fatto che si sta verificando una maggiore neutralizzazione del plasma, in cui gli ioni vengono convertiti in neutroni. Una tendenza opposta si riscontra per quanto riguarda He e Ar. Infatti, l’iniezione di miscele di gas H\(_2\)+He e H\(_2\)+Ar ha portato ad un aumento del flusso di calore in entrambi i casi rispetto al solo H\(_2\). Un analizzatore a spettrometria di massa è stato utilizzato per studiare l’efficienza di conversione di N\(_2\) in ammoniaca, mostrando conversioni tra il 3 e il 5%. La banda di emissione molecolare a 336 nm, corrispondente alla transizione elettronica della specie NH\(_+\) (A\(3\Pi\)\(\rightarrow\)X\(3\Sigma\), \(\Delta v = 0\)), è stata osservata con spettroscopia di emissione ottica. Tale intensità aumenta linearmente con il contenuto di azoto nella miscela. Inoltre, la radiazione al plasma è stata monitorata utilizzando un sistema di bolometria. Non essendo state osservate tendenze significative in funzione dell’azoto inserito, si possono escludere eventuali effetti del fenomeno della ‘limitazione della potenza’, ovvero *power limitation*.

Esperimenti simili sono stati condotti con GAMMA10/PDX, un dispositivo al plasma lineare situato presso l’Università di Tsukuba. L’unicità di quel generatore al plasma risiede nella capacità di raggiungere elevate temperature elettroniche, sebbene con densità elettroniche inferiori di due ordini di grandezza rispetto a Magnum-PSI. Tali esperimenti ci hanno permesso di studiare l’effetto delle
impurita’ sul plasma *detachment* in un’ampia gamma di parametri. I risultati sono in linea con quanto ottenuto in Magnum-PSI, evidenziando il gas \( \text{H}_2 + \text{N}_2 \) come miscela più favorevole per ridurre il flusso di particelle verso il *target*.

Per comprendere la moltitudine di processi atomici e molecolari che si verificano nel divertore, sono necessarie simulazioni numeriche. In questo studio, un approccio suddiviso in tre fasi distinte è stato adottato come segue: inizialmente, un modello “globale”, detto anche *global model*, è stato realizzato sulla base del codice *Plasimo*. I modelli globali sono simulazioni a media spaziale che consentono di implementare una vasta serie di equazioni chimiche del plasma e di evidenziare i processi più rilevanti tra esse. Estesi modelli sono stati generati per studiare scenari al plasma con le specie \( \text{N}_2-\text{H}_2, \text{Ar}-\text{H}_2 \) e He-\( \text{H}_2 \). Questo studio mostra che due principali processi di neutralizzazione di plasma a idrogeno dovuti alla co-presenza di azoto risultano dominanti: la conversione ionica di NH seguita da ricombinazione dissociativa e un trasferimento protonico tra \( \text{H}_2^+ \) e \( \text{N}_2 \), producendo lo ione molecolare \( \text{N}_2\text{H}^+ \). Questi due processi, identificati per la prima volta in questo studio, sono stati indicati come N-MAR (ricombinazione attivata da azoto-molecolare). Nessun significativo processo di neutralizzazione sembra essere guidato dalla presenza di argon o elio. I principali processi evidenziati attraverso lo sviluppo e lo studio di questi *global models* sono stati implementati in Eunomia, un codice Monte Carlo adatto per il trasporto di particelle neutre in dispositivi lineari al plasma. Infine, Eunomia è stato abbinato a B2.5, un codice di dinamica dei fluidi che risolve le equazioni del plasma. I risultati della simulazione di tutti e tre i casi di studio (\( \text{H}_2-\text{He}, \text{H}_2-\text{N}_2, \text{H}_2-\text{Ar} \)) riproducono qualitativamente l’effetto favorevole di \( \text{N}_2 \) confermando l’effetto deteriorante di He e Ar sulle prestazioni di *detachment*. In questo studio, l’importanza della specie NH viene evidenziata e N-MAR confermato come via di reazione di neutralizzazione, rendendo più tollerabili i carichi di calore sulla *target* del divertore. Questo lavoro rappresenta un ulteriore passo avanti verso la piena comprensione del ruolo dei processi volumetrici in un *detached* plasma nella regione del divertore.
Samenvatting

Plasmachemie in divertor relevante plasma's

Een van de grootste uitdagingen van de energieproductie door middel van kernfusie is het probleem van de warmteafvoer. Een aanzienlijk deel van het in de plasmakern opgewekte vermogen wordt door de zogenaamde scrape-off layer (SOL) afgevoerd, en komt uiteindelijk in de zogenaamde divertor op de wand terecht. Deze wand in de divertor, die in ITER zal bestaan uit actief gekoeld wolfram, wordt blootgesteld aan extreem hoge hitte- en deeltjesbelastingen, maar kan technologisch gezien slechts tot 10 MW/m² verdragen. Om een acceptabele warmte- en deeltjesstroom op de divertor-wand te bereiken, is het essentieel om het plasma gecontroleerd los te koppelen van de wand, een toestand die we plasma-detachment noemen. Detachment is een operationeel regime waarbij bepaalde plasmacondities leiden tot ionenrecombinatie in het volume van het plasma, wat resulteert in een lagere deeltjesflux, en wordt gekenmerkt door een plasmadrukval langs de magnetische veldlijnen naar de wand. Het is uitvoerig bewezen, zowel theoretisch als experimenteel, dat het introduceren van onzuiverheden in het plasma het bereiken van detachment vergemakkelijkt. Er is echter weinig bekend over de door onzuiverheden veroorzaakte chemische processen in het divertor-gebied tijdens detachment. Om hier duidelijkheid over te krijgen zijn speciale experimenten uitgevoerd in het lineaire plasma-apparaat Magnum-PSI. Lineaire plasmamachines, vaak aangeduid als divertor-simulatoren, maken het mogelijk om detachable-relevante plasma’s te genereren, met goede toegankelijkheid voor diagnostieken.

Plasma-detachment is allereerst bereikt door injectie van waterstofgas (H₂) in Magnum-PSI, met neutrale achtergronddrukken variërend van 0,3 tot 16 Pa. In dit werk is de invloed van drie verschillende onzuiverheden op de mate van detachment in waterstofplasma’s onderzocht, namelijk stikstof (N₂), argon (Ar) en helium (He). Deze drie onzuiverheden zijn actief ingeblazen in het vacuüm vat van Magnum-PSI, samen met H₂, in fluxverhoudingen van 0, 5, 10, 15 en 20%. De neutrale achtergronddruk werd hierbij gefixeerd op 2 en 4 Pa, d.w.z. op divertor relevante drukken. De resultaten benadrukken de gunstige invloed van het gasmengsel N₂ + H₂; het verlaagt de plasmadruk dichtbij de wand en het verminderd de warmteflux naar de wand. Interessant is dat wanneer we kijken naar plasmadichtheid- en temperatuurprofielen, we waarnemen dat de elektronentemperatuur constant blijft, terwijl de elektronendichtheid afneemt met het verhogen van het gehalte aan N₂ in het gasmengsel. Dit is een verdere indicatie dat er meer recombinatie plaatsvindt, waarbij ionen worden omgezet in neutrale deeltjes in het volume van het plasma. Een tegenovergestelde trend wordt waargenomen met betrekking tot He en Ar. In feite leidde injectie van H₂ + He en H₂ + Ar gasmengsels in beide gevallen tot een verhoogde warmteflux vergeleken met alleen H₂ gas. Een massaspectrometer is gebruikt om de conversie-efficiëntie van N₂ naar ammoniak te bestuderen. Conversies tussen de 3 en 5% zijn waargenomen. De moleculaire emissieband bij 336 nm, overeenkomend met de elektronische overgang van NH⁺ (A^3Π → X^3Σ, \( \bar{v} = 0 \)), is waargenomen met optische emissiespectroscopie. De intensiteit van deze band neemt lineair toe met de fluxverhouding van N₂ in het gasmengsel. Bovendien is plasmasstraling gemeten met behulp van een bolometriesysteem. Het uitgestraalde vermogen is niet afhankelijk gebleken van de hoeveelheid geïnjecteerd stikstof, waardoor het eventuele effect van een vermogenstekort is uitgesloten.

Soortgelijke experimenten zijn uitgevoerd met GAMMA10 / PDX, een lineaire plasmamachine aan de universiteit van Tsukuba. Het unieke van die machine ligt in het vermogen om hoge elektronentemperaturen te bereiken, hoewel elektronendichtheden twee orden van grootte lager zijn vergeleken met Magnum-PSI. Die experimenten maakten het mogelijk om het effect van onzuiverheden op detachment in een groter bereik van parameters te onderzoeken. De resultaten zijn
in lijn met wat is waargenomen in Magnum-PSI, waarbij opnieuw werd aangetoond dat H₂ + N₂ het meest gunstige gasmengsel is om de deeltjesstroom naar de wand te verminderen.

Numerieke simulaties zijn nodig om een volledig begrip te geven van de fundamentele atomaire en moleculaire processen die zich voordoen in een divertor-omgeving. Er is gekozen voor een aanpak in drie stappen: allereerst zijn globale plasmamodellen ontwikkeld op basis van de Plasimo-code. Globale modellen zijn ruimtelijk gemiddelde simulaties waarmee men een reeks chemische plasma-vergelijkingen kan implementeren en de meest relevante processen onder hen kan afleiden.

Uitgebreide modellen zijn ontwikkeld voor N₂-H₂, Ar-H₂ en He-H₂ plasma-scenario’s. Deze studie toont aan dat er twee dominante stikstof-gerelateerde recombinatie-reactiepaden een rol spelen: de ionenconversie van NH gevolgd door dissociatieve recombinatie en een protonoverdracht tussen H₂⁺ en N₂, waarbij N₂H⁺ wordt geproduceerd. Deze twee processen worden N-MAR (stikstof Moleculair geactiveerde Recombinatie) genoemd. Wat betreft de Ar-H₂ en He-H₂ plasma-scenario’s, lijkt geen significant ionenrecombinatie-proces te worden veroorzaakt door de aanwezigheid van Ar en He.

Vervolgens is het resulterende gereduceerde reactie-schema voor H₂-N₂-chemie geïmplementeerd in Eunomia, een ruimtelijk opgeloste Monte-Carlo-code die geschikt is voor het simuleren van het transport van neutralen in lineaire plasma-apparaten. Ten slotte is Eunomia gekoppeld aan B2.5, een vloeistofcode die de plasma-vergelijkingen oplost. Simulatieresultaten van alle drie scenario’s (H₂-He, H₂-N₂, H₂-Ar) reproduceren het gunstige effect van N₂ kwalitatief, terwijl het ongunstige effect van He en Ar op de mate van detachment wordt bevestigd. Het belang van NH als elektronendonor wordt benadrukt en N-MAR bevestigd als reactieroute die de conversie van ionen naar neutralen verbetert, waardoor de warmtebelasting naar de wand wordt gereduceerd.

Dit werk betekent een verdere stap in de richting van een volledig begrip van de rol van plasmachemische volumeprocessen in een divertor-plasma tijdens detachment.
Curriculum Vitae

Renato Perillo was born on 21-09-1989 in Feltre, Italy. After finishing his Diploma degree in 2008 at Liceo Scientifico Jacopo da Ponte in Bassano del Grappa, he studied Environmental Sciences and Technology at Universita’ degli Studi di Padova, in Padova, Italy. In 2014 he graduated within the group of Professor Paradisi, at the Department of Chemical Sciences, in Chemistry of Plasmas. From November 2015 he started a PhD project at DIFFER Institute in Eindhoven, The Netherlands, of which the results are presented in this dissertation. From November 2019 he will be employed at University of California San Diego as a Post Doc researcher.
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