A chemical reduction method based on pathway analysis

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A Chemical Reduction Method based on Pathway Analysis

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Abstract

Numerical simulations are a great tool to study plasma physics. However, the nature of a plasma leads to the significant presence of a particle’s or a molecule’s (ro-vibrational) excited and/or ionized states. For a single atom, this might still be computable in reasonable time, but when a molecule or multiple different atoms are present the computational cost quickly skyrockets.

The sheer amount of particles and reactions makes full-fledged plasma simulations infeasible. To still be able to model complex plasmas, chemical reduction must be applied. Chemical reduction decreases the complexity by reducing the number of species and/or reactions taken into account. This is done in a way such that the simulated physics can still be represented accurately and relevant for the application. The goal of chemical reduction is two-fold, on the one hand it achieves computational cost reduction, on the other hand it allows for better analysis of the underlying chemistry.

In this work a new mechanism reduction method is developed based on the results of the pathway analysis [24] method. An extension of the pathway analysis implementation [26] within the PLASIMO [18] toolbox is created that allows for automated reduction of chemically complex plasmas in zero-dimensional models. The automated tool limits the required user effort and knowledge of the chemistry to a minimum.

The pathway reduction method is capable of removing significant parts of the chemistry, in the form of reactions and species. This is done for both constant input power as well as pulsed input power simulations. Besides taking an extensive look at the effect of removing species and reactions on the accuracy of the reduced model, the reduction method is analysed in a number of ways, including a comparison to a naive method and a timescale analysis of the reduction’s effect on the stiffness of the system.

Large steps have been made in developing and testing a new mechanism reduction method based on pathway analysis. An automated reduction tool is established and is a very promising basis for subsequent reduction work. An extensive look at possible future work is taken including a detailed proposal and some initial work for a side-by-side comparison between pathway reduction and the Intrinsic Low-Dimensional Manifold [21] method.
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.2.2 Pulsed input power plasmas: Reducing reactions only</td>
<td>39</td>
</tr>
<tr>
<td>4.3 Reducing reactions and species</td>
<td>42</td>
</tr>
<tr>
<td>4.3.1 Constant input power plasmas: Reducing reactions and species</td>
<td>43</td>
</tr>
<tr>
<td>4.3.2 Pulsed input power plasmas: Reducing reactions and species</td>
<td>44</td>
</tr>
<tr>
<td>4.4 Reduction analysis</td>
<td>46</td>
</tr>
<tr>
<td>4.4.1 Comparison with a naive reduction</td>
<td>47</td>
</tr>
<tr>
<td>4.4.2 Timescale analysis</td>
<td>49</td>
</tr>
<tr>
<td>4.4.3 Relating species and timescales: Schur/Eigenvalue decomposition</td>
<td>51</td>
</tr>
<tr>
<td>5 Conclusions and Outlook</td>
<td>53</td>
</tr>
<tr>
<td>5.1 Conclusions</td>
<td>53</td>
</tr>
<tr>
<td>5.2 Outlook</td>
<td>54</td>
</tr>
<tr>
<td>5.2.1 Error calculation of pathway reduction</td>
<td>54</td>
</tr>
<tr>
<td>5.2.2 Allowing the tool to run till a requested error is achieved</td>
<td>54</td>
</tr>
<tr>
<td>5.2.3 Different approach to a comparison with the naive reduction</td>
<td>55</td>
</tr>
<tr>
<td>5.2.4 Using Schur decomposition as a species and timescales analysis tool</td>
<td>56</td>
</tr>
<tr>
<td>5.3 Outlook: ILDM versus Pathway Reduction</td>
<td>56</td>
</tr>
<tr>
<td>5.3.1 The ILDM method</td>
<td>57</td>
</tr>
<tr>
<td>5.3.2 Simple hydrogen chemistry</td>
<td>58</td>
</tr>
<tr>
<td>5.3.3 Future work</td>
<td>60</td>
</tr>
<tr>
<td>Appendix</td>
<td>64</td>
</tr>
<tr>
<td>A Sample system decomposition</td>
<td>64</td>
</tr>
<tr>
<td>B Model information</td>
<td>65</td>
</tr>
<tr>
<td>C Heatmaps of species-timescale relation</td>
<td>67</td>
</tr>
</tbody>
</table>
Chapter 1

Introduction

Mankind has always been fascinated by what it cannot explain. Curiosity has driven people to explore and explain natural phenomena. Where in the distant past, many things we see in our daily lives were still unexplained, nowadays everything we see, is at least understood to some extent if not completely. Science, therefore, is no longer a discipline of big discoveries per se. Besides discovering new methods and/or phenomena, a large part of the scientific society focuses on improvement of old methods and obtaining a better understanding of known processes.

As mentioned, it is in human nature to try and explain things we observe, at first this was of course focused on Earth’s phenomena. With more and more obtained knowledge, our eyes turned to space more recently. It turned out that 99% of all observable mass is in the, so-called, fourth state of matter, the plasma state. In the last century, research into this plasma state has grown strongly to becoming one of the hot topics in physics research.

Not just interstellar matter is comprised of plasmas but also some prominent features on Earth, including possibly humanity’s biggest invention, fire can at times be considered a plasma, and the mighty lightning discharges during a thunderstorm are definitely examples of plasmas. However, a plasma was only first called plasma in official writing by Langmuir in 1928 [1] when researching low-pressure arcs.

A plasma has since been defined as a (partly) ionized gas. Neutral atoms have lost one or more electrons due to (often high-energy) collisions and split into one ion and one (or more) free electrons. Nevertheless, not all ionized gases are plasmas. Plasmas are very different to gases because of their electrical behaviour. Due to the significant presence of charged particles in a plasma, it responds strongly to externally applied electric and magnetic fields. The collective behaviour shown by the charged particles is something unique to a plasma and only occurs when there are enough charges present in a certain volume and the total negative charge is very close to equaling the total positive charge, which is called quasi-neutrality [2].

Due to a large amount of positive and negative charge carriers any space charge found within a ionized gas will be shielded and “invisible” to other charges after a certain distance, called the Debye length. Before the ionized gas qualifies as a plasma the dimensions have to be larger than this Debye length, effectively screening most parts of the plasma from possible space charges in other parts of the plasma.

Plasma research nowadays is very diverse, spanning a multitude of dedicated research groups worldwide. Studies are still performed to increase the understanding of lightning inception and fully explain this process [3] that has been observed ever since humans existed.
The biggest application of plasmas in the past century and up to this day is its use in lighting applications, which therefore still remains a hot topic [4]. Industrially, plasmas are very interesting for production processes, as in for example the world of semiconductor production [5]. Even though plasmas are ionized gases, there is also the possibility to create and use them in and around liquids, which is a relatively new field of study [6]. Among many other applications, another very interesting aspect of plasma research is the usage of plasmas in medicine [7,8].

In order to investigate all these applications, advanced diagnostic tools have been developed [9] over the past century and a bit. Even today, extensions of diagnostic tools and new methods are in development [10]. However, with just experimental diagnostics much information about plasmas is still unobtainable. Often, the measurable quantities cannot be explained either. To provide understanding of the inner workings of plasmas, experimental work has to be complemented by modelling of said plasma. Modelling of plasmas has a similarly rich past as experimental research into plasmas [11]. This thesis deals explicitly with the modelling part of plasma research, therefore no experimental set-ups or apparatus will be discussed in the remainder of this work. A more in-depth introduction into plasma modelling and its field will be given in the next section.

1.1 Plasma modelling

Plasma modelling is a discipline that has been in development since research into plasmas started. In the past modelling would either imply theoretical calculations of processes or mimicking one of nature’s phenomena in an experiment. This could either be a small-scale version of a large feature, or a larger version of a small feature. In the last half of the century, however, numerical simulations have become the dominant modelling process. Where experiments either mimic observable phenomena or create new features, modelling requires more knowledge or educated guesses to be able to function. Finding a resulting observable is often just a side-goal of a model. A model requires and gives knowledge of the inner workings of a process. Modelling is a means to understand what happens in the world, in the case of this work modelling aims to understand the inner workings of plasmas.

In numerical simulations a plasma is recreated as well as it can be and the plasma is simulated using known equations for interactions and processes. This way a numerical approximation can be made for plasma models that are not solvable analytically. A numerical simulation deals with three main segments of a plasma [12]:

- **The configuration** describes the size (and geometry) of the plasma (vessel), its boundary conditions and the energy input into the plasma.

- **The transport** describes how the species in the plasma are transported within the plasma and with its surroundings. The same goes for the transport of energy and momentum.

- **The chemistry** describes the interaction between species in the plasma, especially the creation and destruction of the species.

These are in principle separate concepts of the plasma, however there is a lot of interaction between the different segments and they are therefore strongly dependent on each other.
Together these can be used to calculate, for example, the electromagnetic field, the electron temperature/density, densities of all other species and radiated power or all of these at the same time. This can be done at a certain point in time and/or space, but also time-resolved and/or on a 1D, 2D or even 3D grid. With the broad range of possible plasma models also comes a broad range of complexities.

As mentioned by J. van Dijk et al [11], a combination of many features are necessary to achieve a self-consistent plasma model. Even then, it is completely dependent on the application what the output of a plasma model will be. This research is focused on the plasma chemistry and will therefore not discuss calculations of the electromagnetic field, solving the Boltzmann equation and defining transport in detail unless necessary. In the field of chemistry well-known examples of dedicated simulation toolkits include the HPEM (Hybrid Plasma Equipment Model) code developed on the University of Michigan [13], ZDPlasKin (Zero-Dimensional Plasma Kinetics solver) developed at LAPLACE [14] and PLASIMO (PLAsma SImulation & MOdeling) developed at Eindhoven University of Technology [15].

The HPEM code focuses on modelling low pressure plasma processing reactors and is suitable for plasma tool development and improvement [16]. A range of different types of plasmas can be simulated and especially plasma-surface interactions are modelled, making it very useful for industrial (for example the semiconductor industry) applications. All of the code is capable of 2D simulations, whilst a large part is also available for 3D work.

ZDPlasKin is a model developed to keep track of species densities and gas temperature in non-thermal plasmas. No spatial information is calculated and the results are volume-averaged or local densities [17]. This saves enough computation time that the considered chemistry can be arbitrarily large. More details of zero-dimensional modelling will be given in chapter 2.

PLASIMO is a toolbox that is more universal compared to the other two examples. Instead of focusing on a specific type of application or plasma it is meant to be a universal plasma simulation software. Plasma simulations of both steady-state and transient processes are supported. Various degrees of equilibrium from Local Thermodynamic Equilibrium (LTE) till non-LTE and non-thermal plasmas are supported [18]. It can calculate electromagnetic fields, transports and flows, radiation as well as species densities and temperatures. Modules are available from zero-dimensional, 1D, 2D and 3D simulations. The configuration and usage is entirely user-controlled. The work described in this thesis is performed within the PLASIMO environment and was meant to add extra functionality to the already diverse toolbox.

1.2 Plasma chemistry

The focus of this work is on the complex chemistries that can arise within plasmas. Chemistry in this case is the generalization of interactions between different species and between species and the surrounding. A species in this sense is one unique state of an atom or molecule. The most basic example is an argon atom in the ground state, which will be represented by the abbreviation Ar. All species in simulations are given some properties like charge, internal energy and mass. In the case of Ar the charge is 0, the internal energy is also 0 (internal energies are measured compared to the ground state) and the mass is 39.948 u. Not just the ground state of atoms can be considered, but also more complicated excited states of atoms, (multiply) ionized versions of the atom (ions), molecules and even excited and/or ionized molecules.
The last species to mention, often the most important one, is the electron, known as e. Though it is the smallest and lightest of them all, it plays the largest role in the formation of a plasma. As a plasma can only exist when enough of the background gas is ionized. The most prominent ionization method is electron-impact ionization. Electrons are also the negative charge carriers in most plasmas (electronegative plasmas are the exception, but are quite rare).

In a plasma chemistry these species do not just interact with the electromagnetic field (if charged) but also with each other. The most basic interaction is a collision between two particles. During a collision, energy and/or momentum may be interchanged between the two particles. Kinetic energy may be lost in a collision but momentum is conserved. In the case that a collision changes the state of either one of the particles, it is called a reaction. This way one or more “new” species can be formed and one or more of the “old” species can be destroyed. Looking back at the case of electron-impact ionization as discussed before, this reaction is given by equation (1.1):

\[
\text{Ar} + e \rightarrow \text{Ar}^+ + 2e. \tag{1.1}
\]

In this simple reaction an electron (e), with a high enough kinetic energy, impinges on an argon atom (Ar) and transfers (part of) its energy to the outermost electron of the atom, which in turn gains enough energy to free itself from the electromagnetic pull of the atom’s core. After this collision the argon atom is left ionized and forms an argon ion (Ar\(^+\)), the freed electron is released and the original electron changes direction, leaving an argon ion and two electrons as net result. However, this is not the only possible reaction that can occur when Ar and e meet, another example is given in equation (1.2),

\[
\text{Ar} + e \rightarrow \text{Ar}^* + e. \tag{1.2}
\]

Here Ar\(^*\) is an excited argon atom, where the outermost electron has been pushed into a higher energy orbital than its ground-state position. Again the electron transfers (part of) its energy to the atom, but now the atom is not ionized and no new electron is released. In general, all reaction equations contain a number of species on the left-hand side (LHS) and a number of species on the right-hand side (RHS). The number of times species \(X_i\) appears on the LHS of reaction \(r\) is given by \(\nu_{\text{LHS}(i,r)}\), and on the RHS by \(\nu_{\text{RHS}(i,r)}\). With this, every reaction can be written according to,

\[
\sum_i \nu_{\text{LHS}(i,r)} X_i \rightarrow \sum_i \nu_{\text{RHS}(i,r)} X_i, \tag{1.3}
\]

which shows that, mathematically, a reaction is just the conversion of species on the LHS to species on the RHS.

Which of the two reactions (1.1) or (1.2) occurs is not determined beforehand. It depends on the energy of the incoming electron and even when that is known it is still a matter of probability whether (1.1) or (1.2) occurs or any other elastic (energy is conserved) or inelastic (energy is not conserved) collision occurs.

Exactly determining how a (series of) reaction(s) plays out is therefore impossible. Nature’s inherent randomness makes it so that starting from the same initial situation the final result is not unique. In plasma simulations this is solved by either introducing said randomness in the simulation itself, for example by solving chemical kinetics using a Monte Carlo
method \[19\], or by considering many occurrences of the same collision and determining the
average amount of times that a certain result occurs.

This last case leads to the introduction of reaction rates for specific processes. A reaction’s
rate dictates the number of times per unit of volume the reaction takes place per unit of time.
A volumetric reaction rate, \( Z_r \), is given by,

\[
Z_r = K_r \prod_{i \in \text{LHS}} n_i \nu_{\text{LHS}(i,r)}. \tag{1.4}
\]

Here \( n_i \) is the density of a species \( X_i \) that appears in the left-hand side (LHS) of reaction \( r \)
and \( \nu_{\text{LHS}(i,r)} \) is the number of \( X_i \) on the LHS. \( K_r \) is the quantity known as the rate coefficient,
this coefficient contains all dependencies of the reaction rate on external parameters (besides
concentrations of target species), most notably the (electron) temperature.

In order to determine the effect of reactions on the densities of species the net produced
amount of said species needs to be known. Knowing the number of a species \( i \) present on the
LHS of a reaction \( r \), \( \nu_{\text{LHS}(i,r)} \), and the number on the the right-hand side (RHS), \( \nu_{\text{RHS}(i,r)} \),
one can calculate the net production, \( \nu_{ir} \), according to,

\[
\nu_{ir} = \nu_{\text{RHS}(i,r)} - \nu_{\text{LHS}(i,r)}. \tag{1.5}
\]

This is what is called the stoichiometric coefficient for species \( i \) in reaction \( r \). Combining
this with the reaction rate given in equation \[1.4\] leads to the source (or sink) of particle \( i \)
due to reaction \( r \), \( \nu_{ir} Z_r \). Combining the effects of all reactions in the chemistry gives the
chemical source, \( S_i \), of species \( i \) at a certain point in time in a certain volume,

\[
S_i = \sum_{r=1}^{N_r} \nu_{ir} Z_r, \tag{1.6}
\]

which gives the resulting equation for the chemical source of a species, where \( N_r \) is the amount
of reactions in the system.

As will be described later in chapter \[2\] the chemical source term is one of the terms that
determines the evolution of a species’ density. The reaction rate \( Z_r \) depends on the densities
of all the species that occur on the LHS of a reaction. Therefore the system becomes strongly
non-linear and the chemical sources of species are strongly interwoven.

For simple chemistries evolution of species densities is still possible in a timely manner,
for example a simple argon plasma can be simulated quite accurately with only 4 species and
6 reactions. However, when more accuracy and information on different states is needed, the
amount of species and reactions can grow out of control. An extensive chemistry for a molec-
ular oxygen plasma contains 53 species connected by a total of 1442 reactions. Chemistries
like this are (near) impossible to simulate in more than one dimension.

1.3 Plasma chemical reduction

In order to be able to simulate such complex plasmas in reasonable periods of time, these
chemistries have to reduced. Reduction is this case very simply means removing reactions and
species from the system. In a few exceptional cases, the modeller might know and understand
the inner workings of the system and be able to thin out the reactions and species based on
this knowledge. However, this is the ideal case and often not much simulation is still needed
if the system is already known that well.
More often, the modeller has only a limited knowledge of what is important in the system. In that case, it is a possibility to remove intermediate species from the chemistry. These species are destroyed very fast after being created and the large reaction rate that spawn from their destruction can significantly slow down a simulation. The method where these are removed is called the Quasi Steady State Assumption or QSSA [20]. The disadvantage is that the modeller needs some knowledge to determine these intermediate species.

A chemical reduction technique that is based on the same principle of fast equilibration of some of the species and reactions is Intrinsic Low Dimensional Manifold (ILDM) [21]. The main difference, however, is that it does not require manual input and analysis from the user. The user only defines a timescale above which they are interested in the system’s response. The method then determines which processes are in equilibrium after this time and the slow and fast processes are decoupled. This method reduces the dimensionality of the system by removing differential equations associated with intermediate species. A manifold is constructed that shows the evolution of this lower-dimensional system.

Another method that is well-known as a dimensional reduction, is Principal Component Analysis (PCA). Although, like ILDM, not originally developed for plasma simulation, this has been applied to plasmas before [22]. Exploiting the fact that the system moves on a lower-dimensional manifold than the chemistry originally shows, it is possible to describe complicated non-equilibrium plasmas using only a few parameters. Through the use of training sets generated from the full chemistry the species densities are projected on a lower dimensional basis spanned by the so-called Principal Components (PCs). By solving the system for these PCs and then translating back to the original variables the plasma can be simulated efficiently.

ILDM and PCA are both examples of dimension reduction through reparametrization of the chemical state space. The other main method of dimension reduction is mechanism reduction [23]. QSSA, as mentioned above, is an example of mechanism reduction, where parts of the chemistry are removed in order to reduce the dimensionality of the problem. Another example that is often given of mechanism reduction is the Pathway Analysis Algorithm (PWA) by R. Lehmann [24], even though it is an analysis tool at heart and does not decrease the dimensionality of the chemistry. The advantage of mechanism reduction versus reparametrization is that it gives a lot of insight in the chemistry itself. Though it can be used to reduce the dimensionality its use is preferred for deep understanding of the chemistry.

Since QSSA requires knowledge of the system beforehand, which is often not available, it is desirable that a new method of mechanism reduction is developed that does not require the user to have this knowledge but is still able to reduce the system and give insight into the inner workings. The question this thesis aims to answer is:

- **Can a Pathway Analysis Algorithm be used to develop an automated mechanism reduction method?**

An implementation of PWA already exists within the PLASIMO toolbox [25,26], but was not yet complete and suitable for chemical reduction. The goal of this thesis is to expand on the existing PWA implementation and use its results to reduce plasma kinetics models. An update to the pathway analysis implementation and a coupling between its result and a newly created reduction technique is needed. A semi-automatic tool that only requires a few variables as user-input is developed that takes a full chemistry and in the end returns a reduced chemistry for the user to use in further modelling. In order to achieve this, a
translation algorithm has to be developed that interprets the result of pathway analysis and uses it to remove species and/or reactions from the chemistry automatically. The resulting reduction will then be crosschecked with the full chemistry’s results and an analysis of its features is performed.

1.4 Outline

This thesis is continued in chapter 2 with an in-depth explanation of zero-dimensional models, which is the type of simulation that this work is focused on. The essential equations are introduced and the effect of reduction on these equations is explored.

Following this, chapter 3 explains the pathway analysis algorithm as it was originally developed. The end of this chapter details the differences between the original and the implementation in the PLASIMO toolbox.

After the analysis algorithm has been detailed, chapter 4 explains how this is used to form an automated reduction method. A first look is taken at some early results where only reactions are removed from the chemistry in both constant and pulsed input power plasmas. The next step is including the removal of species as well, followed by a comparison to what a “naive” reduction would do. In order to explain why the method works, a short look is taken at the timescales of the system before and after reduction as well as looking at the relation between species densities and said timescales.

The final chapter, chapter 5, shortly revisits the previous chapters and ties them up in short and clear-cut conclusions. A proposal for a comparison study with the ILDM method is suggested. Where applicable, the faced challenges are discussed and used at the end of the chapter to give recommendations for future work.
Chapter 2

Zero-Dimensional Models

Considering the computational cost of modelling complex chemistries, a trade-off has to be made between the spatial information gathered and the complexity of the chemistry. When simulating three-dimensional plasmas one can only include a small amount of species and reactions. A 2D-model already allows for a larger system and so on. Whenever chemistry is the chosen focal point from the three main aspects of a plasma given in section 1.1, the usual choice is a zero-dimensional model. By removing information regarding spatial gradients in all three dimensions the computational cost is drastically reduced, leaving more computational power to tackle the complex chemistry.

In essence the transport and configuration aspects of the plasma are replaced by frequencies accounting for their effect. For example, incorporation of wall effects is done by adding rates of addition and deletion of the species affected. The brunt of the model is the actual chemistry, i.e. the reactions between species as described in section 1.2. In the next section 2.1 a short overview of the types of zero-dimensional models is given with their characteristics. Afterwards the type used in this thesis is discussed in more detail as well as the chemical reduction of this type of model. The last section 2.4 focuses on the timescales associated with global plasma models as this is used in section 4.4.2 and section 4.4.3 to analyze the power of the method developed in this thesis.

2.1 Zero-Dimensional Chemistry models

Within the plasma research field, three common types of zero-dimensional models exist [12], namely:

- Collisional Radiative Models (CRM)
- Reaction Exploration Models (REM)
- Global Plasma Models (GPM)

First of all, CRMs have been around for a long time, originating from plasma spectroscopy halfway through the 20th century, around 1962 [27]. But they are still relevant today [28], as the light coming from plasmas is still often its main goal, i.e. in lithography, or a means to gaining knowledge about the plasma, i.e. understanding fusion plasmas. These models concern themselves with determining the state populations of emitters in a plasma, thus
being able to model their light output. This is done by considering the relevant radiative and collisional processes between these states and other plasma particles.

Any intermediate, i.e. excited level, that decays faster than it can move by a form of transport is not treated but instead converted into transition frequencies between the states that do participate in transport processes. This way the atomic state distribution is kept accurate whilst still leaving out fast transient species. Often, linearity of the system is kept intact by considering the agents of transition (for example electrons and photons) as external parties to the system. Their state is not recorded and therefore the transitions are treated as frequencies based on the given circumstances.

This is where REMs differ from CRMs, in these the transitions can also be initiated by all other species present within the chemistry, which now also includes electrons. Reactions as in equation (1.1) and (1.2) occur and these processes depend on the densities of the species involved in them as in equation (1.4). Non-linearity is created by definition and to calculate species densities a differential equation for each species has to be solved in time.

The goal of REMs is to determine the evolution of species densities and to analyse reaction kinetics. By solving the differential equations the species that are present in large densities can be identified for a given set of input parameters. At the same time, the species that decay into these states quickly can be identified. This way, it is possible to use a REM to determine these states for a CRM. An example of a REM is ZDPlasKin [14], mentioned before in section 1.1.

Lastly, GPMs aim to predict general plasma values like electron density and temperature based on user-given input settings. Input settings can include factors like the size and geometry of the plasma vessel, and often the applied input power. However, in order to do this a GPM needs to be able to model the effect of reactions and species on these internal plasma parameters. Therefore, a GPM cannot exist without the aid of either a CRM or REM. The type of zero-dimensional model used in this thesis is a GPM with a built-in REM, as described in [12]. The following section 2.2 describes this type of model in detail and addresses the equations solved.

### 2.2 Global Plasma Models

As mentioned above, Global Plasma Models (GPMs) or Global Models predict internal plasma parameters based on user-defined plasma aspects like configuration, transport and chemistry. Research using global models has been conducted for a few decades in order to analyse and develop complex chemistries [29, 30]. These are usually calculated for an average across a volume and not a single point as a zero-dimensional model might suggest. Section 2.2.2 details on the semantic difference between the two definitions. The equations governing this type of model are given and explained in the following section 2.2.1.

The main plasma aspect contained within a GPM is the chemistry of the plasma. The configuration and transport are only included in the form of frequencies at which species enter or leave the system as is the case for all zero-dimensional models. The model solves the evolution of species densities by calculating how the chemical reaction sources affect them.
2.2.1 Species and electron energy density balance

All types of particles within the plasma should adhere to the particle balance that is contained in the zeroth moment of the Boltzmann equation,

\[
\frac{\partial n_i}{\partial t} + \nabla \cdot n_i \mathbf{v}_i = S_i, \tag{2.1}
\]

where \( n_i \) is the density, \( \mathbf{v}_i \) is the mean velocity and \( S_i \) is the chemical source of species \( s \). Transport is, however, not included directly and therefore the second term disappears or must be modelled in approximate form. In this approximate form (i.e. \( f_{i,\text{trans}} n_i \)) it will become part of the RHS of equation (2.1). Replacing the right-hand side with equation (1.6) leaves,

\[
\frac{\partial n_i}{\partial t} = \sum_{r=1}^{N_r} \nu_{ir} Z_r. \tag{2.2}
\]

Since there is not just one species present in a mixture, these can be replaced by vectors and matrices, simplifying both notation and implementation. When presenting all the densities by \( \mathbf{n} \), all the sources by \( \mathbf{S} \), all the stoichiometric coefficients by \( \mathbf{\nu} \) and all the rates by \( \mathbf{Z} \) this gives,

\[
\frac{\partial \mathbf{n}}{\partial t} = \mathbf{S} = \mathbf{\nu Z}. \tag{2.3}
\]

The electron energy density balance determines the evolution of the electron energy density of the system and is governed by all processes that take energy from or give energy to the electrons in the mixture. When the assumption is made that all input power is initially absorbed into the electrons’ shared pool of energy, the input power \( P_{\text{in}}(t) \) adds a positive term.

Reactions in which electrons participate and where there is an internal energy difference between the RHS and LHS, this energy difference is attributed to the electron energy pool, with some exceptions like radiative recombination. Take, for example, the reaction given by equation (1.1), it takes 15.76 eV to ionize an argon atom, this energy is taken from the incoming electron. This way every reaction \( r \) has a certain electron energy impact \( E_{e,r} \) (note that this can be both positive and negative or zero, positive indicating a loss of energy). The combined effect of these reactions is given by \( \mathbf{E_e} \cdot \mathbf{Z} \), this is the inelastic source term. This leads to the following balance equation,

\[
\frac{\partial}{\partial t} \left( \frac{3}{2} n_e k_B T_e \right) = P_{\text{in}}(t) - \mathbf{E_e} \cdot \mathbf{Z} + Q_{\text{extra}}, \tag{2.4}
\]

where \( Q_{\text{extra}} \) is the effect of so-called extra sources on the energy of electrons.

These extra sources contain any process or reaction that either contain species that are not present in the mixture, do not change species or do not conserve charge or mass. The most prominent examples are wall reactions and elastic collisions. For more information on the implementation of these extra sources, see Graef (2012) [12].

2.2.2 Differential versus integral balance

Zero-dimensional modelling can be considered from two different perspectives. Either one can start from the differential balance equation like the one in equation (2.2) or one can use
a integral balance as a starting point. The general differential balance for a species with a, local, density \( n \) is given by,
\[
\frac{\partial n}{\partial t} + \nabla \cdot \mathbf{\Gamma} = S,
\]
where \( S \) is the local source and \( \mathbf{\Gamma} \) is the local flux density of said species. It is important to stress that these values are all \textit{local} and therefore are to be evaluated at that point. When, for example, the flux is diffusive, the second term can be replaced with Fick’s law [31] to give:
\[
\frac{\partial n}{\partial t} - \nabla \cdot D \nabla n = S,
\]
where \( D \) is the local diffusion coefficient. Adding the definition of the diffusion length \( \Lambda \) sanitizes the equation to give,
\[
\frac{\partial n}{\partial t} - D \frac{n}{\Lambda^2} = S
\]
by using the definition,
\[
\nabla \cdot D \nabla n \equiv \frac{D n}{\Lambda^2},
\]
which leads to an evaluation of \( \Lambda^2 \) at all times by:
\[
\Lambda^2 \equiv \pm \frac{D n}{|\nabla \cdot D \nabla n|},
\]
whose sign depends on the sign of \( \nabla \cdot D \nabla n \).

Solving a global model using the differential balance directly implies the use of local values and the calculation of local densities. This intuitively suggests a detailed required knowledge of the system, which might concern users when building such a model. The alternative is to use the integral balance, which is given by,
\[
\frac{d}{dt} \int_V n \, dv + \int_{\delta V} \mathbf{\Gamma} \cdot d\mathbf{A} = \int_V S \, dv,
\]
where \( V \) is the volume over which the integral is taken and \( \delta V \) is that volume’s surface with (local) normal vector \( d\mathbf{A} \). Using this balance in a global model would require a division by the volume \( V \), which is given by,
\[
\frac{d}{dt} \frac{1}{V} \int_V n \, dv + \frac{1}{V} \int_{\delta V} \mathbf{\Gamma} \cdot d\mathbf{A} = \frac{1}{V} \int_V S \, dv,
\]
where the first and last term now contain the average density \( \langle n \rangle \) and average source \( \langle S \rangle \). When the second term is multiplied and divided by the surface area, it can be replaced according to,
\[
\frac{1}{A} \int_{\delta V} \mathbf{\Gamma} \cdot d\mathbf{A} \equiv \frac{1}{V} \frac{1}{A} \int_{\delta V} \mathbf{\Gamma} \cdot d\mathbf{A} = \frac{1}{V} \int_V S \, dv,
\]
with \( \langle \mathbf{\Gamma}_A \cdot n \rangle \) the average flux over the surface area with normal vector \( n \). Together these lead to a balance for the average density based on other averaged quantities given by,
\[
\frac{d}{dt} \langle n \rangle + \frac{A}{V} \langle \mathbf{\Gamma}_A \cdot n \rangle = \langle S \rangle.
\]
In the end, the integral balance \((2.13)\) looks very similar to the differential case \((2.7)\). There are however subtle differences. A good example of where the two approaches diverge is in the calculation of the source. Let’s take a look at the source of \(\text{Ar}^+\) due to the reaction \(r\) in equation \((1.1)\). One \(\text{Ar}^+\) is created every time this reaction occurs and therefore its source \(S_r\) (in \(\text{m}^{-3}\text{s}^{-1}\)) is exactly the reaction rate, given by \((1.4)\). This source then look as follows,

\[
S_r = K_r n_{\text{Ar}} n_e. \tag{2.14}
\]

However, equation \((2.14)\), only applies in the differential case, as this is the local rate coefficient and these are the local densities. When the integral case is considered, the source \(<S_r>\) due to reaction \(r\) would look like:

\[
<S_r> = <K_r n_{\text{Ar}} n_e > \neq < K_r > < n_{\text{Ar}} > < n_e >. \tag{2.15}
\]

The differential version works out fine as the known quantities in the simulation are indeed the local values of the densities and rate coefficient. In the integral case, one knows the averages of the densities and the rate coefficients, but not the averages of any products of these. Only in the case of a completely homogeneous system of densities will the integral case be able to apply equation \((2.15)\) properly. The case where the system is homogeneous is also the case where the integral and differential approach are identical.

As far as working with global models goes, this difference in approach will not cause significant differences in results, if it does at all. It is, however, important that the modeller is aware of this subtle difference. One should be careful in the communication of the results from a global model as simply stating it is a volume-averaged result or a result for a specific point is not always entirely true.

### 2.2.3 The PLASIMO Global Model

Within the PLASIMO toolbox, an implementation of a global model exists that has been developed by W. Graef \([12]\). This Global Model includes a REM in order to calculate the chemical interactions. The sources are included like equation \((2.14)\). The most important input for the model is the input power that is coupled to the electron energy balance. Besides that, the user defines the chemistry in the form of species and reactions, including the rate coefficients. Multiple different types of reactions are supported, i.e. lists of regular reactions, scaled reaction groups for vibrational interactions, reactions taken from external sources like LXCat \([32]\) and many more.

Wall reactions, elastic collisions, configuration and transport access are included in the form of extra sources that change one or more species’ density based on frequencies. Recently, this model has been updated to include the possibility to calculate the temporal evolution of the gas temperature besides the calculation of the electron temperature. Processes that add or remove translational or internal energy to neutral species are calculated and the gas temperature is changed accordingly. Users can make use of declarations of constants and functions in order to improve the readability of input files and simplifying the declaration of rate coefficients and other values that require complicated formulas.

The Global Model is coupled with BOLSIG+ \([33]\) in order to solve the electron Boltzmann equation and determine electron transport coefficients and collision rate coefficients based on the chemistry included in the input file. The resulting electron energy distribution (EEDF) is then used to determine the cross-sections of the included reactions.
Different types of output can be produced using the global model, entirely based on user preference. All of them are available with temporal evolution. There is also a GUI available where the user can make alterations to the input data, where data can be visualised during the simulation and general data and a chemistry analysis are available. The list below gives a grasp out of the possible data collected from the Global Model:

- Species densities
- Energy density, electron temperature and gas temperature
- Reaction rates, rate and stoichiometric coefficients and relative reaction contributions to chemical sources
- BOLSIG+ in/output files
- Reduced electric field
- Mobilities and diffusion coefficients

Different solvers are available within the general PLASIMO toolbox and these can also be chosen for the Global Model. The starting and end time of the simulation can be chosen as well as the initial timestep. The initial conditions, in terms of species densities, can be supplied by the user and the user can indicate exactly what output the global model will produce based on the given input parameters.

### 2.3 Plasma Chemical Reduction of Global Models

As pointed out in section 1.3, plasma chemistries become so complex that reduction can be (or sometimes just plain is) necessary. This is still the case when opting for a global model specifically focusing on the chemistry. The reason for reduction is two-fold, on the one hand chemical reduction strongly decreases the computational costs of a model, on the other hand reduction allows for better analysis of the chemistry itself.

However, it is important to note the effects of reduction on the system itself. Assuming that all included reactions and species are correctly implemented, a reduction will always lower the accuracy of the model compared to the full chemistry. The modeller needs to be aware of this when deciding how and what to reduce from the system and care has to be taken to not produce unphysical or untrue results.

In the end, it all depends on the **goal of the simulation** (and therefore the goal of the reduction). If the goal is simply to find a reduced chemistry that can calculate global plasma parameters quicker whilst still having a certain accuracy, the modeller can push the reduction until the maximum error is reached. However, if the goal is to analyse the creation or destruction of one or more species, the modeller has to be more careful in the reduction approach.

#### 2.3.1 Source term effects

In order to understand the effect of removing one reaction from the chemistry the chemical source as given in equation (2.3) has to be considered again. This vector contains terms of the sort given in equation (2.11), for every reaction one of these terms arises for every species it
affects. Removing a reaction would then entail that the term corresponding to that reaction would be removed from the source elements it appears in.

Removing a non-essential reaction would not change the values in the source term by a lot and only for a few species. However, the effect of removing a reaction is more subtle than that. Considering the equilibrium state of the system, given by,

\[
\frac{\partial n_{eq}}{\partial t} = S_{eq} = 0, \tag{2.16}
\]

this means that the source elements have to be zero to achieve steady state. Removing a single reaction disturbs this equilibrium and the system will relax to steady state again, but this steady state will not be the same. Suppose, for an arbitrary species density \( n_1 \) the original equilibrium source is given by,

\[
S_{eq} = -K_1n_1n_2 + K_2n_2n_3 + K_3n_3n_4 = 0, \tag{2.17}
\]

where the \( K_i \) correspond to a rate coefficients of reaction \( i \) and \( n_s \) correspond to a density of species \( s \). This source shows that there three reactions affecting \( n_1 \), one consuming and two producing reactions. The equilibrium density of \( n_1 \) can then be calculated by:

\[
n_{1,eq} = \frac{n_3}{K_1} \left( K_2 + \frac{K_3n_4}{n_2} \right). \tag{2.18}
\]

If, for example, the rate of reaction 3 is very low, it could be a candidate for removal from the system. The new equilibrium condition for \( n_1 \) would then be given by,

\[
S_{eq}^{new} = -K_1n_1n_2 + K_2n_2n_3 = 0, \tag{2.19}
\]

and the equilibrium would be given by,

\[
n_{1,eq}^{new} = \frac{K_2}{K_1} n_3. \tag{2.20}
\]

However, this is not the full answer. Since the deleted reaction contains \( n_3 \) as well, it is already apparent that the equilibrium value of \( n_3 \) will also change and therefore equation (2.18) and equation (2.20) are not directly comparable. Besides that, the removed reaction also involves \( n_4 \), which means another equilibrium position will change. On top of that, when the condition for \( n_1 \) and \( n_3 \) change, the reaction rates of the first and second reaction here will change as well, meaning that \( n_2 \) will be affected as well. This ripple effect will, in the end, affect all species densities and therefore the effect of removing a reaction is far from trivial.

Since it is impossible to form a mathematical description of the effect that is valid for all systems, the effect will be illustrated by examples. In order to stay within the range of systems that is still analytically computable, only linear systems will be shown here. Any reaction containing two active acting species introduces non-linearity to the system.

An illustrative example contains a fictional system with 3 species and 4 reactions. For the sake of clarity the system is assumed to be the classical three-level argon system, schematically given in figure 2.3.1, with reactions between the argon ground state and two of its excited states. As the system is fictional, the energy levels of these states are not of importance. The
Figure 2.1: Fictional 3 level argon system with 4 reactions. Used rate coefficients for these reactions are given in table 2.1.

The system contains three densities \( n_{\text{Ar}}, n_{\text{Ar}^*}, \) and \( n_{\text{Ar}^{**}} \) and four reactions \( r_1, r_2, r_3, \) and \( r_4 \), given by,

\[
\begin{align*}
Ar + h\nu \xrightarrow{K_1} Ar^*, \\
Ar^* + h\nu \xrightarrow{K_2} Ar^{**}, \\
Ar^{**} \xrightarrow{K_3} Ar + h\nu, \\
Ar^* \xrightarrow{K_4} Ar + h\nu.
\end{align*}
\]

According to equation (2.3), the temporal evolution of this system can be described by,

\[
\frac{\partial}{\partial t} \begin{pmatrix} n_{\text{Ar}} \\ n_{\text{Ar}^*} \\ n_{\text{Ar}^{**}} \end{pmatrix} = \begin{pmatrix} -K_1 n_{\text{Ar}} + K_3 n_{\text{Ar}^{**}} + K_4 n_{\text{Ar}^*} \\ K_1 n_{\text{Ar}} - K_2 n_{\text{Ar}^*} - K_4 n_{\text{Ar}^*} \\ K_2 n_{\text{Ar}^*} - K_3 n_{\text{Ar}^{**}} \end{pmatrix},
\]

which is solvable by decomposition of this matrix. The eigenvalues and eigenvectors found are not pretty and are therefore given in appendix A in equation (A.1) and equation (A.2).

To test the effect of removing a reaction on the temporal evolution, three cases are considered. They are given in table 2.1. The rate coefficient \( K_4 \) is altered between the situations. System A is the baseline with all four reactions included, in System B the fourth reaction is excluded. These two systems are compared in figure 2.2, which shows that the deviation is quite small when a low rate coefficient reaction is removed.

System C is designed so that \( r_4 \) is important. When B and C are compared, one can see that removing a significant reaction from the system can cause large errors. Even though this
Table 2.1: Rate coefficient values for the sample systems in this section.

<table>
<thead>
<tr>
<th>System</th>
<th>$K_1$</th>
<th>$K_2$</th>
<th>$K_3$</th>
<th>$K_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1</td>
<td>0.5</td>
<td>6</td>
<td>0.15</td>
</tr>
<tr>
<td>B</td>
<td>1</td>
<td>0.5</td>
<td>6</td>
<td>0</td>
</tr>
<tr>
<td>C</td>
<td>1</td>
<td>0.5</td>
<td>6</td>
<td>1.5</td>
</tr>
</tbody>
</table>

**Figure 2.2:** Temporal evolution of species densities in System A (left) and System B (right) from table 2.1. The units are arbitrary and the initial condition has all 100 a.u. in the argon ground state. Little deviation occurs due to removal of $r_4$.

Example is very simple and not representative of a physical system it shows how strong the chemical sources can be influenced by single reactions and rate coefficients.

**Figure 2.3:** Temporal evolution of species densities in System C (left) and System B (right) from table 2.1. The units are arbitrary and the initial condition has all 100 a.u. in the argon ground state. Major deviation occurs due to removal of significant $r_4$.

Additional to that, it is apparent that System C reaches its steady state faster than A and B. Table A.1 in appendix A shows the eigenvalues for the three systems, where the second eigenvalue of System C is an order of 2 larger than those of System A and B. As will be explained in section 2.4, this indicates that its slower timescales is shorter than those of the others and therefore it reaches equilibrium faster. Besides the steady state difference, a different temporal evolution is observed as well.

Considering the values of the rates of the reactions in this system, given in figure 2.4, it
makes sense that the reduction from system A works whilst the reduction of System C does not. The rate of $r_4$ is by far the lowest in A, whilst in C it is second only to the ground state excitation. An approach of removing reactions that have the lowest rate would correctly leave $r_4$ unaltered in System C whilst removing it from A.

![Figure 2.4: Temporal evolution of reactions rates in System A (left) and System C (right)](image)
The units are arbitrary and the initial condition has all 100 a.u. in the argon ground state. The rate of $r_4$ (equation (2.21d)) is of low importance on the left, whilst being of high importance on the right.

A second idea that figure 2.4 promotes is the fact that both reactions associated with Ar** have low rates during the whole evolution in System C. This suggests the possibility of removing this species from the system altogether. The reduced system would then only contain two species and two reactions between them. The temporal evolution of System C and its reduction is shown in figure 2.5. The differences in steady state values for $n_{Ar}$ and $n_{Ar^{**}}$ are only 6.25% and 2.70%, respectively.

![Figure 2.5: Temporal evolution of species densities in System C (left) and its reduction (right)](image)
The units are arbitrary and the initial condition has all 100 a.u. in the argon ground state. Only small deviation occurs after removal of the species.

The effect of removing reactions and species from a chemistry is comprehensible but the effect itself is quite more extensive than intuitively expected. There are more, sometimes unwanted, side-effects of removing reactions from a chemistry, the next section 2.3.2 deals with a few of those effects.
2.3.2 Reduction error examples

Whenever a reaction is removed from a chemical system, the system inherently changes. Careful and smart removal is necessary to preserve the accuracy and physical value of the remainder of the chemistry. Even then, unpredicted (and sometimes unwanted) effects can occur.

According to equation (2.2) the source for a single species is the sum of all reactions that either produce or consume this species. Removing or deactivating reactions changes the elements in this sum. What can occur is that, for some reason, either all producing or all consuming reactions are deleted whilst there is/are still one/some of the other type present. In this case the species is either only produced or only consumed.

Both cases can have strong unwanted consequences. In the case of pure production, the density of this species will continue to rise. This does not only lead to unphysical values, but can influence other species as well. In chemical simulations, often values are used for reactions coefficients that are dependent on for example the neutral density. If the continuously produced species is a neutral this would lead to wrong calculations for other species as well. The same goes for ions when the charge density is used, but ions often play a role in quasi-neutrality questions too, giving rise to extremely high electron densities to compensate.

When a species is only consumed its density will keep dropping till there are (almost) no more left. However, due to the nature of stepper algorithm, this can also lead to negative density values, which are purely unphysical. Other than that, even though a species is not produced very much (which is why the production would be deleted) it can still be an important source for another species of interest. When the value of the short-lived species density goes to zero, the other species’ production path dries up, causing all its relations to become faulty as well.

Besides purely producing or consuming species, which causes wrong results, there is also the possibility that unpredicted effects hinder the analysis of a certain chemistry. When a reduction behaves differently than expected, it is possible that the modeller interprets this with the wrong conclusions. An example of this is the fact that it is possible that reducing more reactions leads to a results that is closer to the original system than a lesser reduction would give. The modeller could then wrongly conclude that the strong reduction is a proper reduction as it gives accurate results. Reductions like that are very volatile to small changes due to the small amount of reactions that are left, they might not work for a small change of input parameters already.

For example, assuming a chemistry with the three species Ar, Ar$^*$ and e, with the reactions given by,

\[
\begin{align*}
\text{Ar} + e & \rightarrow \text{Ar}^* + e \quad \text{with rate: } 2, \quad (2.24a) \\
\text{Ar}^* + e & \rightarrow \text{Ar} + e \quad \text{with rate: } 3, \quad (2.24b) \\
\text{Ar}^* & \rightarrow \text{Ar} + h\nu \quad \text{with rate: } 10. \quad (2.24c)
\end{align*}
\]

If this system were to be reduced step by step by removing one reaction at a time, something peculiar happens. If we look at the total source of Ar$^*$, $S(\text{Ar}^*)$, this is $-11$ for the full system. When the lowest rate reaction, in this case reaction (2.24a), is deleted, $S(\text{Ar}^*)$ becomes $-13$. In that case $\Delta S(\text{Ar}^*) = -2$ and $\Delta S_T = \frac{2}{7}$. When a second reaction is also deleted, now reaction (2.24b), $S(\text{Ar}^*)$ becomes $-10$. Now $\Delta S(\text{Ar}^*) = 1$ and $\Delta S_T = \frac{-1}{11}$. Even though more reactions are deleted, the final approximation is closer to the original value due to the fact that the effect of removing the reactions can be in both directions.
What is left of the system works for the current density values, which is not guaranteed for a different operation condition. I.e. if the electron density were to increase strongly, reaction (2.24b) would increase in rate and the system with just one reaction removed would give more accurate results than the system with two removed.

It is advisable to monitor the deviation from the full system by using stepwise reduction to be able to notice effects like this. When the deviation reaches a maximum and then decreases again, the system is expected to be more stable when a reduction before the maximum deviation is used.

2.4 Timescales of a global model

Later on in this work an analysis is done that evaluates a reduction based on the timescales of the system that are left after reduction. In order to determine these timescales it has to become clear what these timescales mean for a system.

This starts with the set of differential equations given in equation (2.3). By linearizing the source term on the right-hand side the following equation is formed,

\[ S(n) = S(n_0) + \frac{\partial S(n_0)}{\partial n} (n - n_0) + O(\delta n)^2. \]  

(2.25)

The source vector \( S \) is given by equation (2.3), where \( \nu \) is constant. The derivative of the sources to the densities can then be given by the Jacobian matrix, \( J \), defined as,

\[ J = \frac{\partial S}{\partial n} = \nu \frac{\partial Z}{\partial n}, \]  

(2.26)

and ignoring the higher order terms leads to a new source term given by,

\[ S(n) = S(n_0) + J(n - n_0). \]  

(2.27)

When looking at a perturbation \( \alpha \equiv n - n_0 \), the balance equation (2.3) can be written as:

\[ \frac{\partial \alpha}{\partial t} = J\alpha. \]  

(2.28)

2.4.1 Timescales and species: The relation

The differential equation set (2.28) has to be solved for each species individually. The largest impact from a chemical reduction is achieved by removing species as each species corresponds to its own differential equation that has to be solved each timestep. However, species are not just represented in one differential equation as they are strongly correlated.

The Jacobian matrix \( J \) has off-diagonal elements, causing mixing of factors in the equation system. However, the matrix can be diagonalized, a spectral decomposition of \( J \) is given by:

\[ J = V \Lambda V^{-1}, \]  

(2.29)

where \( \Lambda \) is a matrix with the eigenvalues of \( J \) on the diagonal and \( V \) is the corresponding left eigenvector matrix. The new balance for \( \alpha \) now looks as follows,

\[ \frac{\partial \alpha}{\partial t} = V \Lambda V^{-1} \alpha, \]  

(2.30)
left multiplication by $V^{-1}$ gives,

$$V^{-1} \frac{\partial \alpha}{\partial t} = \Lambda V^{-1} \alpha. \quad (2.31)$$

Assuming $V^{-1}$ is constant in the timeframe of interest, it can be added within the differential and with the definition $\psi \equiv V^{-1} \alpha$ a new balance is formed:

$$\frac{\partial \psi}{\partial t} = \Lambda \psi. \quad (2.32)$$

Since $\Lambda$ is a diagonal matrix the system of equations is now decoupled. The individual elements of the vector $\psi$ have their own equation now, governed by their own eigenvalue. For a single element $\psi_i$, the evolution equation is given by,

$$\frac{\partial \psi_i}{\partial t} = \lambda_i \psi_i, \quad (2.33)$$

where $\lambda_i$ is the corresponding eigenvalue. Solving this gives the evolution of $\psi_i$ over time, given by,

$$\psi_i(t) = C_i \exp(\lambda_i t). \quad (2.34)$$

Every element $\psi_i$ now has its own timescale, given by equation (2.35). Now the relation between $\psi$ and individual timescales is known, it is important to be able to link the elements $\psi_i$ to species densities. The definition of $\psi$ shows that every element of this vector is some linear combination of $(n_i - n_{0,i})$, where the elements of the right eigenvector show the relative importance of the individual species densities. If species are to be removed, the impact on the timescales of the system can be analyzed by looking at this decomposition of the Jacobian matrix.

### 2.4.2 Timescales and stiffness

Taking another look at equation (2.28), this differential equation leads to solutions with linear combinations of the form $\alpha_n \exp(\lambda_n t)$, where $\lambda_n$ with $n \in \{1, 2, ..., N_s\}$ are the eigenvalues of the Jacobian $J$, of which there are just as many as there are different species in the system. Assuming that the system is approaching equilibrium (i.e. $n_0$ is the equilibrium composition and $n$ is a small perturbation thereof), all these eigenvalues will have a negative real component and the solution will converge towards equilibrium. The time it takes for this to occur is dependent on the eigenvalues themselves, they are directly relatable to the timescales according to:

$$\tau_i = \frac{1}{|\text{Re}(\lambda_i)|}, \quad (2.35)$$

where $\tau_i$ is one of the timescales of the system. Again, there are the same amount of timescales as there are different species in the chemistry. It is, however, possible that two or more of the timescales have the same value. Eigenvalues of 0 are also possible, these correspond to a conserved $\psi_i$, meaning that one linear combination of densities is constant in time. Examples of this are elemental and mass conservation.

In order to determine the timescales of a chemical model, one therefore needs to determine the Jacobian of the system according to equation (2.26) and calculate its eigenvalues. The stoichiometry matrix as well as the matrix containing the derivatives of the reactions rates to
the species densities are computable from the input chemistry. These derivatives are not constant in time as most reactions are non-linear and therefore depend on two or more densities. The $\frac{\partial Z}{\partial n}$ matrix contains elements depending on current species densities and therefore the Jacobian is time-dependent. This means that at different times in the simulation, different timescales govern the evolution of the system, which stems from the co-dependency of species densities.

A model has to take into account the effect of all different timescales, which means that the timesteps must always be small enough to deal with the shortest timescales accurately. Since timesteps cannot be taken differently for different processes, the long timescale processes are also evaluated in these short time intervals, even though they do not contribute much in that time. To quantify this effect, the concept of stiffness was introduced. The stiffness, $S_t(t)$, is directly related to the ratio between the longest and shortest timescales and is given by,

$$S_t(t) = \frac{\tau_{\text{max}}(t)}{\tau_{\text{min}}(t)}.$$  \hspace{1cm} (2.36)

A larger stiffness increases the computation time and effort needed to complete a simulation. Wherever possible, a reduction in stiffness will contribute to a strong decrease in computational cost. There are two ways to achieve this, either increasing the shortest timescale or decreasing the longest timescale. Since stiffness has such a strong effect on computational cost, the stiffness of reduced models is analysed later in this work in section 4.4.2.
Chapter 3

Pathway Analysis (PWA)

One of the tools to analyze a chemistry is Pathway Analysis. When performing a pathway analysis reactions chains and their effect on the density of species of interest are investigated. As opposed to a more general analysis in the form of, for example, a sensitivity analysis [34], pathway analysis uses the stoichiometric information of a system. Reactions are connected to form chains of reactions called pathways.

The basis for the connection of reactions lies in the expected lifetime of the species involved in the reactions. If a reaction produces species A with a very short lifetime, it makes sense to see which other reaction(s) consume species A so effectively. By adding up the effects of a producing reaction with one (or more) consuming reaction(s) a chain of reactions is made. If, for example, the producing reaction turns species B into species A and the consuming reaction turns species A into species C, the effective combination of those would be a process which turns species B into species C. This chain shows the relation between species that do not participate in the same reaction. Even though there is no direct link between their densities, an indirect link is revealed.

By repeating this process whenever another one of these short-lived species, like species A before, is encountered at the end of the chain, long chains representing the flow of conversion from the “starting” species (i.e. species B) to the “final” species (i.e. species C or even further species that species C turns into). Performing such an analysis for a timescale of species of interest can give meaningful information of the relevant species and reactions related to the interested species and might give clues on how to understand or improve the modeled system.

However, as mentioned before in section 1.2, chemical models can quickly become complex. Performing a pathway analysis manually is cumbersome and prone to human errors for such models, if not impossible. To automate the process of pathway analysis, R. Lehmann suggests an algorithm for computational analysis in [24]. This algorithm is used in this work when performing pathway analyses and is described in section 3.1.

3.1 Lehmann’s Algorithm

The following section summarizes [24] in order to present the required knowledge for the rest of this work. The basic algorithm for pathway construction starts with individual reactions as the initial pathways. Then for each intermediate species, the so-called branching species, the pathways producing the species are connected to the pathways consuming them. A next step is to remove unnecessarily complex pathways by checking if any pathway contains another
pathway as a sub-pathway. This can all be done without knowledge of the reaction rates in the system. A general schematic overview is given in 3.1 where the deletion step was not yet included in this version of the algorithm.

R. Lehmann expanded on this algorithm by requiring knowledge of the reaction rates, which lead to the following changes [24]:

- A rate is determined for each pathway.
- If a pathway contains sub-pathways it is not deleted, but split into its sub-pathways. The original pathway’s rate is then divided over its sub-pathways in order to keep conservation of rates and density changes.
- The order in which species are treated as a branching point is automated. Species with the shortest lifetime are used first.
- If a new pathway has a small rate, it is deleted in order to reduce memory consumption.
- The rates of deleted pathways is recorded and updated in order to keep conversation.

### 3.1.1 Lehmann’s Algorithm: Definitions

Under consideration is a set of reactions $R_j$ with rate $r_j$, $j \in \{1, 2, ..., n_R\}$ where $n_R$ is the total amount of reactions in the system. These reactions occur between the set of species $S_i$, $i \in \{1, 2, ..., n_S\}$ where $n_S$ is the total amount of species. To keep track of the role species play (produced, consumed or intermediary species or no part at all) in these reactions, the stoichiometry of species $S_i$ in reaction $R_j$ is stored in a matrix with elements $s_{ij}$. 
Whenever pathways, $P_k$ with rate $f_k$, $k \in \{1, 2, ..., n_P\}$ where $n_P$ is the total number of pathways, are created two new variables are needed to keep track of the pathways:

- $x_{jk}$ denotes the multiplicity of reaction $R_j$ in the pathway $P_k$.
- $m_{ik}$ denotes the stoichiometry of species $S_i$ in the whole set of pathway $P_k$. This can be linked to the previous definitions by equation (3.1),

$$ m_{ik} = \sum_{j=1}^{n_R} s_{ij} x_{jk}. \quad (3.1) $$

In order to prevent overuse of memory at some point in the algorithm pathways may be deleted. However, to keep conservation of reaction rates and species’ densities the deleted values are stored and updated each time. The quantities $\tilde{r}_j$, $\tilde{p}_i$ and $\tilde{d}_i$ record the deleted reaction rate of reaction $j$ and the deleted production and destruction rate of species $i$, respectively. With this the total production ($p_i$) and destruction ($d_i$) of a species and the total reaction rate ($r_j$), which are the conserved quantities, can be given by equations:

$$ r_j = \tilde{r}_j + \sum_k x_{jk} f_k, \quad (3.2a) $$
$$ p_i = \tilde{p}_i + \sum_{\{k|m_{ik}>0\}} m_{ik} f_k, \quad (3.2b) $$
$$ d_i = \tilde{d}_i + \sum_{\{k|m_{ik}<0\}} |m_{ik}| f_k. \quad (3.2c) $$

In order to calculate the pathway rates later on in the algorithm one more quantity needs to be defined, this is the maximum value of either the destruction or production of a species $D_i$ and is given by equation (3.3),

$$ D_i = \max(p_i, d_i). \quad (3.3) $$

### 3.1.2 Lehmann’s Algorithm: The Algorithm

Looking back at figure 3.1 at the start of the algorithm the first set of pathways are created. Every reaction from the original set is given its own pathway with a rate equivalent to the reaction’s rate. The species with the shortest lifetime, rather the mean density divided by the destruction rate, will be treated as the first branching species. Every pathway producing the branching species is connected to every pathway consuming the branching species. This way the species is in essence “recycled” in the newly created pathways. In order to conserve the net production or net destruction of the branching species the pathways consuming or producing the species, respectively, are kept with an adjusted rate that accounts for their effect on this species density changes. Afterwards, all the pathways that originally contained the branching species in their stoichiometry are deleted from the set of pathways. This process is repeated for the next lowest lifetime species, which will then be the new branching species. This is continued until either all species are treated this way or a user-defined lifetime or species is reached.
Figure 3.2: Schematic overview of the connection step when treating a single branching species. An explanation of the individual part is given in the sections sections 3.1.3 and 3.1.4.

In order to have a proper connection step between two pathways a few steps have to be done. First of all, the composition of the pathway itself, in terms of the multiplicity of the included reactions, has to be determined. After this, a rate has to be assigned to the newly formed pathway. If this rate is not high enough, the pathway can be deleted based on an user-defined threshold. In that case the pathway’s contribution to the overall chemistry has to be recorded in deleted reaction, production and destruction rates. After a new pathway has been determined and has a high enough impact on the chemistry a check has to be done to make sure that the new pathway is not a linear combination of already existing pathways. If so, the new pathway’s rate will be distributed to the pathways it is a combination of. This way, no unnecessarily complicated pathways are created and proper analysis of the chemistry is still possible. A description of these steps is given below.

3.1.3 Connecting pathways sharing a branching species

The process of connecting the pathways that affect a branching species is schematically given in figure 3.2. The following two sections detail the individual parts of this figure.

For a given branching species $S_b$ all producing and consuming pathways are to be connected. For a given producing pathway $P_p$ and consuming pathway $P_c$, combining into the resulting pathway $P_r$, the connection step is done as follows. Since the new pathway will no longer produce or consume $S_b$, all $S_b$ produced in $P_p$ will be consumed by $P_c$. This is done using the stoichiometric information of $S_b$ in both pathways. A combination of $m_{bp}$ times $P_c$ with $|m_{bc}|$ times $P_p$ is made, where the $m_{ik}$’s are the ones given by equation (3.1). The newly created pathway will then consist of the reactions that were contained in both original pathways with a given multiplicity $x_{jr}$ which is only non-zero for reactions $j$ that were in one or both of $P_p$ and $P_c$. If the set of reaction multiplicities has a common divisor, they will be divided by this divisor in order to keep the $P_r$ as simple as possible. If this is done the resulting rate will have to be multiplied by this divisor though.

In order to calculate the rate of the new pathway the probability that the produced $S_b$ in pathway $P_p$ is actually consumed by $P_c$ has to be determined. This is equal to the proportion of $S_b$ consumed by $P_c$ and the total consumption of $S_b$. In the case that species $S_b$ has a net consumption this is equal to the destruction $d_b$, given in equation (3.2c), in the case that $S_b$
has a net production this is equal to \( d_b \) plus the net production, which is equal to \( p_b \), given in equation (3.2b). In both cases this is equal to \( D_b \) as defined in equation (3.3). This leads to a probability \( \pi_c \) that a produced particle of \( S_b \) is consumed by \( P_c \), given by equation (3.4),

\[
\pi_c = \frac{|m_{bc}|f_c}{D_b}.
\] (3.4)

Knowing that the rate of particles produced by \( P_p \) is given by \( m_{bp}f_p \) this leads to equation (3.5) for the rate \( \phi_{pc} \) at which \( S_b \) produced by \( P_p \) is consumed by \( P_c \),

\[
\phi_{pc} = \pi_cm_{bp}f_p = \frac{|m_{bc}|f_c m_{bp} f_p}{D_b}.
\] (3.5)

On the other hand, the rate at which this happens in the new pathway \( P_r \) is also known and given by equation (3.6) with \( f_r \) the rate of \( P_r \),

\[
\phi_r = |m_{bc}|m_{bp}f_r.
\] (3.6)

From this \( f_r \) can be calculated as in equation (3.7) and this allows for the determination of a connected pathways’ rate,

\[
f_r = \frac{f_pf_c}{D_b}.
\] (3.7)

### 3.1.4 A pathway’s contribution to density changes

As mentioned in the previous section 3.1.3 a rate can be attributed to a connection of pathways by determining the chance that the created species is consumed by the corresponding pathway. The same principle is applied when looking at conservation of density changes. In order to have a final set of pathways that is capable of containing the full initial chemistry, the net density change of the branching species has to be preserved. There are three different situations, shown below.

- The branching species, \( S_b \), has no net production or destruction. In this case no extra action has to be taken.
- The branching species, \( S_b \), has a net production. In this case the pathways producing \( S_b \) have to be retained as a portion of the produced \( S_b \) will contribute to this net production. Their rate will be adjusted to correspond to the contribution these pathways have to the production.
- The branching species, \( S_b \), has a net destruction. In this case the pathways consuming \( S_b \) have to be retained as a portion of the consumed \( S_b \) will contribute to this net destruction. Their rate will be adjusted to correspond to the contribution these pathways have to the destruction.

In the second case, a part of the \( S_b \) produced by producing pathway \( P_p \) will contribute to the net production of the branching species. The probability that this happens is given by equation (3.8), where \( \delta_b \) is the net production of the species,

\[
\pi_\Delta = \frac{\delta_b}{D_b}.
\] (3.8)
To show this a new pathway \( P_d \) is created which is the same as \( P_p \) which has rate equal to:

\[
f_d = \pi \Delta f_p = \frac{f_p \delta_b}{D_b}.
\]  
(3.9)

This is also valid for the third case, only then \( f_p \) becomes the rate \( f_c \) of the consumptive pathway \( P_c \) and \( \delta_b \) becomes \( |\delta_b| \) as the net destruction is a negative value.

### 3.1.5 Pathways below user-defined threshold

When a multi-component mixture or molecular gas is present, a plasma’s chemistry can quickly become very complex due to the sheer amount of species and reactions. In that case, the amount of created pathways explodes, causing memory and computational issues. Figure 3.3 shows how to deal with this problem using a user-defined threshold \( f_{\text{min}} \) that can be applied to pathway rates. If a newly created pathway has a rate below \( f_{\text{min}} \), this particular pathway is deemed not important enough to represent the chemistry. However, measures have to be taken to ensure overall conservation if pathway \( P_u \) is thrown away. First of all, the rate of all the reactions contained in \( P_u \) has to be accounted for. Next to that, the net production and destruction of species by the pathway has to be recorded. The deleted reaction rate \( \tilde{r}_j \), production \( \tilde{p}_i \) and destruction \( \tilde{d}_i \) rate of the involved reactions and species are updated according to equations:

\[
\begin{align*}
\tilde{r}_j &= \tilde{r}_j + x_{ju} f_u, \quad (3.10a) \\
\tilde{p}_i &= \tilde{p}_i + m_{iu} f_u \quad \text{if } m_{iu} > 0, \quad (3.10b) \\
\tilde{d}_i &= \tilde{d}_i + |m_{iu}| f_u \quad \text{if } m_{iu} < 0. \quad (3.10c)
\end{align*}
\]

With that, the removal of pathways as a whole is not done. Since there is now presence of deleted rates in the algorithm, these have to be dealt with in pathway connections as well. Whenever a branching species \( S_b \) is treated all producing pathways will also be connected to the deleted rates of consuming reactions in previous steps, given by \( \tilde{d}_b \). This leads to a ‘deletion rate’ \( \tilde{f}_p \) of productive pathway \( P_p \), given by,

\[
\tilde{f}_p = \frac{f_p \delta_b}{D_b}.
\]  
(3.11)
The values given in equation (3.10) are updated accordingly with this deletion rate. The same goes for the connection between $\tilde{p}_b$ and a consuming pathway $P_c$. Lastly, the previously deleted productive pathways are also connected to the deleted consumptive pathways, with a rate $\frac{\tilde{p}_b \tilde{d}_b}{D_b}$, and the fraction of deleted pathways that contribute to density changes are also calculated.

### 3.1.6 Making a pathway elementary

Due to the nature of the algorithm it can occur that a newly created pathway is a combination of other pathways. This newly created pathway does not give any new information and only hinders the analysis of the chemical system. In order to circumvent this issue, whenever a new set of pathways is created a check is done whether a new pathway $P_{\text{new}}$ is actually a combination of others. Checking whether or not another pathway is a subset of the new one is not enough, as these might have already been deleted. Therefore a new loop with connection steps is initiated, illustrated by figure [3.3]

This is done analogously to section [3.1.3], every reaction in $P_{\text{new}}$ (with $f_{\text{new}} > f_{\text{min}}$) is given its own pathway and the same order of branching species $S_b$ as in the main algorithm is used. Whenever two pathways, $P_x$ and $P_y$, are connected a check is done according to equation [3.12],

$$R(P_i) \nsubseteq R(P_x) \cup R(P_y),$$

(3.12)
where \( R(P_a) \) represents all of the reactions in a pathway \( P_a \). \( P_i \) is a pathway from the set of pathways created in this elementary algorithm, but \( i \neq x \land i \neq y \). Only if this is valid, the connection of \( P_x \) and \( P_y \) will be added to the list. In simpler words, if there is already a pathway in the set that has reactions that are a subset of the combined reaction pool of \( P_x \) and \( P_y \), the connection of \( P_x \) and \( P_y \) is too complex as it contains at least one smaller pathway. Therefore, it cannot be elementary and should not be part of the final set of pathways.

In the end, either \( P_{new} \) is formed again or a list of candidates \( P_{el} \) of sub-pathways for \( P_{new} \) are formed. However, these sub-pathways often do not form a complementary set to describe \( P_{new} \) uniquely. Therefore, the definitive sub-pathways still have to be determined. In order to deal with this issue systematically an order of preference is determined for the found sub-pathways. The pathways that are already present in the full list of pathways are preferred over those that are not present yet. So the already existing pathways with the highest rate in the main algorithm are put on top of the list. The pathways that are not yet present are sorted based on their simplicity. The pathway with lowest total multiplicity, \( \sum_{j=1}^{n_R} x_{jz} \), is put on top for the rest of the list.

With this list known, weights \( w_{el}^{el} \) are attributed to all of the sub-pathways using the Simplex method [35]. Using these weights the rate of the complicated pathway is divided over its elementary pathways, like equation (3.13). If the elementary pathway already existed, the rate is added to the existing rate of the pathway. If it did not exist yet, it will be created with the rate according to equation (3.13).

\[
\Delta f_{el}^{el} = w_{el}^{el} f_{new}.
\]  

### 3.1.7 Output

In the end the algorithm outputs a list of pathways \( P_f \) with a rate above \( f_{min} \), along with the multiplicities \( x_{ik} \) of reactions \( i \) in that particular pathway. Also the value of deleted rates, species’ production and destruction, according to equations (3.10) are available. Along with those are the pathways that contribute to density changes in order to keep the system’s initial state intact.

The only parameter that these results depend on is the value of \( f_{min} \), which can be changed by the user at any time depending on the required accuracy and amount of information for the analysis.

### 3.2 PLASIMO Implementation

In the PLASIMO [18] implementation of the PWA algorithm, there are some differences compared to section 3.1. First of all, the reaction rates are not taken as averages over the model’s simulation time, but are instead taken as reaction rates at a certain point in time. By using this way it is possible to investigate the system’s chemistry at specific points in the evolution. Fast, early reactions will not play a role in averages over the simulation time, but can still be investigated by looking at the early stages of a plasma this way. Same goes for reactions that do not play a role early on, but become important later on due to processes like heating. As all reaction rates are calculated by equation (1.4), whenever the density and/or rate coefficient changes throughout the temporal evolution, so will the impact of the reactions. Density changes will occur through the source terms of the species and the rate
coefficients are dependent on many factors, often, most importantly either the gas or electron temperature.

As addition to the algorithm, a record of the electron power density associated with each pathway is kept [26]. Every pathway $P_q$ has an electron power density $Q_q$ which is, initially, defined by,

$$Q_q = f_q \sum_{j} x_{jq} \varepsilon_j,$$  \hspace{1cm} (3.14)

where $\varepsilon_j$ is the reaction energy of reaction $j$. This also has to be accounted for in the connection of two pathways. When productive pathway $P_p$ and destructive pathway $P_c$ are connected to form $P_n$, the electron power density follows the same logic which leads to equation (3.15) for the combined electron energy density,

$$Q_n = f_n \sum_{j} x_{jn} \varepsilon_j.$$  \hspace{1cm} (3.15)

With the addition of the electron power density of pathways it becomes possible to add a second user-defined parameter $Q_{\text{min}}$. Now, when a new pathway is created, it will only be deleted when both its rate is below $f_{\text{min}}$ and its electron power density is below $Q_{\text{min}}$. Pathways which do not have a high rate but have a big impact on the electron energy distribution are still recorded by the algorithm and available for analysis.

Lastly, with a new parameter, whenever a pathway is deconstructed into its elementary sub-pathways the candidates are sorted, based on four criteria, before the weights are determined using the Simplex method:

- Pathways which already exist in the main algorithm with a higher rate are above pathways which already exist with lower rates.
- If pathways have the same rate, the pathway with the higher electron power is first.
- If pathways have the same rate and electron power density, the pathways with the least amount of reactions (the least complex pathway) is on top.
- If that is also equal, the pathway that was originally created first is higher, this is based on their index in the algorithm.

Whenever a pathway’s rate is distributed to its elementary sub-pathways as in equation (3.12), the same is done for its electron power density, as shown in equation (3.16),

$$\Delta Q_{z}^{el} = w_{z}^{el} Q_{\text{new}}.$$  \hspace{1cm} (3.16)

Here, $Q_{\text{new}}$ is the electron power density of the newly created pathway that is to be divided over its sub-pathways. Weights $w_{z}^{el}$ are calculated using the Simplex method and $\Delta Q_{z}^{el}$ is the difference in electron power density of the elementary pathways.
Chapter 4

Chemical Reduction based on Pathway Analysis

In the chapter 3, Pathway Analysis (PWA) has been explained and shown to be a systematic method for analysis of complex chemistries. Whereas it helps to understand the chemistry, it does not directly offer a tool to reduce this complex chemistry. One could use the results of PWA to manually adjust and tweak a chemistry in order to reduce it. However, as explained, the strength of the method is the automation and the objectivity. Therefore a tool has been created to offer automatic reduction of a complex chemistry based on PWA results.

4.1 Pathway Analysis interpretation

PWA does not provide a handle for a mathematical reduction technique like ILDM or PCA as explained in section 1.3. It does give a lot of direct information about the reactions in the set and indirect information on the species related to those reactions. A reduction based on this method must perform based on the input thresholds, $f_{\text{min}}$ and $Q_{\text{min}}$. By tweaking these parameters the degree of reduction should change accordingly. In order to keep the system modular and user-friendly, it was chosen to not introduce any new parameters for reduction. Now, it is up to the user of PWA to decide whether or not a reduction is done, but in any case, this reduction would not require any more input from the user than the already supplied input for the pathway analysis.

4.1.1 Interpretation methods

There are a couple of ways to use PWA results for reduction, listed below:

- **Method 1**: The system can be transformed into a different basis, the pathway basis. In this case, the original reactions are replaced by the final pathways found by PWA. Some species need to be excluded as branching species in order to end up with pathways that actually have a net effect. By changing $f_{\text{min}}$ and $Q_{\text{min}}$, the amount of pathways used in the new reduced system changes, effectively reducing the system.

- **Method 2**: Reactions and species can be treated as they were originally. In this case, the result of PWA is used to distinguish important and unimportant reactions and/or
species. Like before, the amount of species and/or reactions that are taken into account in the reduced model depends on the input parameters $f_{\text{min}}$ and $Q_{\text{min}}$.

There are some pros and cons for both of these methods. Transforming to a pathway space allows for a more direct link between PWA and the PWA reduction. The full strength of the analysis method is translated into a reduction. However, this method is complex to implement and either will require a whole automatic change of basis or a lot of manual work to achieve its goal. Besides that, this method is not suited for using to understand the simplified chemistry, as the reduced system does not represent the species and reactions as they are.

Using PWA to reduce the given species and/or reactions has the opposites of these pros and cons. The direct link between PWA and the reduction is not present as there has to be some translation from important pathways to important reactions and species. But once this translation is determined this method is straightforward to implement and automate. Also, the reduced chemistry still consists of regular reactions and species and is therefore suitable for analysis. Added to this, is the fact that this method is complementary to the framework that is given within the PLASIMO software [18] in which this work was executed.

As the goal is to develop an automated method, which implies a minimization of user-effort, the implementation should be compatible with the current PLASIMO toolbox. PLASIMO supports the use of all types of reactions and species, but all of them represent physical processes and particles. The resulting reduction should thus directly be usable with the PLASIMO software. Therefore the second method was chosen. For this, a translation between PWA results and a corresponding reduction had to be found. A very simple pathway analysis result is shown below. There are two types of pathways that are reported, the first type is of pathways that contribute to the density changes of species in the chemistry. The second type are the Null pathways that are left over when the algorithm has been completed.

Active pathways that have contribution on the densities changes:
0: rate = 1.34291e+24
  1x Reaction 0 ("Ar_ion") @ 1.34291e+24 1/m^3/s and -3.39089e+06 J/(m^3*s)
-------------------------------
Net: Ar -> e + Ar+

Active pathways:
10: rate = 7.21788e+24
  1x Reaction 1 ("Ar_exc") @ 7.21788e+24 1/m^3/s and -1.33684e+07 J/(m^3*s)
  1x Reaction 4 ("Ar*_rad") @ 7.21788e+24 1/m^3/s and -1.33684e+07 J/(m^3*s)
---------------------
Net: Null

In this, fictional, example result, only two pathways had high enough rates and/or electron power densities associated with them to not be deleted. For each pathway the reactions it contains, and their multiplicities, are shown and a net result of the full pathway is calculated. Besides that, the rate and electron power density are given per pathway. Out of the 10 reactions that were present in the original chemistry there are just 3 that are present in the important pathways. These pathways represent the most prominent chemical conversion flows through the system, so these reactions appear to be the most important for chemical flow.
4.1.2 The Reduction

That is the basis the used reduction is based on. In essence, all reactions that are part of the pathways in the result of a PWA analysis are deemed as “important reactions”. All the others are now named “unimportant reactions”. Throughout this work the system is reduced using these unimportant reactions in different ways.

The main function of the reduction is to exclude the unimportant reactions from future simulations. A blacklist is automatically generated that allows for a re-run of the same simulation with a reduced chemistry. With the lower amount of reactions the system becomes less complex. The extent to which this reduction blacklists reactions is user-determined by the input parameters of the PWA algorithm. If the thresholds are higher, generally, more reactions will be blacklisted. It is therefore possible to find a maximal reduction for a given accuracy of the final result.

Since not just reactions are important for both analysis and computation time, the reduction also reports about species. Species that no longer have any reaction associated with them are reported as “unimportant species”. These species can then be deleted from the chemistry, allowing for a reduction in both reactions and species.

Besides species that have no reactions at all anymore, there might also be species which have exclusively either sinks or sources left. These are not necessarily unimportant but may cause unwanted effects like unphysical densities or extreme energy sinks. Situations like these are reported beforehand and the user is advised to look at these species critically.

As the PLASIMO implementation of PWA, see section 3.2, is taken at a certain point in time, it is possible that a reduction captures the behaviour around that time but not at other times in the plasma evolution. Therefore it is possible to perform a reduction based on multiple analyses at different times. To combine said analyses two techniques are supported for combination of two blacklists $B_a$ and $B_b$, these are given by,

$$B_c = B_a \cup B_b,$$  \hspace{1cm} (4.1a)

$$B_c = B_a \cap B_b.$$  \hspace{1cm} (4.1b)

In the first case, the system is reduced even more by blacklisting all reactions that are unimportant at either one of the timestamps. This will decrease the accuracy at both points but will lead to increased reduction where it might be difficult to reach at the same point in time due to the presence of only a few, but large, pathways. In the second case, only those reactions are blacklisted that are deemed insignificant at both times. This makes sure that reactions (and species) that are important at either of the timestamps are kept. The evolution of the plasma is retained better, at the cost of lowered reduction.

In the end, a tool is developed that automatically runs a model, followed by a PWA step and then the reduction. Only in this case the output is not just a blacklist for reactions and species, but a whole new mixture section is created fully automated. This can then be used to alter the input files in a few seconds to be able to run a model with the reduced chemistry. Optional information about the reduced species and reactions are still available for analysis, but little to no analysis is necessary to be able to find a reduced model and run that reduced model.

Several different implementations were employed during this project, each of these will have its own subsection below. First the method and goal for each section will be shortly
addressed before looking at the resulting plasma behaviour before and after reduction. More information about the models used is given in appendix B.

4.2 Reducing reactions

In the first stage of the research a method was developed that allowed for reduction of reactions only. In this process a framework was developed to process PWA data and determine the insignificant reactions. The found list was subsequently deactivated from the original chemistry and the simulation was redone. The results for the original and reduced model were compared for the important parameters and species. At first, this was only done for plasmas with a constant input power, assuming that in this case the important and unimportant reactions at a certain point in time are valid enough to represent the temporal evolution. The focus of many constant input power models is on the steady state condition, which can be approximated by performing the reduction with the reaction rates at that point in time.

4.2.1 Constant input power plasmas: Reducing reactions only

At first this method was applied to a helium-water chemistry with 56 species and 623 reactions. This model is a zero-dimensional model as described in section 2.2.3. The aim of this model is to describe the steady state of said plasma for given mixing ratios and input power. More information can be found in appendix B. By varying the input parameters for pathway reduction, $f_{\text{min}}$ and $Q_{\text{min}}$, a different amount of reactions can be deactivated from the chemistry. Since many of the reactions involve species with very low densities or are very dependent on environment parameters like gas- and electron temperature, a significant part of the 623 reactions can be deactivated. In figure 4.1, the electron density and temperature, respectively, are shown for the full model and for the same model with 387 reactions deactivated through pathway reduction. With 62% of the reactions deleted only 13.9% and -3.9% deviation in electron density and electron temperature is observed in steady state situations.

Figure 4.1: Electron density (left) and temperature (right) versus time of a helium-water chemistry, with 56 species, for the full and the reduced system. In the reduced system 387 of the 623 reaction are deactivated, the steady state differences are 13.9% and 3.9% for density and temperature, respectively.

Increasing the thresholds, increases the amount of reactions that are to be deactivated. This does, however, not necessarily mean that the deviation from the full chemistry increases.
An example is shown in figure 4.2 for the same model, here 500 reactions have been deactivated. Both the steady state electron density and temperature are closer to the real model’s values. This might sound counter-intuitive, however it is perfectly explainable by looking at example 2.3.2.

What is noticeable though is that the evolution of the plasma does not follow a similar trajectory anymore. By taking a rigorous reduction based on steady state values, information about the early development of the plasma is lost by ignoring reactions that are only important at early stages of the plasma. This effect can be better seen in figures 4.3 where the early stages differ significantly.

If one would be interested in the early evolution of the plasma, the pathway analysis should be done at an early stage in the plasma. The price is loss of accuracy at steady state, but the development of the plasma is followed more correctly. Figure 4.4 illustrates this for the helium-water chemistry. In this case, an important ion, $H_3O^+$, is shown. The reduction also conserves densities of important species besides electrons. As is visible, the steady state solution differs more but the early stages match a lot better.

Figure 4.2: Electron density (left) and temperature (right) versus time of a helium-water chemistry, with 56 species, for the full and the reduced system. In the reduced system 500 of the 623 reaction are deactivated, the steady state differences are 8.1% and 2.1% for density and temperature, respectively.

Figure 4.3: Electron density versus time of a Helium-water chemistry for a full and reduced version of the model. On the left 387 reactions have been deactivated and on the right 500 reactions have been deactivated out of the total 623 reactions.
4.2.2 Pulsed input power plasmas: Reducing reactions only

Last section 4.2.1 showed that the reduction method is capable of recreating certain states of the plasma, but information about other periods in the transient behaviour is lost. Therefore it is interesting to look at the effect of reduction on pulsed plasma sources, as these repeat the transient behaviour and might therefore enhance errors in the reduction over periods of the input power density. To test this a molecular hydrogen chemistry will be used. The model used contains 41 species and 334 reactions, more information again in appendix B. In order for a proper comparison to be made, the same model is first run and reduced for a constant input power (of 1e7 Wm\(^{-3}\)). In that case 305 reactions can be deleted with a 1.02% difference in electron density and a 0.09% difference in electron temperature, this is shown in figure 4.5.

![Figure 4.4](image1.png)

**Figure 4.4:** \(H_2O^+\) density versus time for the helium-water chemistry for a full and reduced model. In the reduction 379 of the 623 reactions are deactivated. The steady state difference is 15.8%, but the early evolution behaviour is the same.

![Figure 4.5](image2.png)

**Figure 4.5:** Electron density (left) and temperature (right) versus time of a molecular hydrogen chemistry for a full and reduced version of the model. This model originally consists of 41 species and 334 reactions. After 305 reactions have been deactivated, the steady state differences are 1.02% and 0.09% for density and temperature, respectively.

In the case that a pulsed input power source is applied on this chemistry the evolution of
both electron temperature and density is, of course, different. The pulse is a sinusoidal signal where only the positive values are applied, see figure B.1. Since the system never reaches equilibrium, there cannot be a measure for difference at steady state. What can be compared between a full and reduced model is the trend and the difference in extrema. In figure 4.6 the difference in the peak electron density and temperature during one pulse is compared. Less reactions can be deleted, 300 here, and the peak density differs by 0.26\%, whilst the temperature differs by 5.56\%. The trend is the same as in the full model. The quick response of the electron temperature to the start of the pulse is captured and the resulting increase in electron density follows the same trend as well.

![Figure 4.6: Electron density (left) and temperature (right) versus time for a pulsed, molecular hydrogen model with 45 species and 334 reactions. The reduced version has 300 of these reactions deactivated. The peak electron density differs by 0.26\% and the temperature by 5.56\%. The corresponding pathway analysis was taken at 4.1 ms into the simulation which corresponds to the peak in electron density.](image)

For the figures mentioned above, a pathway analysis was done at the middle of the pulse, at 4.1 ms, where most activity takes place as both electron density and temperature are high here. Many reaction coefficients and rates depend on these two values. In order to check how robust the method is, reductions based on pathway analysis at different times are done. Both the start of the pulse, where the electron temperature peaks, and the time between pulses are other interesting times. In figure 4.7 the results for analysis at the temperature peak are shown. A lot less reactions (234) are reducable in this case, and the differences are bigger than before, with 18.56\% and 16.36\% difference in peak electron density and temperature respectively.

As shown in equation (4.1), two methods to combine two PWA results are available. To test the effect of combining two pathways a molecular oxygen chemistry is considered. This is quite a big chemistry with 53 species and a total of 1442 reactions. At first this chemistry is tackled by using similar rate and energy density thresholds as before. This results in a reduction of 1411 reactions as shown in figure 4.8.

In order to improve this reduction a second PWA is added at the time (1.75 ms) of the peak temperature and minimum density. The method of equation (4.1b) is chosen, as this makes sure that reactions that are important at one (or both) of the time stamps are kept in the system. If some reactions plays an important role at the start of the pulse, at low density and high temperature, but loses its impact during the pulse, this is now kept. However, as it turns out this does not prevent the large difference around the start and end of the pulse.
Figure 4.7: Electron density (left) and temperature (right) versus time for a pulsed, molecular hydrogen model with 45 species and 334 reactions. The reduced version has 234 of these reactions deactivated. The peak electron density differs by 18.56% and the temperature by 16.36%. The corresponding pathway analysis was taken at 4.0 ms into the simulation which corresponds to the peak in electron temperature at the start of a pulse.

Figure 4.8: Electron density (left) and temperature (right) versus time for a pulsed, molecular oxygen model with 53 species and 1442 reactions. The reduced version has 1411 of these reactions deactivated. The peak electron density differs by 0.17%, as this is the time (1.8 ms) at which a pathway analysis is done. The peak electron temperature and minimum electron density, however, occur at a different time and they differ by a few orders of magnitude.

Both the input parameters at the start and middle of the pulse are tweaked to find a better result. It turns out the maximum amount of reduced reactions with a proper fit of the reduced data is achieved by taking a PWA at the middle of the pulse with a few orders of magnitude lower threshold. In this case, 1386 reactions can still be reduced and the reduced data is an almost exact match to the full data, see figure 4.9.

All in all, reduction of pulsed plasma sources is still possible with the method described in section 4.1.2, however it is more difficult than it is for constant plasma sources. To be precise, reduction of pulsed plasma sources is more effective with, and therefore requires, knowledge of the dynamic behaviour of important parameters in the system. This makes that pulsed source reduction is (much more) difficult to automate completely.
4.3 Reducing reactions and species

Whereas reducing reactions as in previous sections proves to be effective in analysis of complex chemistries by simplifying them, it seems not complete yet. One thing that was noticeable is that some species lose all reactions producing and consuming them. Since this concerns zero-dimensional models, as described in chapter 2, these species are either constant in time or will go to zero density due to extra source terms. These species then either contribute nothing to the simulation or have an effect that is not justified as the actual density of these species is not properly calculated. When no processes related to a species are kept in a simulation, its density will stay at its initial density. If this initial density is not a correct estimated guess by the modeller, this wrong density will stay in the simulation throughout the whole time. For example, some ionized species might still contribute to the electron density through quasi-neutrality constraints even though their density is no longer updated according to the plasma’s current state.

In order to deal with these issues, the reduction method was extended. All species in the chemistry are identified and after reduction of reactions the ones that have no reactions producing and consuming them anymore are given as output for the user. These can then be deactivated from the model’s chemistry in order to improve on its accuracy but also to increase the understanding of the chemistry. A second situation that can occur is that a species only has productive or consumptive reactions related to it, in that case (and without transport) a species’ density will keep increasing or decreasing, reaching unphysical values after long enough simulation times. The user is warned when this situation occurs and pointed to the species that this is valid for and the corresponding reactions that are still left.

Finally, this information was combined in an automated tool that constructs a new mixture (essentially a new, reduced chemistry) for the user. This way reduction can be created and tested quickly with only a few user-actions. Once a satisfactory accuracy and level of reduction has been reached, the user can then use it for either computational efficiency as well as thorough analysis of the reduction.
**4.3.1 Constant input power plasmas: Reducing reactions and species**

Once again, this method was first applied to chemistries with a constant input power. The method was stress-tested by increasing the PWA thresholds as high as possible without causing unphysical behaviour in the reduced chemistry. A possibility to exclude species from deactivation was needed in order to retain species that were essential for declarations used in the model, e.g. the only negative ion was kept in when a negative ion density was set and used in the model. Some rate coefficients are dependent on declarations that do not involve any of the species contained within the reaction. So, even if a species is only consumed by diffusion and/or convection, its initial density will still affect other reactions, until its density drops to negligible values.

For the helium-water chemistry the addition to the reduction was a removal of 7 species from the system completely. The results are shown in figure 4.10. The resulting steady state solution is very similar to the obtained values at earlier sections in this chapter. The amount of removed reactions is also quite small. Some species in this chemistry are vital to the gas temperature calculation done in the global model, therefore it is very difficult to reduce more for this model. Careful consideration of essential species is possible, but outside the scope of this research.

![Figure 4.10: Electron density (left) and temperature (right) versus time for a helium-water chemistry with 623 reactions and 56 species. The reduced version has 383 of these reactions and 7 species deactivated. The final electron density differs by only 14.2% and the final electron temperature by 4.0%.](image)

By considering the point in time at which the gas temperature calculation breaks down as a point of interest and including a PWA position there, the thresholds can be driven up a lot higher whilst still maintaining stability. In the end, this does not lead to many new deactivated species, but about another 100 reactions can be deactivated this way. Figure 4.11 shows that in this case the early behaviour is followed very well, even though the steady state solutions is a factor of 3 off.

When this method is applied to the (constant) hydrogen chemistry, the result looks as shown in figure 4.12. Notable is that the reduced model shows a clear deviation in the microsecond to millisecond range. As is shown on the right side of figure 4.12 the relative error is in the order of tens of percents in this range. If this timescale is important for analysis or when such an error is unwanted, this can again be remedied by combining the steady state analysis with one in the timescale of the deviation. Figure 4.13 details the effect of such an addition. A limited decrease in reduction (8 reactions and 5 species less) leads to an overall
more accurate reduction for all timescales, reaching at most a relative error of a few percents.

Whilst deleting species from the chemistry strongly impacts the computation time of the model due to the dimensionality reduction obtained, it also impacts the quality of reduction too. Similar levels of reduction in the amount of reactions can still be obtained, but these sometimes require more careful consideration of chosen parameters. Stability issues can occur when the gas temperature is calculated instead of assumed constant (which is the case for the helium-water chemistry), which has to be taken into account in the reduction.

4.3.2 Pulsed input power plasmas: Reducing reactions and species

With information about constant input powers known, the next step is the application on pulsed plasma sources. The aim for these kinds of plasmas is to replicate the evolution of the densities and temperatures. Since there is no steady state that will ever be achieved it is more important that evolution is similar as this is the behaviour that would be observed in
experiments. Some experiments are interested in the range of values that can be expected, to for example determine the load on a target. Other experiments might be more interested in the peak values as this is the moment that plasma does its intended work.

Examples of these are applied to the previously used hydrogen chemistry. Between the time that the results from the previous section have been obtained and the time the results in this section were obtained, temporary alterations had been made to the hydrogen chemistry. Now it contained 41 species and 306 reactions in total. For the purpose of this thesis, the change is not important, as the difference between the full and the reduced chemistry is what matters. In the case that the trend and the general order of densities and temperatures are important, one can push the reduction as far as possible. In that case, 273 out of the 306 reactions and 18 out of the 41 species can be deleted. In figure 4.14, it is apparent that the trend is closely followed and little deviation to the full chemistry is found. The maximum error is at all times below 10% and this chemistry allows for evaluation of the most important processes in this particular chemistry.

On the other hand, when the actual peak value is more important, a reduction can still be done that deactivates a significant portion but only shows errors below 0.5%. With just 4 species and 14 reactions less deleted, this accuracy is already reached. The results are shown in figure 4.15. What has to be noted is that, like in section 4.2.2, the time at which the pathway analysis is done is crucial to the result of the reduction.

Comparing to section 4.2.2 the amount of reactions deleted is similar, but the addition of species deletion offers a more interesting and far more effective reduction. The accuracy of both methods is also very similar, thus even in the pulsed case there is no reason to exclusively reduce reactions and not also species.

A final test for the method is to apply it to a significantly larger chemistry than has been done so far. For this, a molecular nitrogen, pulsed chemistry was chosen as it contains a total of 2504 reactions and 66 species. The set contains a large range of vibrational excited states of molecular nitrogen and the interactions between those states. These processes are very much gas temperature dependent and therefore it is to be expected that for a room-temperature
Figure 4.14: Electron density (left) and its relative error (right) versus time for the molecular hydrogen chemistry with a pulsed input power. In this version, the reduction is based on an analysis at 4.35 ms. On the left the electron density of both the full and reduced model (273 reactions and 18 species deactivated) is shown. On the right the relative error of the reduced model compared to the full model’s local value is given. The maximum error does not exceed 10%.

The best result obtained is a trade-off between the degree of reduction and the accuracy of the reduced model, although it is still dependent on the aim of the reduction. In this case it was found that deactivating up to 2461 or 98% of reactions and 41 or 62% of species leads to the “best” reduction. In that case, peak differences of 0.38% and 0.021% are observed for the electron density and temperature, respectively. The left side of figure 4.16 shows the evolution of this plasma for the full and reduced model.

When the (constant) gas temperature is increased to 2000 K, the degree of reduction cannot reach this far. An attempt at reducing to the same degree is shown on the right side of figure 4.16. Due to the higher relevancy of some of these reactions at this gas temperature the reduction shows a larger deviation from the full model. In this case, a more conservative approach should have been taken to accurately reduce this chemistry to its core elements. More reactions (and species) play a significant role now and therefore less should be deactivated.

4.4 Reduction analysis

The two previous sections illustrated some of the results obtained using the developed reduction method. In order to look at these more critically, the method must be looked at "out of its own comfort zone". This means that a test needs to be done compared to another, simpler method. Besides that, the working part of the method should be analysed. The answer to the question how the method realises its effect should be touched upon.

In the next few sections this is done in a few ways. In section 4.4.1 a short comparison study is executed to a so-called "naive" reduction. Following that, in section 4.4.2 the timescales of the system before and after reduction are calculated. The last part of this chapter, section 4.4.3, focuses on the link between species/reactions and the timescales/eigenvalues found in both Schur and Eigenvalue decompositions.
Figure 4.15: Electron density (left) and its relative error (right) versus time for the molecular hydrogen chemistry with a pulsed input power. In this version, the reduction is based on an analysis at 4.35 ms. On the left the electron density of both the full and reduced model (259 reactions and 14 species deactivated) is shown. On the right the relative error of the reduced model compared to the full model’s local value is given. The maximum error does not exceed 0.5%.

Figure 4.16: Electron density versus time for a molecular nitrogen chemistry with a pulsed input power, 2504 reactions and 66 species. In this version, the reduction is based on an analysis at 0.33 ms. On the left the electron density of both the full and reduced model (2461 reactions and 41 species deactivated) at a gas temperature of 300 K is shown. On the right this is shown for the same chemistry, only with a gas temperature of 2000 K. Here 2445 reactions and 41 species are reduced, a similar amount.

4.4.1 Comparison with a naive reduction

To determine whether performing a pathway analysis step before reducing a chemistry is an improvement over performing a similar reduction without pre-analysis, a comparison is done. The reduced models obtained using the tool developed in this work are compared to naive reductions of the same full chemistries. The simplest (and most naive) reduction that was decided to compare with here is the removal of $x$ reactions with the lowest rates at a certain time.

The accuracy of both the naive reduction and the PWA reduction are then compared at the time of interest of the simulation. In figure 4.17 on the left side the electron density is shown for the full, the PWA reduced and the naive reduced model with similar amount of reactions removed. At steady state, the time of interest of this model, the PWA reduced
model differs by 14.2\%, whereas the naively reduced model differs by 68.2\%. On the right the density of the ion H3O+ is shown for all three. This is one of the most important ions in this chemistry, and also this density is conserved quite well by both reductions with 23.3\% and 73.5\% difference respectively.

**Figure 4.17:** Electron density and H3O+ density for the full chemistry, the PWA reduction and a naive reduction. The PWA reduction has 383 reactions and 7 species removed, whilst the naive reduction has 372 reactions removed. The relative errors, at steady state on the left are 14.2\% and 68.2\%, respectively. On the right, they are 23.3\% and 73.5\%.

Here, the PWA reduction performs better, accuracy wise, than the naive reduction. However, when the degree of reduction is increased this does not always have to hold. Figure 4.18 illustrates how for a higher degree of reduction, the naive reduction performs better than the PWA reduction. The error for both models is similar and follows a similar trend. On achieved accuracy levels for similar degrees of reduction this work’s reduction works comparatively to a naive reduction.

**Figure 4.18:** Comparison between reductions for a high degree of reduction of the helium-water chemistry. On the left, the H3O+ density for the full model and the two reductions are shown. On the right, the relative errors of the reductions compared to the full chemistry are shown. The PWA reduction here has 475 reactions and 8 species removed, the naive reduction has 475 reactions removed as well.

However, a side-note to this comparison is that it seems like the naive reduction performs better in the early stages of the simulation. The goal was to have a similar amount of reactions removed in the naive reduction as in the PWA reductions, therefore the naive reduction had to be done at a timestamp of 1 \(\mu\)s or else the reduction was not stable and would not resolve.
Since the reduction is done at that timestamp, it is to be expected that it performs best at the time. Furthermore, this volatility of the naive reduction makes its so that, even though the method is simpler, it requires more user effort and knowledge to perform the reduction.

An unmentioned aspect of a reduction comparison is the computational cost, or clock time, of the models. Here, no attention was given to the time the reductions take to complete the simulation. The PWA reductions were at all times faster to resolve and reach the end of the simulation than the naive reductions. These times were not recorded, which could provide some more insights into the comparison between the two. Some worked out ideas for future comparisons are given in section 5.2. Furthermore, the next section 4.4.2 will investigate the effect of the PWA reduction on the timescales of the system in order to explain (part of) the clock time speed-up.

A second side-note is that the naive reduction is not capable of automatic reduction of species. This would require quite an amount of user effort to check and manually deactivate species. Not removing species leads to the problems mentioned at the start of section 4.3, making the naive reduction more prone to errors.

4.4.2 Timescale analysis

A system’s evolution is partly determined by its timescales. The stiffness of a system is defined by dividing the longest timescale at a certain timestamp by the shortest timescale at that timestamp. In general, when the stiffness of a model increases it will take longer to compute a given simulation time for that chemistry. The PWA reduction decreases the computation costs by more than expected by just removing reactions and species. Therefore, an analysis of timescales and (inherently) stiffness of the realised reductions using this method is performed.

As described in section 2.4 the timescales relevant for a system are dependent on the reaction and species contained within its chemistry. Removing reactions and/or species would then inherently alter the timescales that govern the system. Since the equilibrium position also shifts when this happens, it is not trivial to determine the change of timescales after deleting one or more parts of the chemistry.

The pathway analysis algorithm, see chapter 3, first treats the shortest-lived species as a branching species. This is determined at a specific point in time and the life-time is calculated by dividing the current density by the current destruction rate. Intuitively, these species will correspond to one or some of the smallest timescales in the system. An expectation is that the reduction method based on PWA would then affect the shorter timescales of the system. However, as the effect is not predictable, this should be investigated.

In this section, the Jacobian is calculated, as in equation (2.26), for a whole range of time steps using the (current, at that timestamp) rate coefficients and densities given by the PLASIMO simulation. A spectral decomposition returns the eigenvalues of the Jacobian and with these the reigning timescales can be determined. Timescales that are longer than the equilibration (in case of constant input power) or simulation (in case of pulsed input power) time are deemed infinite. These represent conservation mechanisms within the chemistry.

Said calculations are done for both the full chemistry and the reduced system. An example of such a comparison is shown in figure 4.19. Here, the before-used helium-water chemistry is compared to its reduced version. The reduction does not show a clear effect on the short timescales. What can be seen is that, in this case, the early behaviour of the system is smoothened and at the later stages both the minimum and maximum timescale decrease. For the stiffness this also gives a similar, smoothened trend, with a slightly higher stiffness at the
end of the simulation time.

When taking a look at the constant input power version of the hydrogen chemistry (which now has its original 41 species and 334 reactions again), see figure 4.20, a similar effect is observed. In this case, the early stage is again smoothened out, only up to a certain timestamp though. Around steady state the minimum and maximum timescale now both increase instead of decrease compared to the full model. This in turn, again leads to a small increase in stiffness.

Figure 4.19: Timescale (left) and stiffness (right) analysis of a reduction of the helium-water chemistry where 475 reactions and 8 species are deactivated. On the left, the minimum and maximum timescale of both the full and reduced chemistry are given. On the right, the resulting stiffness is plotted against time for both.

Figure 4.20: Timescale (left) and stiffness (right) analysis of a reduction of the molecular hydrogen chemistry with constant input power. In the reduced model 303 reactions and 17 species are deactivated. On the left, the minimum and maximum timescale of both the full and reduced chemistry are given. On the right, the resulting stiffness is plotted against time for both.

For pulsed power plasmas, a timescale variation will occur during every pulse. When the pulse is first applied, power is deposited in the system and processes that are similar to the early evolution of a DC plasma occur. It will take some time before they equilibrate again, so it is expected that during the pulse the shortest timescale decreases temporarily before increasing again as fast processes equilibrate. The maximum timescale is more difficult to predict, as it is not known beforehand what the slowest process is.
Once again, to investigate this behaviour, the timescales were calculated throughout the simulation time, for a pulsed plasma this time. Figure 4.21 represents this result for the molecular hydrogen plasma. Immediately noticeable is that the predicted drop in the shortest timescale is filtered by the reduction whereas it is present in the full chemistry. This compares to actual simulation speed, as this is the point where the full chemistry would strongly shorten and slow its timesteps while the reduction passes these points significantly faster.

The maximum timescales stay roughly the same throughout the pulses. Some small differences in peak heights and widths can be observed but no large differences. The stiffness of the reduced model also shows how the reduced model can handle the pulses faster than the full model, as the stiffness is generally lower during the pulse.

All in all, no clear effect of the reduction on the timescale is distinguishable. For constant input powers it does not seem to decrease or increase the timescales and/or stiffness. No preferential direction was found either. For pulsed models it does seem that the reduction reduced the time taken in the brunt of the pulse by slightly suppressing the increase in stiffness in that period. However, the timescales and stiffness do not show why the reduction is so much faster than the full model.

![Figure 4.21: Timescale (left) and stiffness (right) analysis of a reduction of the molecular hydrogen chemistry with a pulsed input power. In the reduced model 297 reactions and 15 species are deactivated. On the left, the minimum and maximum timescale of both the full and reduced chemistry are given. On the right, the resulting stiffness is plotted against time for both.](image)

### 4.4.3 Relating species and timescales: Schur/Eigenvalue decompostition

Understanding the effect of removing species requires an understanding of the relation between species and timescales. As explained in section 2.4.1, the eigenvectors can be used to determine the linear combination of densities that is captured in a timescale. Building on the calculations done in the last section, the values of the eigenvectors, or more-so the inverse eigenvector matrix can be plotted in a heatmap. This is comparable to a part of the timescale analysis in [26], only in this work the spectral decomposition is used as this can directly link species to the timescales.

At first, this was done for the helium-water chemistry, used multiple times before in this thesis. Figures C.1 and C.2 showed how, even though the total range of timescales is unaffected, the reduction affects the short timescale processes more that it does the long timescales processes, which remain virtually untouched. Concerning the method and the
speed-up of the reduction this was good news, but this changed when the molecular hydrogen model was also tested. Strange results lead to a re-evaluation of the method. A spectral decomposition can fail to deliver correct and accurate results when duplicate eigenvectors are present as their eigenvectors can then be linearly dependent [21].

A reconstruction of the Jacobian by reversing equation (2.29) showed that, in the case of molecular hydrogen, the reconstructed Jacobian showed major deviation from the original. Therefore the results for this model where not valid and inherently not useful. This realisation made it so that the previously obtained helium-water results had to be checked for correctness. It turned out that, whilst the reconstructed Jacobian mostly showed little to no deviation, there were some differences between the original and the decomposition. To what extent the heatmaps created are valuable is not determinable and therefore these results are only given in the appendix and not discussed further here.

The use of a Schur decomposition as done in [26] would circumvent the issue of collinear eigenvectors, however the Schur vector matrix cannot be related 1-to-1 to species densities like the spectral decomposition can. All but one Schur vectors are related to linear combinations of timescales which prohibits the use as a direct analysis tool. In section 5.2.4 a method is suggested that combines the strengths of both decompositions and should avoid the downside of both.
Chapter 5

Conclusions and Outlook

In this work a mechanism reduction method was developed, expanded and tested for a varying range of circumstances. This chapter first provides the conclusions that can be taken away from chapter 4 followed by suggestions for future work based on the challenges faced during this work or expansions of this work.

5.1 Conclusions

The pathway reduction method is capable of systematically reducing zero-dimensional chemistries by removing reactions and species. The degree of reduction is controllable and the reduced variants capture the original chemistry up to a degree of accuracy the user wishes.

In order to retain the temporal behaviour of a plasma using this reduction method the tool should be applied at the timestamps of interest. When doing so, the behaviour is kept whilst still reducing significantly large parts of the chemistry.

The (maximum) degree of reduction that can be attained depends on the configuration aspects of the plasma. Changing the temperature, pressure and/or input power affects which processes and which amounts of processes are important.

If a zero-dimensional model calculates its gas temperature's temporal behaviour, the amount of species that can be removed from the system is decreased. The gas temperature calculation is heavily influenced by the species composition.

A comparison between pathway reduction and a naive reduction shows that there is no strong difference in final accuracy between the two for the systems studied in this work. However, the clock time is decreased significantly by using pathway reduction. Besides that, the pathway reduction method is more stable and requires less user effort. Therefore, only pathway reduction can be set-up in an automatic fashion.

No preferential effect of pathway reduction on the stiffness of the system was found. The expectation that the pathway reduction method increases the shortest timescales was not confirmed. The method is, however, able to reduce the stiffness of pulsed plasma simulations, during the pulse.

Spectral decomposition is not suitable to analyse the relation between species and timescales. The near-collinearity of eigenvectors causes significant errors, as for collinear eigenvectors the spectral decomposition does not exist, and therefore the results from this analysis are not reliable.

Returning to the research question stated in section 1.3, it is definitely possible to
develop an automated reduction method based on pathway analysis, one that is very successful at reducing complex chemistries autonomously.

5.2 Outlook

This section focuses on the difficulties and opportunities encountered during the work described in this thesis. Where possible these were turned into suggestions for future work as they would have been done if time would have allowed it.

5.2.1 Error calculation of pathway reduction

Currently, the pathway reduction tool uses the input information used for pathway analysis in order to determine its thresholds. However, it is not clear from the beginning to the user what values of thresholds lead to what degree of reduction. Moreover, it is not evident what kind of accuracy can be expected given a certain threshold or degree of reduction. In discussions with potential (future) users of the tool this was one of the most prominent questions asked.

As mentioned in section 2.3.1, it is very laborious to determine the full effect of the removal of a reaction and/or species. The error of a full reduction is equal to the compound effect of each individual reaction and species removed, making it infeasible to calculate directly. There are some important indicators that give some sense of expected error though.

First of all, the pathway analysis algorithm has a record of the total deleted effects in the forms of \( \bar{r}_j, \bar{p}_i \) and \( \bar{d}_i \) shown in equation (3.10). If the system were to be designed like the first method in section 4.1.1 describes, these would be directly relatable to the reduced system’s error. These values show the error for the specific densities at the time the pathway analysis was performed.

However, it is not the first method from section 4.1.1 that is implemented, but the second one. Therefore the values \( \bar{r}_j, \bar{p}_i \) and \( \bar{d}_i \) do not show the exact values deleted in the reduction. Considering a reactions that is present in both important and deleted pathways, the \( \bar{r}_j, \bar{p}_i \) and \( \bar{d}_i \) are updated as if its presence in the deleted pathways was deleted. As the reaction is either kept in or removed, it is not possible that part of its effect is deleted and the \( \bar{r}_j, \bar{p}_i \) and \( \bar{d}_i \) will be overrated values.

Since they are only valid at one specific set of densities and they are overestimations of the actual deleted values, these numbers can only be used as indications for the maximum relative error. As the goal of this research focused on exploring the errors of the reduction this was not implemented in the tool as it is. It would, however, be a good starting point in any future attempt to describe the error of the reduction based on the pathway analysis results. It would then still need refining in order to give proper error expectations for the user. Another option to deal with required errors instead of using pathway analysis thresholds is detailed in the next section 5.2.2.

5.2.2 Allowing the tool to run till a requested error is achieved

Akin to the previous section 5.2.1, this section suggests a way to step away from using the threshold values used in pathway analysis to also perform the reduction. There are cases where the user would want to reduce the chemistry as far as possible whilst maintaining a certain level of accuracy. At the current time, this is possible using the pathway reduction tool, but it does require some user effort in altering the threshold and testing till the desired
accuracy is reached. For most models used in this thesis, this sufficed and could be done, for a given set of conditions, within at most a few hours. However, when for example the oxygen or nitrogen chemistry are used, due to the sheer amount of species and reactions used this would take longer.

For a longer period of time, it is undesirable to require user-input every so often. An improvement suggestion for future work would be to automate this process. The easiest-to-use and most consistent way would be to ask the user’s input to indicate the following:

- The interested point(s) in time at which the accuracy is to be evaluated
- The species of interest at this(/these) timestamp(s)
- The maximum deviation from the full model’s value that this(/these) species’ density(/ies) may be
- How close to that maximum the final reduction needs to be at least, so essentially a range of accuracies that suffice

The way the tool would then work is to start from a default threshold value, then perform a pathway analysis and a reduction, followed by running said reduced model up to the largest timestamp the user specified. If the accuracy for the given parameters is better than the maximum given by the input parameters, a new pathway analysis and reduction will then be done for higher threshold values. If the accuracy is not sufficient, the same would be done but for lower threshold values.

This process would then be iterated until an accuracy is reached that lies within the range for all given parameters. By iterating in this manner an automated process of reaching the best possible reduction for the user is created. The tool would take more time to reach this situation than an experienced user would need with the non-iterative version that exists now. However, the iterative version could be run in the background and that would in the end save the user effort and allow for other work in the meantime.

5.2.3 Different approach to a comparison with the naive reduction

Section 4.4.1 describes a comparison between the pathway reduction developed in this work and a naive reduction that just removes reactions with the lowest rate. This section is focused on the accuracy and error differences between the two methods. It turns out that no major difference is achieved, for the models in question, by pathway reduction compared to the relatively simple naive reduction. However, during the collection of this data is was apparent that the pathway reduction was not only more stable than the naive version, but the reduced models using pathway reduction also were significantly faster in terms of clock time.

Due to time constraints, a clock time comparison between the two methods was not done though. In order to quantify the effective clock time reduction between the two methods, a proper comparison could be done. This would add to the value of the comparison itself and also to the knowledge of pathway reduction itself. Care has to be taken that the two methods are compared fairly, that is on the same processing system and with the same CPU strength allocated. Alternatives are to look at system time or process time instead.
5.2.4 Using Schur decomposition as a species and timescales analysis tool

As mentioned in section 4.4.3, the problem faced when relating species’ densities with system timescales is that no method provides a one-to-one relation consistently. The spectral decomposition does provide a one-to-one relation but linearly dependent eigenvectors give rise to inaccuracies. The Schur decomposition will always give accurate results, but only one timescale can be related with species one-to-one. The Schur decomposition of a jacobian $J$ would look like equation (5.1), with $Q$ the Schur vector matrix and $N$ an upper triangular matrix with the jacobian’s eigenvalues on the diagonal $[^{21}]$.

$$J = QNQ^T. \tag{5.1}$$

Akin to section 2.4.1 this can be filled into equation (2.28) and rewritten to give equation (5.2),

$$\frac{\partial Q^T \alpha}{\partial t} = NQ^T \alpha. \tag{5.2}$$

However, when the definition $\psi \equiv Q^T \alpha$ is added a problem arises. Since $N$ is an upper triangular matrix it does not only have diagonal elements, so only the last differential of $\psi_n$ reduces to a simple form like equation (2.33). For example, the second-to-last differential is given in by,

$$\frac{\partial \psi_{n-1}}{\partial t} = \lambda_{n-1} \psi_{n-1} + N_{(n,n-1)} \psi_n. \tag{5.3}$$

In equation (5.3), two different sets of species’ density are related to one another and no specific timescale can be linked to this relation anymore as in equation (2.34). The Schur decomposition could therefore be used to compute only a single relation, whilst there are as many relations to be made as there are species.

In order to circumvent this problem, one can take advantage of a property of the Schur decomposition. A Schur decomposition of a given matrix is not unique, meaning that there are different possible decompositions that satisfy equation (5.1). For a Jacobian of a system of $S_n$ species, which has $S_n$ eigenvalues (and $S_n$ timescales), there are $S_n!$ ways to arrange the eigenvalues over the diagonal. Every one of these solutions can be made from every other solution through the use of one or more Givens rotations $[^{36}]$.

What this allows is to compute the Schur decomposition of a given Jacobian, record the Schur vector corresponding the eigenvalue in the bottom row, then switch around the rows to place the next eigenvalue in the bottom row, record this eigenvalue’s Schur vector and repeat till all the vectors are recorded. Now a figure, similar to the ones in appendix C can be made for all systems, regardless of the presence of linearly dependent eigenvectors.

5.3 Outlook: ILDM versus Pathway Reduction

The pathway reduction method developed in this work has been tested for a variety of situations and also a variety of inherent properties of the method itself are explored. However, in order to increase the understanding of its strength an additional benchmark test against a different reduction method would be very helpful. There are multiple other well-known chemical reduction techniques, so a suitable comparison partner must first be found. In the
case of pathway reduction it would be interesting to compare it with the Intrinsic Low Dimensional Manifold (ILDM) technique as some similarities might be expected. Although one is a mechanism reduction method and the other a reparametrization of the chemical state space, both methods are (often) focused on reproducing steady state values. The goal of ILDM is to reduce the stiffness the system to strongly reduce the computational cost needed to solve it. Pathway reduction was expected (but this was not confirmed) to have that same effect by tackling short-lived species first.

A comparison with ILDM was always seen as the next step for the work in this thesis, but was not credible within the amount of time allocated for the research. The rest of this section will therefore deal with the plan on how to compare these. The required alterations to one or both methods, if any, will be explored and some initial, simple results will be shown.

5.3.1 The ILDM method

The ILDM method is based on the fact that very fast processes do not play a role in cases where steady states are investigated. Some of the theoretical background of this method is already touched upon in other parts of this thesis. For the sake of this section a concise explanation of the method will be given, for a more detailed description see the work of T. Rehman [21] or P. Koelman [26]. Based on the method described below and the pathway reduction method described in chapter [3] and chapter [4], possible advantages of ILDM over pathway reduction, and the other way around, are identified and described in section 5.3.3.

The Jacobian matrix has been defined in equation (2.26) and its Schur decomposition in equation (5.1). When applying the Schur decomposition in ILDM, the eigenvalues on the diagonal in \( N \) are sorted from low to high. This ensures that the slow timescales are on top and the fast timescales are on the bottom. Doing so enables splitting of \( Q_T \), based on a cut-off timescale \( \tau_{\text{cut-off}} \) using equation (2.35), according to:

\[
Q_T = \begin{pmatrix} Q_T^s & Q_T^f \end{pmatrix},
\]

(5.4)

where the \( Q_T^s \) corresponds to timescales \( \tau > \tau_{\text{cut-off}} \) and \( Q_T^f \) to timescales \( \tau < \tau_{\text{cut-off}} \).

One of the main assumptions in the ILDM method, is that the fast processes, corresponding to the short timescales, equilibrate far before steady state is reached. Under this assumption, there exists some lower-dimensional manifold for the source, \( S(n) \), to which all fast processes are perpendicular. Using this attribute the manifold equation can be set up, given by,

\[
Q_f^T S(n) = 0,
\]

(5.5)

which indicates that on the manifold all fast processes are no longer significant.

In this form, the system of species evolutions is underdetermined though, meaning that more equations are needed to still be able to solve the system. A first addition is the set of elemental conservation equations that dictate that no elements can be created or destroyed by processes within the systems studied. These equations are given by,

\[
\Phi n - \varpi_e = 0,
\]

(5.6)

where \( \Phi \) is a matrix with matrix elements \( \Phi_{ij} \) which is the number of times species \( j \) contains element \( i \). The total amount of elements in a closed system is given by the vector \( \varpi_e \).
In order to construct a manifold the last type of equation is added, the *parameter equation*. The parameter equation part is user-determined and its amount gives the final dimensionality of the manifold. The parameters are (often) species and the equation(s) are given by,

\[ Pn - \varpi^p = 0, \]  

(5.7)

where \( P \) contains rows for each parameter with a single one corresponding to the parameter species. The value these parameters will take are given in vector \( \varpi^p \).

By varying the parameter(s), a manifold can be spanned by solving the following system of equations,

\[ 0 = g(n) = \begin{cases} Pn - \varpi^p \\
\Phi n - \varpi^e \\
Q^T S(n) \end{cases}, \]  

(5.8)

which gives a mapping for all the species densities based on the density of the parameter species. This mapping is stored in a lookup table. This gives an equation for the species densities based on the parameter species densities,

\[ n = n(n_p), \]  

(5.9)

with \( n_p \) the densities of the parameter species. Finding the temporal evolution is then done by solving the differential equation(s) for the parameter species only, using,

\[ \frac{\partial n_p}{\partial t} = S_p(n(n_p)), \]  

(5.10)

with \( S_p \) the source for the parameter species. The dimensionality of the system is strongly reduced and only a few differential equations have to be solved to find the temporal evolution of all the species.

### 5.3.2 Simple hydrogen chemistry

The first step in the comparison is a simple side-by-side evaluation of the same chemistry. The first case studied in the work of T. Rehmann [21] (who took this from E. Kemaneci [37]) is a 3-level hydrogen system including the hydrogen ground state, H, an hydrogen excited state, H*, and the hydrogen ion, H+. The reaction set is given by,

\[
\begin{align*}
    H + e &\rightarrow H^* + e & K_1 &= 2.7 \cdot 10^{10}, \\
    H + e &\rightarrow H^+ + 2e & K_2 &= 9.0 \cdot 10^8, \\
    H^* + e &\rightarrow H^+ + 2e & K_3 &= 1.0 \cdot 10^6, \\
    H^+ + 2e &\rightarrow H^* + e & K_4 &= 17.5 \cdot 10^4, \\
    H^* + e &\rightarrow H + e & K_5 &= 3.8 \cdot 10^4, \\
    H^+ + 2e &\rightarrow H + e & K_6 &= 1.7 \cdot 10^2.
\end{align*}
\]  

(5.11a-f)

Important to note is that, in the ILDM application, the electron density is assumed constant and therefore this density is not calculated. This in turn, leads to the fact that the reaction rates are only dependent on *one* density, which means that the Jacobian matrix is constant and the system is fully linear.
This system is implemented in a PLASIMO global model to find the full solution with the begin condition that the mass fractions are as follows, $y_{H} = 0.01$, $y_{H^*} = 0.30$ and $y_{H^+} = 0.69$. For these conditions the ILDM solution is taken from T. Rehmann. Finally the pathway reduction technique from this work is applied on the full solution, which removes the species H and 4 reactions from the system. The results for all three method for the remaining species are given in figure 5.1.

![Reduction method comparison for 3-level H system](image)

**Figure 5.1:** Comparison for the two remaining species ($H^*$ on the left and $H^+$ on the right) of the 3-level hydrogen system of two reduction methods, pathway reduction and ILDM. The mass fraction is plotted against the simulation time for the full, pathway reduced and ILDM reduced solutions.

First of all, for this simple case both methods are capable of reducing the system still whilst maintaining relatively accurate results. For the $H^*$ species the results for both methods show little deviation from each other. On the other hand, for the $H^+$ species the pathway reduction performs better at the early stages whilst the ILDM reduction performs better near steady state. This is despite of the fact that the pathway analysis is performed at this steady state. The difference is, however, perfectly explainable as the ILDM method aims to capture the effect of the larger timescale processes after the fast processes are equilibrated. Therefore it captures steady state (almost) perfectly, whilst showing bigger deviation at times when the fast processes are actually not equilibrated yet. Pathway reduction on the other hand, removes 4 out of 6 reactions, still maintaining relative accuracy due to the fact that the important reactions throughout are kept in. By completely removing reactions, an error is introduced at all points in time though.

Another notable feature in this comparison is the dimensionality of the final solution. In the ILDM case, three differential equations (one for each species) are translated into one differential equation for the parameter species (in this case $H^*$) with a look-up table for the other two species based on the density of the parameter species. In the pathway reduction case, one species is removed, leaving two (coupled) differential equations for the other two species. Both of these differential equations are simplified by the removal of 4 out of 6 reactions.

In the end, in the ILDM method one differential equations with 4 reactions has to be solved, followed by a calculation of the other densities from a look-up table. The pathway reduction method has to solve two coupled differential equations, each with two reactions. Expectedly, in all cases, ILDM will have a strong decrease of dimensionality. Accuracy losses are consequently also expected to be higher for larger chemistries using ILDM.
5.3.3 Future work

A next step in this comparison would be to look at other (larger) chemistries that can be reduced by both methods. The interesting qualities and quantities to look into and the reason why they are interesting are listed below.

- **Reduction accuracy**: As done before in this thesis, comparing the reduced model’s accuracy to the full model is a good indicator of the quality of reduction. Important to note here is that the desirable accuracy is very much dependent on the goal of the simulation. Both pathway reduction’s and ILDM’s accuracy for various circumstances should be looked into.

- **Computational cost**: When a reduction’s goal is reached, a secondary goal is always to shorten the time it takes to simulate the plasma. More often than not, this is the first reason why using a chemical reduction technique is even considered at all.

- **Dimensionality reduction**: As shown with the simple example, ILDM reduces the dimensionality of a chemical system strongly. Pathway reduction is also capable of reducing the dimensionality of the problem, but to a lower degree. This effect can be quantified for more complex chemistries to give insight into why the methods work/do not work for the particular application.

- **Automatability**: Large-scale application of reduction methods, and also the possibility for users with limited knowledge of the method, depends strongly on the automatability of the method. It is important to qualitatively define the automatability of both methods to compare the user’s experience with the method.

- **Effort for reduction**: Following up on the automatability of the methods, is the effort it takes to arrive at the reduced model. It is necessary to quantify the number of steps a user has to go through in order to find a reduced version of the full chemistry used.

- **Limitations**: Every method has its limitations and for a proper comparison these have to be mapped for both ILDM and pathway reduction. Possible limitations include system size, computational cost of full model, spatial dimensionality and range of input parameters. I.e. a question that has to be answered, is if it is possible to alter the ILDM method so that it works for pulsed plasmas. For pathway reduction, there is a system size where the pathway analysis step will take so long that is not feasible to reduce it this way, the question is whether there is this limitation for ILDM as well.
Bibliography


Appendix A

Sample system decomposition

The sample system described in section 2.3.1 has been solved analytically, but since its results are not very intuitive or necessary for the section in which it is discussed they are given here. A system according to figure 2.3.1 with 3 species and 4 reactions, characterized by reaction coefficients $K_1$, $K_2$, $K_3$ and $K_4$, can be decomposed using an eigenvalue decomposition as in equation (2.29), which then gives,

$$
\Lambda = \begin{pmatrix}
0 & 0 & 0 & 0 \\
0 & \frac{1}{2} (-K_1 - K_2 - K_3 - K_4 - \sqrt{\alpha}) & 0 & 0 \\
0 & 0 & \frac{1}{2} (-K_1 - K_2 - K_3 - K_4 + \sqrt{\alpha}) & 0
\end{pmatrix},
$$

(A.1)

where $\Lambda$ is the eigenvalue matrix with the eigenvalues $\lambda_1$, $\lambda_2$ and $\lambda_3$ on its diagonal, respectively. The eigenvector matrix is given by,

$$
V = \begin{pmatrix}
\frac{K_3(K_2+K_1)}{K_1K_2} & \frac{K_1-K_2-K_3+K_4+\sqrt{\alpha}}{2K_2} & \frac{-K_1+K_2+K_3-K_4+\sqrt{\alpha}}{2K_2} \\
\frac{K_1K_2}{K_1} & \frac{K_1-K_2-K_3+K_4+\sqrt{\alpha}}{2K_2} & \frac{-K_1+K_2+K_3-K_4+\sqrt{\alpha}}{2K_2} \\
\frac{1}{K_2} & \frac{K_1+K_2-K_3+K_4+\sqrt{\alpha}}{2K_2} & \frac{-K_1+K_2+K_3-K_4+\sqrt{\alpha}}{2K_2}
\end{pmatrix},
$$

(A.2)

which contains combinations of the rate coefficients of the four reactions. To simplify the equation a dummy variable $\alpha$ is added, which is defined by,

$$
\alpha = (K_1 + K_2 + K_3 + K_4)^2 - 4(K_1(K_2 + K_3) + K_3(K_2 + K_4)).
$$

(A.3)

When using the values given by table 2.1 the eigenvalues for the systems look as follows in table A.1.

Table A.1: Eigenvalues for the sample systems in section 2.3.1

<table>
<thead>
<tr>
<th>System</th>
<th>$\lambda_1$</th>
<th>$\lambda_2$</th>
<th>$\lambda_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0</td>
<td>-5.88185</td>
<td>-1.76175</td>
</tr>
<tr>
<td>B</td>
<td>0</td>
<td>-5.886</td>
<td>-1.614</td>
</tr>
<tr>
<td>C</td>
<td>0</td>
<td>-5.82288</td>
<td>-3.17712</td>
</tr>
</tbody>
</table>

64
Appendix B

Model information

The models used in chapter 4 of this thesis were existing models developed by other users of the PLASIMO toolbox. None of them were specifically designed for the work in this thesis. The goal of the pathway reduction is to be universally applicable to all global models developed within the PLASIMO software. Since there will be no description of the development of these models in this work, an overview with the important parameters of all used models is presented in this appendix chapter.

Table B.1 and table B.2 show the important parameters for the constant and pulsed models, respectively. These represent the values that are interesting to change when a different condition is to be modelled. Figure B.1 shows the volume-averaged input power as it was used in all pulsed models.

Table B.1: Important information about the models with constant input power used in this thesis.

<table>
<thead>
<tr>
<th>Model</th>
<th>Helium-water</th>
<th>Hydrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td># of species</td>
<td>56</td>
<td>41</td>
</tr>
<tr>
<td># of reactions</td>
<td>623</td>
<td>334</td>
</tr>
<tr>
<td>Initial electron temp (K)</td>
<td>5000</td>
<td>1000</td>
</tr>
<tr>
<td>Gas temp type</td>
<td>Calculated</td>
<td>Constant</td>
</tr>
<tr>
<td>Initial gas temp (K)</td>
<td>500</td>
<td>300</td>
</tr>
<tr>
<td>Input power (Wm^-3)</td>
<td>300</td>
<td>1e7</td>
</tr>
</tbody>
</table>
Table B.2: Important information about the models with a pulsed input power used in this thesis. Note 1: This model used twice with only 306 reactions in figure 4.14 and figure 4.15. Note 2: This model is used once with a gas temperature of 2000 K on the right-side of figure 4.16.

<table>
<thead>
<tr>
<th>Model</th>
<th>Hydrogen</th>
<th>Oxygen</th>
<th>Nitrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td># of species</td>
<td>41</td>
<td>53</td>
<td>66</td>
</tr>
<tr>
<td># of reactions</td>
<td>334¹</td>
<td>1442</td>
<td>2504</td>
</tr>
<tr>
<td>Initial electron temp</td>
<td>1000</td>
<td>1000</td>
<td>1000</td>
</tr>
<tr>
<td>Gas temp type</td>
<td>Constant</td>
<td>Constant</td>
<td>Constant</td>
</tr>
<tr>
<td>Initial gas temp</td>
<td>300</td>
<td>300²</td>
<td>300³</td>
</tr>
<tr>
<td>Input power (W m⁻³)</td>
<td>see fig. B.1</td>
<td>see fig. B.1</td>
<td>see fig. B.1</td>
</tr>
</tbody>
</table>

Figure B.1: The input power used for all the pulsed plasmas simulations in this thesis. It consists of only the positive parts of a sine with a frequency of 4 kHz.
Appendix C

Heatmaps of species-timescale relation

In section 4.4.3 it turned out that the spectral decomposition was not universally suitable for the determination of the relation between species and timescales, the choice was made to not discuss the results first obtained using this method. The results found for the molecular hydrogen model did not make sense and illuminated the flaw in the method, namely that the spectral decomposition of the Jacobian fails for (near-)collinear eigenvectors. However, the results for the helium-water model showed less discrepancy when the Jacobian was recreated and also seem to make more sense. These results are given for the full model in figure C.1 and for the reduced model in figure C.2.

What is visible in these figures is that species and timescales are correlated in groups, or blocks, akin to the work shown in [26]. These blocks indicate that timescales represent certain types of processes, both in the original model and in the reduced model. The biggest difference between the full and reduced model is a strong decrease in effect of interactions between vibrational states, which is a trend in all of the models discussed in this thesis as often the vibrational states are the first species to be deactivated.
Figure C.1: The relative presence of a species density in the representation of the timescales of the system. These values are calculated using a spectral decomposition, the timescales are represented by rows in the inverse eigenvector matrix. This row is scaled to relative values compared to the maximum and the logarithm of that value is plotted here. This is the full helium-water chemistry used before in this thesis.
Figure C.2: The relative presence of a species density in the representation of the timescales of the system. These values are calculated using a spectral decomposition, the timescales are represented by rows in the inverse eigenvector matrix. This row is scaled to relative values compared to the maximum and the logarithm of that value is plotted here. This is a reduction of the helium-water chemistry used before in this thesis deactivating 475 reactions and 8 species.