Modelling of plasmas with complex chemistry: application to microwave deposition reactors
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DOI: 10.6100/IR771642
Published: 07/04/2014

Document Version
Publisher’s PDF, also known as Version of Record (includes final page, issue and volume numbers)

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Modelling of Plasmas with Complex Chemistry: Application to Microwave Deposition Reactors

PROEFSCHRIFT

ter verkrijging van de graad van doctor
aan de Technische Universiteit Eindhoven,
op gezag van de rector magnificus, prof.dr.ir. C.J. van Duijn,
voor een commissie aangewezen door het College voor Promoties
in het openbaar te verdedigen
op maandag 7 april 2014 om 16.00 uur

door

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geboren te İskenderun, Turkije
Dit proefschrift is goedgekeurd door de promotoren en de samenstelling van de promotiecommissie is als volgt:

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This research is sponsored by the Technology Foundation STW, The Netherlands, and the company Draka Comteq Fibre.


A catalogue record is available from the Eindhoven University of Technology Library ISBN: 978-90-386-3588-0
NUR 925

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This thesis was prepared with the \LaTeX{} documentation system.
Printed by Eindhoven University of Technology Printservice, Eindhoven.
Cover design by Verspaget & Bruinink.
The lines on the cover represent optical fibres (white), control volumes (light turquoise), microwave field propagation (dark turquoise), and manifolds in density space (blue).
Summary

The main goal of this work is to gain a better understanding of a microwave deposition plasma reactor that is used in the production of optical fibres. The plasma is formed in a mixture of O$_2$ and SiCl$_4$ and features a complex chemical composition: It consists of electrons, atoms, molecules and positively as well as negatively charged atomic and molecular ions. The plasma has been studied using a blend of analytic modelling and numerical simulation. The theoretical and numerical aspects employed in the study are briefly explained and regarding discussions are also provided within the context.

A global model for the spatially averaged quantities of interest has been used to better understand the role of the various species and reaction paths in the plasma volume and to investigate the added value of modulating the plasma power. The model is firstly implemented to a radio-frequency plasma setup fed with Cl$_2$, for which these kind of models are developed and widely employed. Following this, it is implemented to the microwave deposition reactor fed with either pure O$_2$ or O$_2$/SiCl$_4$ admixtures. In order to study and understand the effects of transport on the plasma properties, 2-dimensional models that calculate the spatially resolved plasma properties and the external microwave field self-consistently have been constructed.

In order to reduce the complexity of the plasma chemistry without sacrificing the accuracy of the model, a chemical reduction technique that originates from combustion engineering has been introduced in plasma physics. The method has been compared with the collisional radiative modelling strategies that have traditionally been used in plasma physics.
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Chapter 1

Introduction
Chapter 1. Introduction

1.1 A broader view of plasmas

"Let there be plasma..."

Plasma, known as the fourth-state of matter, is simply an ionised and luminous gas, in which the electromagnetic interactions between the particles play a significant role. The plasma particles show great variety and they are mainly composed of ground state atoms or molecules, various excited levels, radicals, numerous ions and electrons. The source of ionisation are mainly the electronic reactions, whereas the luminosity of the plasma is mostly a consequence of the light emission from the excited levels.

The plasmas can be found in numerous conditions, such as, nebulae and stars in space, and they constitute most of the visible matter in the universe. Beside the stellar presence the ionosphere and lightning are the most known examples of plasmas on earth. In addition to these natural encounters, they also appear in everyday life directly as lighting devices or indirectly by their applications in many technological devices, such as computers, smart phones, optical fibres and auto-mobiles. In laboratories, plasmas are used in many research projects in various fields driven by either scientific curiosity or by a technological goal.

A certain amount of energy is required to ignite and sustain plasmas. This energy is coupled with them in various manners: Nebulae via interstellar radiation, stars via gravitational pressure and nuclear processes, ionosphere via solar radiation and lightning via electrical processes. The laboratory plasmas are induced via electromagnetic energy: direct-current, radio-frequency range alternating-current, microwaves and lasers.

The first and closest observation of a plasma dates back to the early ages of the mankind by the encounter with the lightning and the sun. However, back then, they were magical beings controlled by mythological gods. The first experimental evidence of a laboratory plasma is shown by C. de Coulomb himself, and it is later studied by various famous scientists; V. V. Petrov, M. Faraday, J. J. Thomson, J. S. E. Townsend and N. Tesla. For an early history of the plasma science we refer to a fundamental book by Raizer [1]. Together with the advances in astrophysics and nuclear sciences it is later discovered that the stars are composed of plasma.

"Plasma" (πλασµα) is a greek word for “moldable substance” or “jelly”, that is given by Nobel laureate I. Langmuir [2]. It originates from the jelly like substance that diffuse throughout the glass vacuum chambers of the arc plasmas. Rumour says that popular blues song of 1920s “Must be Jelly ’cause Jam don’t Shake Like That” by J. C. MacGregor and S. Skylar played an effective role on the naming. Furthermore, a different name is also employed for
1.2 Plasma applications

Currently, plasma applications cover many areas from daily-life; lighting, microelectronics and communication technologies to scientific fields at the edge, fusion research and plasma thrusters. They are ignited in lamps to produce artificial light \cite{3} and used in the surface treatment \cite{4}, such as etching and deposition. They are commonly implemented as ion source \cite{5}, in radical formation, such as OH \cite{6} and dust particle growth \cite{7}. Furthermore, they find applications in the medical technology, for example, for the purpose of wound healing and bacteria treatment \cite{8,9}. The main reason that plasmas are applied in numerous fields is the unique environment they provide for various reactions. The environment decouples the chemical activity and the thermal features of the plasma and makes many reactions viable that are not possible otherwise.

Due to their common usage in various technologies, the biggest percentage of the applications belong to the surface treatment. This phenomena is mainly composed of two distinct processes. The first one is known as surface etching that is simply removal of a portion on a substrate surface. The second one is the deposition of a material on the surface. Plasma based etchers are commonly applied in the microelectronics technology. For example, they form one of the main steps in the fabrication of transistors \cite{10}. Similarly, the microelectronics technology uses plasmas for deposition purposes, for example in the production of the thin films. They are also actively implemented in solar cell \cite{11} and optical fibre productions \cite{12} for the same purpose. This type of deposition is generally known as Plasma Enhanced Chemical Vapour Deposition (PECVD) as a generalisation of conventional chemical vapour depositions. The processes specific to the implementation is also called Plasma activated Chemical Vapour Deposition (PCVD), whereas the difference is mostly a matter of nomenclature.

1.3 Microwave induced plasmas for the purpose of optical fibre production

Optical fibres form the backbone of the modern communication networks, which are, in simple terms, waveguide structures that guide the light propagation. These structures are fabricated in three successive steps: (1) deposition, (2) collapsing and (3) drawing. The first step is to deposit (PCVD) the SiO$_2$ molecule on a silica surface with layers of distinct refractive index. The microwave reactor employed for this purpose is depicted in Figure \ref{fig:microwave-reactor}. The deposition surface is the inner wall of a hollow cylindrical quartz tube, where the tube contacts the plasma. The quartz chamber is fed with an admixture of O$_2$/SiCl$_4$ and the deposition molecule SiO$_2$ is formed in the plasma. In the second step, the hollow tube is collapsed by heat and surface tension, hence, a rod of silica tube is obtained that is called the preform of...
Chapter 1. Introduction

Figure 1.1: A sketch of deposition reactor that employs a microwave induced plasma for the purpose of the optical fibre production.

The fibre. In the last step, the preform is hanged on a drawing tower, where heat generated vertical stress converts it to a final form.

The quartz tube is surrounded by a metal cylindrical reactor, that feeds the region with the microwave radiation to sustain the plasma. The electromagnetic waves directed towards the discharge vanish within a distance called the skin depth and at the same time they reshape the particle spatial distributions. Additionally, the interface between the plasma and the quartz creates an alternative direction for the propagation. The electromagnetic wave that propagates on such a surface, where a conductor and a dielectric meets, is known as a surface wave (also called a surface-guided wave [13]). Due to its higher decay length it axially enlarges the plasma by transporting the microwave energy farther.

1.4 Project goals and outline

The project is part of a cluster called Building on Transient Plasmas (BTP) program of the dutch technology foundation STW. It is achieved in close collaboration with Draka Comteq Fibre company of the Prysmian group. The main goal is to investigate the microwave induced plasmas for a better control of the deposition and the optimisation. The influence of the modulated power input forms one of the main focuses of the investigation. In this content, the spatial distribution and its evolutionary features due to power modulation are investigated with a combination of the spatially and time resolved models. The numerical simulations are carried out on modular plasma simulation platform Plasimo [14] developed in the applied physics department of Eindhoven university of technology in Elementary Processes in Gas Discharges group.

An initial investigation of the plasma is carried on with the global (volume-averaged) model that is characterised by light computational load. The model provides the essential stationary
and modulated volume-averaged plasma quantities. For a spatial resolution, we implement a stationary two-dimensional model of the plasma, where the electromagnetic phenomena is self-consistently described. The complex chemistry produces large computational load in the simulations. In order to reduce this load, we introduce and discuss simplification of the chemical kinetics.

A brief discussion of the essential plasma theory and the computational aspects are provided in chapters 2 and 3. A global (volume-averaged) model of a radio-frequency chlorine plasma is incorporated in chapter 4. A global model of the microwave O$_2$/SiCl$_4$ plasma is presented in chapter 5 and chapter 6 contains a two-dimensional model of the microwave O$_2$ plasma. We introduce a chemical reduction technique called **Intrinsic Low Dimensional Manifold** and discuss its applicability on the plasma models in chapter 7. In chapter 8 we present the interrelation of this technique with the **Collisional Radiative Models** of the plasmas. The general conclusions are provided in chapter 9.
Chapter 2

Fluid description of plasmas
Chapter 2. Fluid description

2.1 Introduction

In this chapter we discuss the theoretical and computational aspects of the plasma models employed in this work. The discussion covers the fluid description of the plasma and focuses on the balance equations, whereas the kinetic and stochastic models of the description are left out of the scope. These kind of plasmas can not be described by a single fluid; they require a multi-fluid description. As a consequence, each discussion labels a fluid with a subscript representing the corresponding particles, such as electrons.

The chapter starts with the Boltzmann equation that describes the dynamics of a many particle system characterised as a fluid. The balance equations of a fluid are derived from this canonical equation. We provide general forms of the balance equations employed in this study and for fundamental derivation we refer to fundamental plasma physics books [15]. The collisional processes and plasma conductivity for an alternating field are also provided in the contents. The global (volume-averaged) models rely on the same balance equations with the spatial integration over the plasma volume. At the end of the chapter the global model description is presented with a focus on their derivation from the balance equations.

2.2 Boltzmann equation

From cosmology [16] to subatomic particle physics [17], infinitely many particles are described by the Boltzmann equation. In the description, one collective fluid behaviour is assigned to one type of particles, which is assumed to be a Newtonian fluid, i.e., solidification or granular structure are absent under all circumstances. The fluid state is defined by a distribution function \( f(\vec{x}, \vec{u}, t) \) that is expressed in a 6-dimensional phase space of 3 velocity \( \vec{u} \) and 3 position coordinates \( \vec{x} \), while time \( t \) is a parameter. When multiplied by an infinitesimal phase space volume \( d^3u d^3x \) \( f(\vec{x}, \vec{u}, t) d^3u d^3x \), it represents the number of particles in the volume at time \( t \). The Boltzmann equation defines the time evolution of the distribution function \( f(\vec{x}, \vec{u}, t) \) in this volume [18]. For a non-relativistic fluid labelled by \( i \), it is given in the form

\[
\frac{\partial f_i}{\partial t} + \vec{u}_i \cdot \nabla_x f_i + \frac{\vec{F}_i}{m_i} \cdot \nabla_u f_i = \left( \frac{\partial f_i}{\partial t} \right)_C,
\]

(2.1)

where \( \vec{F}_i \) is a force field, \( m_i \) is the mass of a particle, \( \nabla_x \) the position derivative and \( \nabla_u \) is the velocity derivative. The term \( \left( \frac{\partial f_i}{\partial t} \right)_C \) is the local source due to the collisions with another fluid, which is either elastic and alters the velocity of the fluid or inelastic and creates or destructs particles. The position derivative \( \vec{u} \cdot \nabla_x f_i \) represents the velocity induced net flux over the position walls in the volume. Similarly, the velocity derivative \( \frac{\vec{F}_i}{m_i} \cdot \nabla_u f_i \) is the force induced net flux over the velocity walls.

In a plasma, solving the Boltzmann equation is numerically challenging due to the phase space dimension and it is not always practical. If the force field is known, it is solved with certain simplifications, e.g. the two-term expansion [19] [20]. Furthermore, the plasma may
be composed of multiple fluids, which interact via the particle collisions, and the problem becomes even more challenging. In this respect, its moments are defined and used to describe the fluid instead. They are set of equations and obtained by integrating the Boltzmann equation over the velocity component of the phase space. The number of the moments is generally infinite, however, not all of them are necessary and only the first three moments are taken into account. In this work we solve these moments to describe the plasma and we assume a Maxwellian distribution function to calculate the required coefficients.

## 2.3 Balance equations

The moments are balance equations in the position space and describe the evolution of the macroscopic quantities. These quantities are particle, momentum and energy densities of a particular fluid and they are position space analogues of the distribution function in the phase space.

The 0\textsuperscript{th} moment is called the particle balance equation, which is the continuity equation of the particle density. It is acquired by integrating the Boltzmann equation over the velocity component. The equation for a particle \( i \) is

\[
\frac{\partial n_i}{\partial t} + \vec{\nabla} \cdot \vec{\Gamma}_i = S_i, \tag{2.2}
\]

where \( n_i \) is the number density, \( \vec{\nabla} \) is the position derivative, \( \vec{\Gamma}_i \) is the flux density and \( S_i \) is the net source. The source \( S_i \) incorporates all the chemical reactions that create or destruct the particles. The description of the source is given in section \([2.6]\). The flux density \( \vec{\Gamma}_i \) is defined as

\[
\vec{\Gamma}_i = n_i \vec{\bar{v}}_i, \tag{2.3}
\]

where \( \vec{\bar{v}}_i \) is the average velocity.

The 1\textsuperscript{st} moment is acquired by multiplication with the momentum of the particle \( m_i \vec{u}_i \) and integrating over the velocity. It is known as the momentum balance equation and for a particle \( i \) it is expressed by the relation

\[
\frac{\partial \left( m_i n_i \vec{v}_i \right)}{\partial t} + \vec{\nabla} \cdot \left( m_i n_i \vec{v}_i \vec{v}_i \right) = -\vec{\nabla} p_i + \vec{\nabla} \cdot \vec{\tau}_i + \vec{F}_i + \vec{R}_F^i, \tag{2.4}
\]

where \( p_i \) is the scalar partial pressure, \( \vec{\tau}_i \) is the viscous stress tensor, \( \vec{F}_i \) is the force field and \( \vec{R}_F^i \) is the friction force due to the elastic collisions. The left hand side contains the temporal and inertial terms whereas the right hand side incorporates the source for the momentum density. The viscous stress tensor is specific for the fluid type and is defined in each section and chapter it is used. The gravitational and magnetic forces are neglected in the plasmas associated with this work. The force field is of an electrical nature and is described by the Lorentz force

\[
\vec{F}_i = n_i q_i \vec{E}, \tag{2.5}
\]
where \( q_i \) is the charge and \( \vec{E} \) is the electric field. The friction force \( \vec{R}_i^F \) is defined by a momentum transfer collision frequency \( \nu_{ij} \) between two species \( i \) and \( j \). Introducing the friction coefficient \( f_{ij} = m_{ij} n_i \nu_{ij} \), where \( m_{ij} \) is the reduced mass, this force is expressed as

\[
\vec{R}_i^F = - \sum_j f_{ij} (\vec{v}_i - \vec{v}_j) .
\]  

The 3rd moment is the energy balance equation and it is similarly derived after multiplying with the energy \( \frac{1}{2} m_i u_i^2 \) of the fluid. The energy balance equation for a particle \( i \) is given by the relation

\[
\frac{\partial (n_i \epsilon_i)}{\partial t} + \nabla \cdot (n_i \epsilon_i \vec{v}_i) + p_i \nabla \cdot \vec{v}_i - \tau_i : \nabla \vec{v}_i + \nabla \cdot \vec{q}_i = Q_i ,
\]  

where \( \epsilon_i \) is the mean kinetic energy, \( \tau_i : \nabla \vec{v}_i \) is the viscous dissipation term, \( \vec{q}_i \) is the convective flux and \( Q_i \) is the local energy source. The convective flux is calculated based on the Fourier’s law of thermal conduction

\[
\vec{q}_i = -\lambda_i \nabla T_i ,
\]  

where \( \lambda_i \) is the fluid conductivity and \( T_i \) is the gas temperature. The local energy source incorporates the net energy gained or lost due to the chemical reactions or the elastic collisions. The electromagnetic energy provided to the plasma also couples to the source, for example, ohmic heating of the electrons in a microwave induced plasma. The explicit form of the source is specific to the particles and discussed in sections 2.5 and 2.6.

In this work, particle densities and velocities are determined from the particle and the momentum balance equations, respectively. The temperature of a fluid is computed from the energy balance equation. In the calculation of the velocity, the momentum balance equations are either simplified or converted. In the next section, we present the velocity calculation in the spatially-resolved model of the thesis. The velocity is not calculated in the global models (see section 2.8).

### 2.4 Particle flux

In the spatially resolved models with a net mass flow, the particle velocity is split into two distinct parts. Each part of the velocity is described with a different implementation of the momentum balance equation 2.4

\[
\vec{v}_i = \vec{v}_b + \vec{v}_{d,i} ,
\]  

where \( \vec{v}_b \) is the bulk velocity due to the barycentric motion of the plasma and \( \vec{v}_{d,i} \) is the diffusive velocity caused by the particle interactions. The bulk velocity is created by the collective dynamics of all distinct particles as a single fluid, which we call bulk motion. The diffusive velocity of each fluid is defined distinctively for the neutral and the charged particles due to the electromagnetic interactions. The calculation of these velocities are discussed in the following sections.
2.4. Particle flux

2.4.1 Bulk motion

The collective bulk motion is governed by the mass balance and the Navier-Stokes equation, which describe the whole plasma as a single fluid. These equations correspond to the first two moments of the Boltzmann equation. The mass balance equation is the mass analogue of the particle balance equation and describes the mass continuity. The Navier-Stokes equation corresponds to the momentum balance equation and relates to the net momentum continuity. The difference in the nomenclature is due to historical reasons, i.e., the theory of the fluid dynamics was developed earlier than the Boltzmann equations and the moments.

The equations are determined by summing the mass-weighted particle balance and the momentum balance equation of each species. The mass balance equation is given by the expression

\[ \frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \vec{v}_b) = 0, \]  

where \( \rho = \sum_j m_j n_j \) is the total mass density. Since the reactions conserve total mass, the net source disappears with the summation. Assuming a laminar flow of the gas, the Navier-Stokes equation is

\[ \frac{\partial (\rho \vec{v}_b)}{\partial t} + \nabla \cdot (\rho \vec{v}_b \vec{v}_b) = -\nabla p + \nabla \cdot \vec{\tau}, \]  

where \( p \) is the total pressure and \( \vec{\tau} \) is the viscous tensor. The friction losses disappear due to the momentum conservation in the collisions, while the net Lorentz force vanishes because of the plasma quasi-neutrality. The viscous stress tensor for a Newtonian fluid is given by the relation

\[ \tau_{ij} = 2 \mu \left( \Gamma_{ij} - \frac{1}{3} (\nabla \vec{v}_b) \right). \]  

2.4.2 Diffusive velocity

In order to calculate the diffusive velocity, the momentum balance equation (2.13) is not directly solved but initially reduced to a simpler form. Under the assumption that the temporal, inertial and viscosity terms are negligible the momentum balance equation reduces to

\[ -\nabla p_i + q_i n_i \vec{E} + \vec{R}_i^F = 0. \]  

This form of the equation can be solved based on two major approaches in the plasma models: Drift-diffusion [21, 22] and self-consistent diffusion [23] formulations. The former is mostly valid for a dominant background gas, whereas the latter does not possess such a limitation.

An effective diffusive velocity of a neutral particle \( i \) is given by the relation

\[ n_i \vec{v}_{d,i} = D_i \nabla n_i, \]  

where \( D_i \) is the diffusion coefficient [24]. It is based on the Fick formulation, which originates from the spatial inhomogeneity of the particle density in a gas [25].
On the other hand, the ambipolar electric field between the charged particles disturbs such a formulation and requires a distinct approach. Based on a self-consistent diffusion formulation Hartgers et al. [23] derived a simpler diffusion expression for the positive ions called multiple ion Fick-like diffusion. In the derivation, firstly, it is assumed that all the ions in the plasma are singly charged. Furthermore, the electrons differ from the ions by their pace: They possess significantly higher mobility and larger diffusion compared to all other charged particles. Under these assumptions the multiple ion Fick-like diffusion for a positive ion \( i \) is

\[
n_i \vec{v}_{d,i} = -n_i D_i \frac{T_e}{T_i} \vec{\nabla} n_e - D_i \vec{\nabla} n_i. \tag{2.15}
\]

Test cases on electropositive Ar/Hg plasmas show that such flux agrees well with the self-consistent diffusion formulation. Moreover, the relation is valid regardless of the negative ion presence in the plasma. A derivation of the expression from the drift-diffusion formulation is given in appendix 2.B.

In order to simplify the diffusion expression (2.15), we assume that a positive ion \( i \) satisfies

\[
\frac{\vec{\nabla} n_i}{n_i} \approx \frac{\vec{\nabla} n_e}{n_e}. \tag{2.16}
\]

The relation (2.16) reduces the multiple ion Fick-like diffusion of a positive ion \( i \) to the form

\[
n_i \vec{v}_{d,i} \approx - \left( 1 + \frac{T_e}{T_i} \right) D_i \vec{\nabla} n_i. \tag{2.17}
\]

In this work, the diffusive velocity expression (2.17) is employed in the spatially resolved model. However, the relation (2.16) does not rely on a solid theory but rather on an observation. In this respect, if an exact diffusion formulation is available, it should be preferred instead. In the model, we neglect the role of the ambipolar electric field on the negative ions and regarding discussion is provided at the end of appendix 2.B.

### 2.5 Ohm’s law: Conductivity for microwave induced plasmas

In this section, we derive the plasma conductivity for an alternating electric field based on the electron momentum balance equation. We firstly assume that the plasma is a nonmagnetic, linear medium and that the electric field is harmonic in time with a small amplitude and a frequency \( \omega \):

\[
\tilde{E} = \text{Re} \left( \tilde{E} e^{i\omega t} \right), \tag{2.18}
\]

where \( \tilde{E} \) is the amplitude.

The flux of a species \( \tilde{\Gamma}_i \) is by definition coupled with its current density \( \tilde{J}_i = q_i \tilde{\Gamma}_i \). In this respect, the momentum balance equation also describes the relation with the current density and the electric field, that is commonly known as Ohm’s law. Due to their large mobility the
2.5. Ohm’s law

Electrons respond quickly and dominantly to any alternating field. In other words, we assume that the electron flux dominates the net current $J$:

$$\vec{J}_e \approx \vec{J} = \sum_i \vec{J}_i.$$  \hfill (2.19)

As a consequence, we are interested in the electron flux in particular. Similar to previous sections we assume that inertial and viscous terms are negligible in the electron momentum balance equation (2.4). In order to investigate the role of the time dependent electric field we keep the temporal term. Furthermore, we assume the cold plasma approximation: $p_e = 0$. With these assumptions the electron momentum balance equation (2.4) is written as

$$m_e n_e \frac{\partial \vec{v}_e}{\partial t} = -e n_e \vec{E} + \vec{R}_e^F$$  \hfill (2.20)

The reduced mass for an electronic collision approximately equals to the electron mass due to its significantly lower value. Additionally, defining an effective momentum transfer frequency $\nu_{eh} = \sum_j \nu_{ej}$, the friction force for the electrons reduces to

$$\vec{R}_e^F = -m_e n_e \nu_{eh} \vec{v}_e.$$  \hfill (2.21)

Furthermore, we assume that the velocity and the current density have the same time dependence

$$\vec{v}_e = \text{Re}(\vec{v}_e e^{i\omega t}), \quad \text{and} \quad \vec{J} = \text{Re}(\vec{J} e^{i\omega t}),$$  \hfill (2.22)

so that the electron current density satisfies

$$\vec{J} = -e \vec{v}_e = -en_e \vec{v}_e.$$  \hfill (2.23)

Equation (2.20) provides the velocity in terms of the electric field

$$\vec{v}_e = -\frac{e}{m_e (\nu_{eh} + i\omega)} \vec{E}.$$  \hfill (2.24)

Putting this expression into equation (2.23) we acquire

$$\vec{J} = \hat{\sigma} \vec{E},$$  \hfill (2.25)

where the conductivity is defined as

$$\hat{\sigma} = \frac{e^2 n_e}{m_e \nu_{eh} + i\omega}.$$  \hfill (2.26)

Using the electron plasma frequency $\omega_p = e^2 n_e/\varepsilon_0 m_e$, it can be written in a more compact form

$$\hat{\sigma} = \frac{\varepsilon_0 \omega_p^2}{\nu_{eh} + i\omega}.$$  \hfill (2.27)

In case the field frequency is negligibly small compared to the plasma and momentum transfer collision frequencies ($\omega \ll \omega_p$ and $\omega \ll \nu_{eh}$), the expression turns into the time-independent (DC) conductivity. According to this, the ohmic energy source for the electrons due to the electromagnetic fields is given by the relation

$$Q_{\text{Ohm}} = \frac{1}{2} \text{Re}(\hat{\sigma}) |\vec{E}|^2.$$  \hfill (2.28)
Chapter 2. Fluid description

2.6 Collisional processes

The collisions define the right hand side of the Boltzmann equation \( \text{(2.1)} \) and they are incorporated as a source in all the balance equations. There are two types of collisions, each is of a distinct nature: Elastic and inelastic. The elastic collisions only alter the energy and momentum of the particles whereas the inelastic ones also destruct and create particles. The latter are also associated with chemical reactions since they modify the internal structure of particles. In this section we discuss these sources and the reaction rates of electronic collisions, for which the collision rates are calculated from the electron energy distribution function. For the sake of simplicity we only show the velocity dependency of the distribution function \( f_e(|\vec{u}_e|) \), where \(|\vec{u}_e|\) is the modulus of the electron velocity. We assume that it is a Maxwellian electron energy distribution function given by the relation

\[
f_e(|\vec{u}_e|) = \frac{2\pi}{(\pi k_B T_e)^{3/2}} \sqrt{\frac{1}{2m_e|\vec{u}_e|^2}} \exp\left(-\frac{m_e|\vec{u}_e|^2}{2k_B T_e}\right), \tag{2.29}\]

In general, the rate of a chemical reaction labelled by \( j \) is given by the relation

\[
R^j = k_j \prod_j n_j^{\nu_{jj}^l}, \tag{2.30}\]

where \( l \) represents the reactant, \( \nu_{jj} \) is the stoichiometric coefficient and \( k_j \) is the rate coefficient. In the particle balances the source is defined by

\[
S_i = \sum_j \nu_{ij} R^j. \tag{2.31}\]

The reaction is described by the net amount of energy absorbed or emitted \( \epsilon_j \), and the energy source is expressed by

\[
Q_i = \sum_j \epsilon_j R^j. \tag{2.32}\]

For an electronic collision, which includes an electron as a reactant, the rate coefficient is

\[
k_{ej} = \int_{\epsilon_j}^{\infty} \sigma_{ej}(|\vec{u}_e|)|\vec{u}_e|f_e(|\vec{u}_e|)d^3u_e, \tag{2.33}\]

where \( \sigma_{ej} \) is the cross-section of the reaction.

The energy loss via an elastic collision of an electron with a heavy particle \( l \) is

\[
Q^l_{Ela} = 3k_B(T_e - T_l)n_e n_l k_{el} \frac{2m_e}{m_l}, \tag{2.34}\]

where \( k_{el}(T_e) \) represents the rate coefficient of collision and \( m \) represents the mass. If the electron temperature is significantly larger than the heavy particle’s this reduces to

\[
Q^l_{Ela} = 3k_B T_e \frac{m_e}{m_l} n_e n_l k_{el} \tag{2.35}\]
2.7. Numerical approach: Spatial discretisation

Assuming that the plasma has settled to a steady-state and temporal variations disappear, we solve the balance equations of a 2-D model with the condition:

$$\frac{\partial}{\partial t} = 0.$$  \hfill (2.37)

Furthermore, an important property of all the equations is the fact that they can be written in a canonical form, which simplifies implementation of the discretisation. This form is called \(\phi\) equation and we refer to [5] for detailed discussion. A simple \(\phi\) equation is given in the form

$$\vec{\nabla} \cdot \vec{\Gamma}_\phi = S_\phi,$$  \hfill (2.38)

where \(\vec{\Gamma}_\phi\) in general is divided into diffusive and convective parts

$$\vec{\Gamma}_\phi = f_\phi \rho \vec{v}_\phi \phi - \lambda_\phi \vec{\nabla} \phi.$$  \hfill (2.39)

The \(\phi\) equation is discretised using the control volume technique, which is based on the spatial integration in each grid cell called control volume [25]. Such a formulation combined with the divergence theorem [29], allows a smart positioning of the quantities: \(\phi\) and \(S_\phi\) values are placed at the centre and fluxes \(\vec{\Gamma}_\phi\) are calculated at the cell walls (see Figure 2.1). As a result, any extra computational load due to extrapolation is removed. As a caveat, in the discretisation, the type of the orthogonal coordinate system plays an effective role. In this respect, the discretised equations differ, for example, from spherical to cylindrical coordinates. In Plasimo, a general ortho-curvilinear description is used in order to simplify their implementation [5]. In the control volume technique, finite differences provide the discretised derivatives [30].
2.8 Global (volume-averaged) models

The balance equations are derived from the Boltzmann transport equation by integration over the velocity component. The global model equations are acquired by further integration of them over the position coordinates \[^{31}\], where the limits of the integration are determined by the constant plasma volume \(V\). Therefore, these models deal with the volume-averaged plasma quantities. They have less computational load than spatially resolved models and relatively simple implementations, yet they also suffer from certain limitations.

The transport terms in these equations are defined by the divergence of the particle flux. Combining such a term with the Gauss’s theorem of the integration \[^{29}\], the transport inside the volume is not important, but only matters at the plasma boundary. Compared to the spatially resolved models, such a formulation removes the necessity of spatial discretisation and hence simplifies the numerical implementation. Furthermore, the computational load due to the discretisation is eliminated in the simulations and the results are easily accessible.

Beside the aforementioned benefits of the implementation, global models also show certain disadvantages due to the same formulation. Firstly, they are only capable of determining the volume-averaged plasma quantities without spatial resolution. Secondly, they assume that the plasma is spatially homogeneous inside the volume and in case that there are strong deviations from homogeneity, the model validity expires. Additionally, a quantitative measure of the homogeneity assumption is absent. Finally, a self-consistent derivation of the transport at the plasma boundary is not available in the model. This transport is effectively defined with a preliminary study, which in general contains an analytic model.

In the following sections, we derive the Global (volume-averaged) model equations from the balance equations. In the derivation, we consider a two-temperature description of the plasma, i.e., all heavy particles are in thermal equilibrium with same temperature \(T_h\) and electrons deviate from this equilibrium with a distinct temperature \(T_e\). We further assume that the density of a particle \(n_i\), the electron temperature and the heavy particle temperature are spatially homogeneous:

\[
\begin{align*}
n_i & \approx \frac{1}{V} \int_V n_i \, d^3x, \\
T_e & \approx \frac{1}{V} \int_V T_e \, d^3x, \\
T_h & \approx \frac{1}{V} \int_V T_h \, d^3x,
\end{align*}
\]

and that the power is uniformly absorbed within the volume. Additionally, the plasma volume \(V\) is assumed to be constant in time within the time-scale considered in the model.

Since the volume transport is not important, the momentum balances are irrelevant in the physical model. Furthermore, due to their high mobility, the electrons are agents that absorb any input power and distribute it to the rest of the plasma. As a result, the particle balance equations and the electron energy balance equations are treated in the model. The particle balances compute the particle densities whereas the electron energy balance determines the
2.8. Global (volume-averaged) models

electron temperature. The heavy particle temperature is externally provided to the model. The electron density is computed from the quasi-neutrality assumption instead. We define the volume-averaged quantities according to the integration and simplify the form of the equations. In order to differentiate the volume-averaged quantities with the spatially resolved ones, capital letters are used. The temperature and the rate coefficients are exceptions to this, for them we employ the same letter under the the spatial homogeneity assumption.

2.8.1 Particle balance equation

The volume-averaged particle balance equation is given by the expression

\[
\frac{1}{V} \int_V \frac{\partial n_i}{\partial t} d^3 x = -\frac{1}{V} \int_V \nabla \cdot \mathbf{\vec{\Gamma}}_i d^3 x + \frac{1}{V} \int_V S_i d^3 x, \quad (2.40)
\]

where \( V \) is the constant volume of integration, \( n_i \) is the density, \( \mathbf{\vec{\Gamma}}_i = n_i \mathbf{\vec{v}}_i \) is the flux vector and \( S_i \) is the source of the species \( i \).

We firstly introduce an average density of the particle \( i \)

\[
N_i = \frac{1}{V} \int_V n_i d^3 x. \quad (2.41)
\]

Under the assumption that the particle flux is uniform (or piecewise uniform) the transport term and the Gauss’s theorem define a wall source

\[
S_i^W = \frac{1}{V} \int_V \nabla \cdot \mathbf{\vec{\Gamma}}_i d^3 x = \frac{\mathbf{\vec{A}}}{V} \cdot n_i \mathbf{\vec{v}}_i \bigg|_W, \quad (2.42)
\]

where \( |_W \) represents its value at the wall and \( \mathbf{\vec{A}} \) is the plasma surface area vector directing outwards. This represents the losses via the particle flux and wall reactions and its nature generally depends on the particle type \( i \) such as neutrals and ions. The velocity is also divided into mass flow and diffusion velocities. For a detailed description we refer to chapter \( \text{I} \).

The source \( S_i \) is a summation of the reaction rates

\[
R^i = k_j(T_e, T_h) \prod_l n_l^{\nu_{ij}}, \quad (2.43)
\]

where \( j \) represents the reaction. Whether the particle \( i \) is the product or the reactant in the reaction determines the sign of the rate. The rate coefficients depend on either the electron temperature or the gas temperature. In this respect, the source depends on various densities and the rate coefficients and we define the dependencies, which are denoted by the parentheses, in the following

\[
S_i = S_i(k_j(T_e, T_h), n_L), \quad (2.44)
\]

where \( J \) represents these reactions and \( L \) is all involved species. Under the assumption that they are spatially uniform the rate satisfies

\[
k_j(T_e, T_h) \prod_l N_l^{\nu_{ij}} = \frac{1}{V} \int_V k_j(T_e, T_h) \prod_l n_l^{\nu_{ij}} d^3 x, \quad (2.45)
\]
where the same notations are used for the volume-averaged rate coefficients and the temperatures. Keeping this in mind, we define an average volume source

\[ S_V^V = \frac{1}{V} \int_V S_i d^3x = S_i^V (k_J(T_e, T_h), N_L), \quad (2.46) \]

which is now a function of the volume-averaged densities \( N_L \) and the rate coefficients. With these quantities, the volume-averaged particle balance equation reduces to a compact form

\[ \frac{\partial N_i}{\partial t} = -S_W^i + S_V^i \quad (2.47) \]

where the volume \( V \) does not change in time.

### 2.8.2 Electron energy balance equation

Similarly, the volume-averaged electron energy balance equation is

\[ \frac{1}{V} \int_V \frac{\partial (n_e \epsilon_e)}{\partial t} d^3x = -\frac{1}{V} \int_V \nabla \cdot \vec{q}_e d^3x - \frac{1}{V} \int_V \nabla \cdot (\epsilon_e \vec{\Gamma}_e) d^3x + \frac{1}{V} \int_V Q_e d^3x \quad (2.48) \]

where \( \epsilon_e \) is thermal energy, \( \vec{q}_e \) is the conductive heat flux, \( \vec{\Gamma}_e \) is the electron flux term and \( Q_e \) is the local energy source of the electrons. The viscous dissipation of energy for electrons is neglected.

Thermal energy of electrons is \( \epsilon_e = \frac{3}{2} k_B T_e \), where \( k_B \) is the Boltzmann constant. Then the average energy density is defined by the relation

\[ \frac{3}{2} N_e k_B T_e = \frac{1}{V} \int_V n_e \epsilon_e d^3x \quad (2.49) \]

Assuming Fourier’s law for conductive heat flux, \( \vec{q}_e = -\lambda_e \vec{\nabla} T_e \) the corresponding volume-averaged term vanishes due to spatial homogeneity

\[ \frac{1}{V} \int_V \nabla \cdot \vec{q}_e d^3x = -\lambda_e \frac{\vec{A}}{V} \cdot \vec{\nabla} T_e \bigg|_W \approx 0. \quad (2.50) \]

The wall energy source term is only defined by the electron flux at the plasma boundary

\[ Q_e^W = \epsilon_e \frac{\vec{A}}{V} \cdot \vec{\Gamma}_e \bigg|_W. \quad (2.51) \]

At the plasma boundary, net current is zero and hence the electron flux at the wall is determined from the total ion flux

\[ \vec{\Gamma}_e \bigg|_W = \sum_{i \in \text{ions}} \frac{\vec{q}_e}{e} \bigg|_W \cdot \vec{\Gamma}_i \bigg|_W. \quad (2.52) \]
The positive ions are accelerated towards the wall due to the potential drop at the plasma edge, i.e., plasma and sheath potentials. The related energy losses are also included inside the wall flux term.

The local source includes the electromagnetic power absorbed \( Q_I \) and the inelastic or elastic energy losses \( Q_R \)

\[
Q_e = Q_I + Q_R. \tag{2.53}
\]

\( Q_I \) is responsible for the coupling between the power introduced to the volume and the plasma. The power input does not always match the power absorbed due to the energy losses to the environment and a scale is necessary to determine their relation. Similar to \( S_i \), \( Q_R \) depends on various elastic collision or reaction rate coefficients (see section 2.6) and the reactant densities. Generally, it is a function of the electron and heavy particle temperatures due to the rate coefficients. We define the dependencies by the parentheses in the following

\[
Q_R = Q_R(k_J(T_e, T_h), k_{el}^J(T_e), n_L), \tag{2.54}
\]

where \( J \) represents all relevant reactions or inelastic collisions and \( L \) represents the reactant densities. As a result of the integration, this term satisfies

\[
Q_R^V = \frac{1}{V} \int_V Q_R d^3x = Q_R^V(k_J(T_e, T_h), n_L). \tag{2.55}
\]

The volume integrated electron energy balance equation is then

\[
\frac{\partial}{\partial t} \left( \frac{3}{2} N_e k_B T_e \right) = -Q_e^W + Q_I^V + Q_R^V, \tag{2.56}
\]

where \( Q_e^W \) represents the energy losses due to transport to the wall, \( Q_I^V \) is the power absorbed, and \( Q_R^V \) is all the volume source.

### 2.8.3 Numerical approach

In the numerical implementation, we firstly put the set of equations into a matrix form. We define a column matrix \( \mathbf{N} \) that includes the particle densities and the electron energy density. Similarly, a source matrix \( \mathbf{S} \) incorporates the source terms for these densities in the order

\[
\mathbf{N} = \begin{pmatrix}
N_1 \\
N_2 \\
\vdots \\
N_Z \\
3/2N_e k_B T_e
\end{pmatrix}, \quad \mathbf{S} = \begin{pmatrix}
-S_1^W + S_1^V \\
-S_2^W + S_2^V \\
\vdots \\
-S_Z^W + S_Z^V \\
-Q_e^W + Q_I^V + Q_R^V
\end{pmatrix},
\]

where \( Z \) is the number of the particle balance equations. Within the matrix notation, the set of ordinary differential equations (ODE) can be written as

\[
\frac{\partial \mathbf{N}}{\partial t} = \mathbf{S}. \tag{2.57}
\]
For a given initial value $N(t_0)$, the set is solved iteratively with a time-step $\delta t$ until a final time $T$ is reached. We set $T$ large enough for steady state solutions, i.e., the solution does not change in time.

Such a set of equations is split into two types as stiff and non-stiff ODEs based on their numerical characteristics [30]. The non-stiff equations are solved with explicit methods, whereas for stiff problems implicit methods are used. Both methods determine a maximum time-step based on the convergence and/or stability criteria. The stiff problems possess a maximum time-step that is significantly smaller than the non-stiff type. Hence, implicit methods are excessive in computational load and demand more time for the simulation. The classification of the problems are simple for the linear problems. On the other hand, the stiffness of the problem is a dynamic quantity and can change at each iteration due to nonlinearity.

Numerous solvers are developed to deal with such a set of equations [32] that is usually specific to the problem. A first type of ODE solver to be employed is called Livermore Solver for Ordinary Differential equations, with Automatic method switching (LSODA) [33, 34]. This solver classifies the problem based on the previous reference points and chooses the optimum algorithm based on the maximum time-step. Hence, the solver automatically switches between explicit and implicit methods and speeds up the computation, whenever possible.

If there are abrupt changes, for example the power input is switched off, LSODA may use too large time-steps and lead to divergence. One way to handle such a problem is to define these points, then reset the solver, and force it to use the stiff solver if necessary. Another way is simply employing an explicit method, if the computational load is reasonable.

### 2.8.4 Discussion

According to the derivation above, if the spatial homogeneity is strongly breached, the profiles cause deviations in the expressions (2.45, 2.46, 2.55, 2.50). In general, the charged particle spatial profiles, such as parabolic and Bessel-like, are almost homogeneous and acceptable, whereas wavy patterns of these profiles can also be tolerable under a homogeneity definition. The profiles generally drop in the order of $0.1\%$ near the wall, and in case such a drop is bound by a small region, the deviations from the homogeneity can be neglected. Furthermore, in order to define the limits of the validity, a general quantitative measure of the spatial homogeneity is necessary. Unfortunately, the global model studies are phenomenological and such a universal validity measure is impossible. They are still in the development and various studies appear in literature [35, 36, 37]. Moreover, an effective transport description is also a source of deviation in the model. Combining this with the role of spatial inhomogeneity, global models are expected to be correct in scale and a perfect agreement with any experimental data is out of the scope.
Appendix

In section 2.A, we provide the drift-diffusion formulation and define the ambipolar diffusion for a single ion plasma. Based on the drift-diffusion formulation, the multiple ion Fick-like diffusion expression (2.15) is derived in section 2.B. The role of the ambipolar electric field on the negative ions is also discussed at the end of this section.

2.A  Drift-diffusion formulation

An effective collision frequency with the dominant gas $\nu_0$ labelled by the subscript 0 simplifies the friction force. Together with the ideal gas law for an isothermal plasma the equation (2.13) reduces to the form

$$n_i \vec{v}_{d,i} = n_i \mu_i \vec{E} - D_i \nabla n_i,$$

(2.58)

where $\mu_i$ is the mobility and $D_i$ is the diffusion coefficients. They are defined by the relations

$$\mu_i = \frac{q_i}{m_0 \nu_0}$$

and

$$D_i = \frac{k_B T_i}{m_0 \nu_0},$$

(2.59)

where $k_B$ is the Boltzmann constant and are coupled to each other by the Einstein relation

$$\frac{D_i}{\mu_i} = \frac{k_B T_i}{q_i}.$$

(2.60)

The equation (2.58) forms the drift-diffusion formulation, where the first term is the drift due to the electric field and the second term is the diffusion.

2.A.1 Ambipolar diffusion

Consider a plasma that contains one type of ion, which is positively charged. The negatively charged electron and the ion are attracted by an electrical field known as the ambipolar electric field. The field couples the electron and the ion to each other and alters their diffusive velocities. The coupling simply makes the electron and ion diffusive fluxes equal by decreasing the former and increasing the latter.

The ambipolar electric field is derived from zero net current of the charged particles [27, 15]

$$\frac{1}{|q_e|} \sum_i q_i n_i \vec{v}_{d,i} = 0,$$

(2.61)

which also assures the quasi-neutrality of the plasma. This condition defines a unique ambipolar electric field

$$\vec{E} = \frac{|q_e| \sum_i q_i D_i \nabla n_i}{\sum_i q_i^2 \mu_i n_i}.$$

(2.62)
For a plasma composed of one ion, the quasi-neutrality defines equal charged densities $n_e = n_+$. and the ambipolar electric field is given by the relation

$$\vec{E} = \frac{D_+ - D_e}{\mu_+ + \mu_e} \vec{\nabla} n_e.$$  

(2.63)

Such a field sets a common diffusive flux and the ion and the electron fluxes reduce to

$$\vec{v}_d,i = -D_{ai} \vec{\nabla} n_e$$  

(2.64)

where $i$ represents either the ion or the electron and $D_{ai}$ is the ambipolar diffusion coefficient

$$D_{ai} = \frac{\mu_+ D_e + \mu_e D_+}{\mu_+ + \mu_e}.$$  

(2.65)

The mobility of the electrons is much higher than of the ions, hence, the coefficient can be simplified by the approximate expression

$$D_{ai} \approx D_i \left(1 + \frac{T_e}{T_i}\right).$$  

(2.66)

### 2.B Multiple ion Fick-like diffusion: Derivation from the ambipolar electric field

The multiple ion Fick-like diffusion (equation (2.15)) is derived in the self-consistent diffusion formulation for singly charged positive ions denoted by $j$  

$$n_j \vec{v}_{d,j} = -n_j D_j \frac{T_e}{T_j} \vec{\nabla} n_e - D_j \vec{\nabla} n_j,$$  

(2.67)

where we changed the subscript for the sake of clarity. In this section we also derive this expression under the same assumptions, within the drift-diffusion formulation. In this formulation the diffusive flux of a charged particle $i$ is expressed by the equation (2.58). For the sake of simplicity we introduce a charge factor $z_i = q_i / |q_e|$ so that the ambipolar electric field equation (2.62) takes the form

$$\vec{E} = \frac{\sum_i z_i D_i \vec{\nabla} n_i}{\sum_i z_i^2 \mu_i n_i}.$$  

(2.68)

We consider a plasma where all the charged particles are singly charged, i.e., $|z_i| = 1$. Furthermore, we assume that the electron mobility satisfies:

$$\frac{\mu_e}{\mu_i \neq e} \gg 1,$$  

(2.69)

and hence the electron diffusion coefficients

$$\frac{D_e}{D_{i \neq e}} \gg 1$$  

(2.70)
due to the Einstein relation (2.60). Additionally, the quasi-neutrality assumption provides the electron density $n_e$ in the derivation

$$n_e = \sum_{i \neq e} z_i n_i.$$  \hfill (2.71)

### 2.B.1 Derivation

In order to simplify the expression we take the denominator in the ambipolar electric field (2.68)

$$T = \sum_i z_i^2 \mu_i n_i.$$  \hfill (2.68)

Firstly, we put the electron outside of the sum, then $T$ is

$$T = \sum_{i \neq e} z_i^2 \mu_i n_i + \mu_e n_e.$$  \hfill (2.68)

Using the quasi-neutrality assumption (equation (2.71)) this becomes

$$T = \sum_{i \neq e} z_i^2 \mu_i n_i + \mu_e \sum_{i \neq e} z_i n_i.$$  \hfill (2.68)

We now partition the sums with the value of charge number $z_i$ and put this value into the sums

$$T = \sum_{i \neq e, z_i < 0} \mu_i n_i + \sum_{i \neq e, z_i > 0} \mu_i n_i - \sum_{i \neq e, z_i < 0} \mu_e n_i + \sum_{i \neq e, z_i > 0} \mu_e n_i.$$  \hfill (2.68)

Rearranging this we have

$$T = \sum_{i \neq e, z_i < 0} \mu_i n_i - \sum_{i \neq e, z_i > 0} \mu_e n_i + \sum_{i \neq e, z_i > 0} \mu_i n_i + \sum_{i \neq e, z_i > 0} \mu_e n_i.$$  \hfill (2.68)

Taking common parentheses of $\mu_e$ for all and $n_i$ sums respecting $z_i$ values we have

$$T = \mu_e \left[ \sum_{i \neq e, z_i < 0} \left( \frac{\mu_i}{\mu_e} - 1 \right) n_i + \sum_{i \neq e, z_i > 0} \left( \frac{\mu_i}{\mu_e} + 1 \right) n_i \right],$$

where the summation is partitioned onto only ions and separate for the negative and the positive ions. Using the mobility assumption (equation (2.69)) this becomes

$$T \approx \mu_e \left[ \sum_{i \neq e, z_i < 0} (-1) n_i + \sum_{i \neq e, z_i > 0} (+1) n_i \right].$$

By replacing the $(-1)$ and $(+1)$ terms with $z_i$ we get

$$T \approx \mu_e \sum_{i \neq e} z_i n_i.$$
Together with the quasi-neutrality assumption (equation \((2.71)\)) this can be written as
\[
T \approx \mu_e n_e. \tag{2.72}
\]

Now we will look at the numerator of equation \((2.68)\)
\[
A = \sum_i z_i D_i \vec{\nabla} n_i.
\]

Again taking the electrons outside the sum gives
\[
A = \sum_{i \neq e} z_i D_i \vec{\nabla} n_i - \sum_{i \neq e} D_e z_i \vec{\nabla} n_i,
\]
and using the quasi-neutrality assumption this becomes
\[
A = \sum_{i \neq e} z_i D_i \vec{\nabla} n_i - \sum_{i \neq e} D_e z_i \vec{\nabla} n_i,
\]
where we used the fact that gradient of the densities commute with the sum
\[
\vec{\nabla} n_e = \sum_{i \neq e} \vec{\nabla} n_i.
\]

Again we partition the sums with the value of charge number \(z_i\) and put this value into the sums
\[
A = \sum_{i \neq e} \left[ (-1) D_i \vec{\nabla} n_i - D_e z_i \vec{\nabla} n_i \right] - \sum_{i \neq e} D_e z_i \vec{\nabla} n_i,
\]
Rearranging this gives
\[
A = \sum_{i \neq e, z_i < 0} (-1) D_i \vec{\nabla} n_i + \sum_{i \neq e, z_i > 0} D_i \vec{\nabla} n_i - \sum_{i \neq e, z_i < 0} D_e (-1) \vec{\nabla} n_i - \sum_{i \neq e, z_i > 0} D_e \vec{\nabla} n_i,
\]
and taking the common parentheses of \(-D_e\) for all and \(\vec{\nabla} n_i\) sums respecting \(z_i\) values we have
\[
A = -D_e \left[ \sum_{i \neq e, z_i < 0} (-1) \left( 1 - \frac{D_i}{D_e} \right) \vec{\nabla} n_i + \sum_{i \neq e, z_i > 0} (+1) \left( 1 - \frac{D_i}{D_e} \right) \vec{\nabla} n_i \right].
\]
Using diffusion coefficient assumption (equation \((2.70)\)) this expression becomes
\[
A \approx -D_e \left[ \sum_{i \neq e, z_i < 0} (-1) \vec{\nabla} n_i + \sum_{i \neq e, z_i > 0} (+1) \vec{\nabla} n_i \right].
\]
Again, putting \(z_i\) values for the \((-1),(1)\) inside the sums again and combining the sums we have
\[
A \approx -D_e \sum_{i \neq e} z_i \vec{\nabla} n_i.
\]
Using the quasi-neutrality assumption (equation (2.71)) this reduces to
\[ A \approx -D_e \vec{\nabla} n_e. \] (2.73)

Putting equations (2.72) and (2.73) back into the ambipolar electric field (2.68) we get
\[ \vec{E} \approx z_i - D_e \frac{\vec{\nabla} n_e}{\mu_e n_e}. \] (2.74)

Using this relation in equation (2.58) and employing the Einstein relation (2.60) the diffusive flux of a charged particle \( i \) is given by
\[ n_i \vec{v}_{d,i} = -z_i n_i D_i \frac{T_i}{T_e} \frac{\vec{\nabla} n_e}{n_e} - D_i \vec{\nabla} n_i. \] (2.75)

If the charged particle \( i \) is a positive ion, this expression is identical to equation (2.67) and it is a consequence of the ambipolar electric field under the same assumptions. For a plasma containing only one positive ion and one electron, this reduces to the well known ambipolar diffusion equation (2.66).

2.B.2  Negative ions

According to the derivation above, the negative ions can also be described by expression (2.75). Furthermore, the derivation by Hartgers et al. [23] can also be extended to contain the negative ions that leads the same expression as (2.75). However, the negative ion case is not compared with a self-consistent diffusion formulation. Furthermore, we observe that the model presented in chapter (6) is numerically unstable for a negative ion density assumption \( \vec{\nabla} n_i/n_i \approx \vec{\nabla} n_e/n_e \) (see equation (2.16)). Additionally, Lichtenberg et al. [38] defines a different proportionality constant for the negative ions instead of the assumption made here. It is based on the Boltzmann equilibrium between the electrons and the negative ions
\[ \frac{\vec{\nabla} n_i}{n_i} \approx \frac{T_i}{T_e} \frac{\vec{\nabla} n_e}{n_e} \] (2.76)
and its validity is discussed by Bogdanov et al. [39]. As a consequence of the relation (2.76), the negative ion ambipolar diffusion coefficient completely vanishes according to the multiple ion Fick-like diffusion. An analysis of this situation for the negative ions is still under investigation.
Electromagnetic model
### 3.1 Introduction

In this section, we describe a model that computes the spatially resolved electromagnetic fields. The model forms one of the electromagnetic modules in Plasimo and it is employed in the plasma simulations of chapter 6. It is based on the Maxwell curl equations [15] with the assumption that the fields are time-harmonic in a homogeneous linear and isotropic media. The equations are discretised by the finite difference approximations in the frequency domain by the help of the Yee algorithm [41]. Furthermore, we consider example cases of cylindrical waveguides including circular and coaxial waveguides. In these cases, the analytic descriptions are available and we compare them with the numerical solutions.

### 3.2 The Maxwell equations

The macroscopic electromagnetic phenomena are described by the Maxwell equations, which determine the spatial and temporal behaviour of the electric and magnetic fields. Inside a dissipative, neutral and non-magnetic linear medium, the Maxwell equations are

\[
\nabla \times \vec{E} = -\mu_0 \frac{\partial \vec{H}}{\partial t}, \\
\nabla \times \vec{H} = \vec{J} + \epsilon_0 \epsilon_r \frac{\partial \vec{E}}{\partial t}, \\
\nabla \cdot (\epsilon_0 \epsilon_r \vec{E}) = \rho, \\
\nabla \cdot \vec{H} = 0.
\]

(3.1)  
(3.2)  
(3.3)  
(3.4)

where \(\vec{E}\) is the electric field intensity, \(\vec{H}\) is the magnetic field intensity, \(\vec{J}\) is the electric current density, \(\rho\) is the electrical charge density, \(\mu = \mu_0\) is the permeability of free space, \(\epsilon_0\) is the permittivity of free space and \(\epsilon_r\) is the relative permittivity of the medium.

#### 3.2.1 Harmonic fields: Complex notation

We assume that these fields are harmonic, i.e., the time dependence is given by a common term \(e^{i\omega t}\). For such fields, it is convenient to use the complex (also known as phasor) notation, so that a physical field \(\mathcal{F}\) is given by

\[
\mathcal{F} = \text{Re} \left( F e^{i\omega t} \right),
\]

(3.5)

where \(F\) is the complex amplitude.

Due to the common term, the notation transforms the instantaneous vector fields \(\vec{E}, \vec{H}\) and \(\vec{J}\) into the corresponding complex amplitudes \(\vec{E}, \vec{H}\) and \(\vec{J}\), respectively. In this notation, the
3.2. The Maxwell equations

Maxwell equations are expressed as
\[ \nabla \times \vec{E} = -i\omega \mu_0 \vec{H}, \]  \hfill (3.6)
\[ \nabla \times \vec{H} = \vec{J} + i\omega \varepsilon_0 \varepsilon_r \vec{E}, \]  \hfill (3.7)
\[ \nabla \cdot (\varepsilon_0 \varepsilon_r \vec{E}) = \rho, \]  \hfill (3.8)
\[ \nabla \cdot \vec{H} = 0. \]  \hfill (3.9)

Furthermore, assuming Ohm’s law, that is in the same notation \( \vec{J} = \sigma \vec{E} \) with a complex conductivity \( \sigma \), equation (3.7) reduces to
\[ \nabla \times \vec{H} = i\omega \varepsilon_0 \left( \varepsilon_r + \frac{\sigma}{i\omega \varepsilon_0} \right) \vec{E} \equiv i\omega \varepsilon_0 \varepsilon_r \vec{E}, \]  \hfill (3.10)
where a complex relative permittivity is also introduced
\[ \varepsilon_r \equiv \varepsilon_r + \frac{\sigma}{i\omega \varepsilon_0}. \]  \hfill (3.11)

3.2.2 Maxwell curl equations

The equations (3.6) and (3.7) are also known as Maxwell curl equations and they describe the electromagnetic waves propagating in a medium. For the sake of simplicity, we introduce a scaled magnetic field \( \tilde{H} \)
\[ \tilde{H} = iZ_0 \vec{H}, \]  \hfill (3.12)
where \( Z_0 = \sqrt{\mu_0/\varepsilon_0} \) is the impedance of free space, and the vacuum wave number \( k_0 = \omega/c_0 = \omega \sqrt{\varepsilon_0 \mu_0} \). In terms of these, the equations (3.6) and (3.10) satisfy
\[ \nabla \times \tilde{E} + k_0 \tilde{H} = 0, \]  \hfill (3.13)
\[ \nabla \times \tilde{H} + k_0 \varepsilon_r \tilde{E} = 0. \]  \hfill (3.14)
Equations (3.13, 3.14) are the governing equations in the electromagnetic model and numerically integrated over the spatial grids.

3.2.3 Helmholtz wave equation

The Maxwell curl equations (3.13,3.14) can be put into a single wave equation for the magnetic field intensity. Taking the curl of equation (3.11) and substituting in equation (3.3), we acquire
\[ \nabla \times \nabla \times \tilde{H} - k_0^2 \varepsilon_r \tilde{H} + k_0 \frac{\nabla \varepsilon_r}{\varepsilon_r} \times \nabla \times \tilde{H} = 0. \]  \hfill (3.15)
The last term on the left-hand side vanishes for a medium with a piecewise uniform complex permittivity:
\[ \nabla \times \nabla \times \tilde{H} = k^2 \tilde{H}, \]  \hfill (3.16)
where the wave number \( k \) has been defined as
\[ k = k_0 \sqrt{\varepsilon_r}. \]  \hfill (3.17)
Equation (3.16) is called the Helmholtz equation and can be used in plasma models \[12\]. It is employed in this chapter to obtain the analytic solutions.
3.3 Boundary conditions

The boundary conditions are divided into four distinct types: (1) material interfaces, (2) symmetry axis, (3) excitation and (4) propagation boundary conditions.

The interface between two materials with distinct dielectric permittivities forms a discontinuity in the media and defines a boundary condition of type (1) (for details see [43]). There are different materials in a system and the boundary conditions are specific to each material. The boundary conditions between two dielectric media is given by the continuity of the parallel electric field. We assume that a metal is a perfect conductor and that the electric field vanishes inside a metal. In this respect, if one of the materials is a metal, then the tangential electric field vanishes.

The boundary between a conductor and a dielectric is of special importance since it allows a wave propagation along their interface, which is known as surface-guided waves [13]. If the conductor is a plasma, the surface wave feeds it and at the same time the plasma itself sustains the wave propagation. Such configuration, where a dielectric tube, i.e., quartz, and a plasma meet, is known as a surface wave discharge and it is discussed in detail by various authors [44, 45, 46]. In some cases, air may also serve as a dielectric, which will allow surface propagation along its boundary with the plasma [47]. For this boundary condition, we also assume that the net surface charge is zero. In a plasma model, for example presented in chapter 6, we neglect the plasma sheath next to a dielectric wall. This region is generally characterised with a net space charge and the zero surface charge assumption may seem unrealistic. On the other hand, if a net surface charge is present at the interface, this gives rise to various higher order hybrid microwave modes that break the axial symmetry. Such modes are outside the scope of this work, and their investigation is left for 3-D electromagnetic models.

A symmetry axis is the boundary condition of type (2) and states that the derivative that is normal to the symmetry axis is zero. The excitation boundary condition (type (3)) has a different characteristic compared to the aforementioned conditions since it specifies the incoming electromagnetic field configuration through a waveguide. We assume that this configuration in the waveguide is known and that there is no reflection from the setup back into this boundary. The scale of the incoming electric field is arbitrary and it is iteratively re-scaled to match the input and the absorbed power.

All these boundary conditions describe physical phenomenon, for which the propagation boundary condition differs from them: It does not reflect a physical situation, but it is an artificial one only to restrict the computational domain bound to a finite region. In this respect, this boundary condition lets the waves propagate through the boundary without any reflection. It is imposed by assigning an analytic form to the wave at the boundary [48].
3.4. Discretisation

The time-harmonic fields are discretised via so called Finite Difference Frequency Domain (FDFD) method [49]. The method is based on the finite difference approximations of the spatial derivatives of the Maxwell curl equations given in the form (3.13, 3.14).

For the sake of simplicity, the discretisation procedure is generalised to an ortho-curvilinear coordinate system. Then the coordinate system can be easily converted by specifying its characteristics. An ortho-curvilinear coordinate system is described by a diagonal metric, in which the coordinates are orthogonal to each other [29]. The best known examples are the cartesian, cylindrical and spherical coordinate systems. In the discretisation procedure, a general ortho-curvilinear coordinate description is employed and the coordinate system is defined by identifying its metric. This greatly simplifies the implementation of distinct ortho-curvilinear coordinates in the models.

In the discretisation, the field vector components are differently positioned on the grid cells according to the Yee algorithm [41] (see Figure 3.1). Similar to the control volume approach, the Maxwell curl equations are integrated over each grid cell and together with Stokes’ theorem of integration the components are placed accordingly. The electric field components are located on the cell walls and they overlap with the material interfaces parallel to them. A Yee grid cell and the smart positioning of the field components are shown in Figure 3.1 (a). The material interfaces are associated with the discontinuities in the medium and form a mutual boundary condition for both materials. As a consequence of the smart positioning, the Yee algorithm provides an easy implementation of the boundary conditions for the material interfaces. The neighbouring Yee cells for the boundary condition implementation are shown in Figure 3.1 (b).
3.5 The TM\textsubscript{01} mode in cylindrical coordinates

In the remainder of this chapter, we are concerned with a cylindrical setup with axially symmetric field profiles. Furthermore, we consider TM\textsubscript{01} mode of the electromagnetic wave that propagates along the $z$ direction of a cylindrical coordinate system $(z, r, \phi)$. This mode is composed of the field components $\vec{E} = (E_z, E_r, 0)$ and $\vec{H} = \left(0, 0, H_\phi\right)$. The field $\vec{H}$ is governed by equation (3.16), for the field component $H_\phi(z, r)$ this yields

$$\frac{\partial^2 H_\phi}{\partial z^2} + \frac{1}{r} \frac{\partial H_\phi}{\partial r} - \frac{1}{r^2} H_\phi + k^2 H_\phi = 0.$$  \hspace{1cm} (3.18)

Using the method of separation of variables for $H_\phi = R(r)Z(z)$, we find that

$$\frac{1}{Z(z)} \frac{\partial^2 Z(z)}{\partial z^2} + \frac{1}{R(r)} \left[ \frac{\partial^2 R(r)}{\partial r^2} + \frac{1}{r} \frac{\partial R(r)}{\partial r} \right] - \frac{1}{r^2} + k^2 = 0.$$  \hspace{1cm} (3.19)

The first term is independent of $r$ and $\phi$. As a consequence, it must be also independent of $z$ if the sum of all terms equals zero

$$\frac{1}{Z(z)} \frac{\partial^2 Z(z)}{\partial z^2} = -k_z^2,$$  \hspace{1cm} (3.20)

where $k_z$ is the complex axial wavenumber. The solutions to $Z(z)$ are the harmonic functions $h(k_z z)$

$$h(k_z z) \propto \exp(\pm ik_z z), \sin(k_z z), \cos(k_z z)$$  \hspace{1cm} (3.21)

By including the definition of the axial wavenumber, $k_z$ of equation (3.20) into equation (3.19) we get

$$\frac{1}{R(r)} \left[ \frac{\partial^2 R(r)}{\partial r^2} + \frac{1}{r} \frac{\partial R(r)}{\partial r} \right] - \frac{1}{r^2} + k^2 - k_z^2 = 0.$$  \hspace{1cm} (3.22)

We introduce the complex radial wavenumber as

$$k_r^2 = k^2 - k_z^2.$$  \hspace{1cm} (3.23)

Substitution of equation (3.23) into equation (3.22) yields

$$\frac{\partial^2 R(r)}{\partial r^2} + \frac{1}{r} \frac{\partial R(r)}{\partial r} + \left(k_r^2 - \frac{1}{r^2}\right) R(r) = 0.$$  \hspace{1cm} (3.24)

This is the Bessel differential equation and the solutions to $R(r)$ are the Bessel functions $B_n(k_r r)$

$$B_1(k_r r) \propto J_1(k_r r), Y_1(k_r r), H_1^{(1)}(k_r r), H_1^{(2)}(k_r r)$$  \hspace{1cm} (3.25)

with $n = 1$.

The Bessel functions of first and second kind, $J(k_r r)$ and $Y(k_r r)$, are analogous, respectively, to $\cos(k_r r)$ and $\sin(k_r r)$ both describing a standing wave for real arguments and an evanescent field for imaginary arguments. Similarly, the Hankel functions or Bessel functions of third kind, $H_1^{(1)}(k_r r)$ and $H_1^{(2)}(k_r r)$, are equivalent to $\exp(ik_r r)$ and $\exp(-ik_r r)$, describing
a propagating solution in negative or positive direction for real argument and an evanescent field for imaginary argument. Therefore, the general solution for $\tilde{H}_\phi$ in a TM mode with rotational symmetry is

$$\tilde{H}_\phi = \propto B_1(k_r r)h(k_z z).$$

(3.26)

Depending on the boundary conditions the corresponding Bessel and harmonic functions are used. Note that a linear combination of the solutions will also be solution of the wave equation. It is also important that when $k_r = 0$, the degenerated Bessel functions are

$$B_0(k_r r)|_{k_r=0} = 1, \log(r)$$

(3.27)

$$B_n(k_r r)|_{k_r=0} = r^n, r^{-n}.$$  

(3.28)

In the following sections, we apply the electromagnetic module to a circular and a coaxial waveguide filled with air. We acquire the analytic solutions via the Helmholtz equation and compare with the simulation results. In order to investigate the accuracy of the method, we define a relative local error of the solution

$$\epsilon \equiv \text{Max} \left( \frac{\tilde{H}_\phi^N - \tilde{H}_\phi}{\text{Max}(\tilde{H}_\phi)} \right),$$

(3.29)

where Max represents the maximum value of different spatial positions and $\tilde{H}_\phi^N$ represents the numerical solution.

In the discretisation scheme finite difference approximations are used, which are provided by Taylor series expansion \[30, 49\]. Let $L$ be a differential operator, $u(x)$ an analytic function and $x$ the spatial coordinate. For a constant grid size $\delta x$, let $\bar{u}$ be the numerical solution and $\bar{L}$ be a numerical operator. The absolute local error is defined as the difference between the analytic and numerical solution and it is position dependent $e(x_n) = |u(x_n) - \bar{u}(x_n)|$, which is in general normalised to the function $\epsilon = e(x_n)/\bar{u}(x_n)$ (see equation 3.29). The consistent error is defined as $e_c(x_n) = |Lu_{x_n} - \bar{L}\bar{u}(x_n)|$.

According to the Taylor series, the consistent error is equal to the remainder terms of the Taylor series expansion and its is related with the absolute local error with $\bar{L}e = e_c$. If the numerical operator is invertible, the relation takes the form $e = \bar{L}^{-1}e_c$. The consistent error can be given by the relation

$$e_c = A(\delta x)^n,$$

(3.30)

where $n$ is the order of the approximation and $A$ is the proportionality constant. The order and the constant are defined by the finite difference approximation, for example $n = 2$ in our case. The grid size is given by the relation $\delta x = l/N$, where $l$ is the length of the computation domain and $N$ is the number of grids. Therefore, the relation between the absolute local error and the number of grid points is

$$\ln e \approx \ln(\bar{L}^{-1}A^n(N)^{-n}),$$

(3.31)

which can be approximately stated by

$$\ln e \approx -\alpha \ln N,$$

(3.32)

where $\alpha$ is defined by the previous parameters defining the differential equation and the order of the finite difference approximation.
3.5.1 Circular waveguide

The geometry of a circular waveguide short-cut at one end \((z = L)\) is shown in Figure 3.2. As \(H_\phi\) must be defined at \(r = 0\), the Bessel function of first kind \(J_1\) is used. Due to the short cut at \(z = L\), a combination of propagating waves appear

\[
H_\phi = J_1(kr) \left[ A \exp(-ik_z z) + B \exp(ik_z z) \right].
\]  

(3.33)

The boundary conditions are

\[
\frac{\partial H_\phi}{\partial z} \bigg|_{z=L} = 0,
\]

(3.34)

and

\[
\frac{1}{r} \frac{\partial r H_\phi}{\partial r} \bigg|_{r=a} = 0.
\]

(3.35)

From the first boundary condition

\[-A \exp(-ik_z L) + B \exp(ik_z L) = 0,
\]

(3.36)

so that

\[A \exp(-ik_z L) = B \exp(ik_z L) = C.\]

(3.37)

Let’s introduce \(L\) into equation (3.33) via multiplying each exponential with the identity \(\exp(ik_z L) \exp(-ik_z L) = 1\):

\[
\tilde{H}_\phi = J_1(kr) \left[ A \exp(-ik_z L) \exp[-ik_z(z-L)] + B \exp(ik_z L) \exp(ik_z(z-L)) \right]
\]

(3.38)

Inserting equation (3.37) into equation (3.38) and dividing by 2

\[
\tilde{H}_\phi = J_1(kr) \frac{C}{2} \{ \exp[-ik_z(z-L)] + \exp(ik_z(z-L)) \} \]

(3.39)

From the second boundary condition, using the formula for the derivative of Bessel functions (see equation 9.1.30 in [50]) we get

\[
\frac{k_r}{k_r} \frac{\partial k_r r J_1(k_r)}{\partial k_r} \bigg|_{r=a} = J_0(k_r a) = 0.
\]

(3.41)
3.5. The TM$_{01}$ mode in cylindrical coordinates

Therefore, the boundary condition at $r = a$ implies that

$$k_r a = x_{01}, \quad (3.42)$$

where $x_{01}$ is the first zero of $J_0$. Remember that the boundary condition at $r = 0$, where the field must be finite, requires using $J$ as $Y$ is infinite at $r = 0$.

From the above condition the complex axial wave number is obtained as

$$k_z = \sqrt{k^2 - \left(\frac{x_{01}}{a}\right)^2}. \quad (3.43)$$

For $k_z$ real, we will use

$$\tilde{H}_\phi = CJ_1 \left(\frac{x_{01}}{a}\right) r \cos[k_z(z - L)]. \quad (3.44)$$

However, when $k_z = i\gamma$ with $\gamma > 0$, i.e., $k_z$ becomes imaginary, we have an evanescent field

$$\tilde{H}_\phi = DJ_1 \left(\frac{x_{01}}{a}\right) r \exp(-\gamma z). \quad (3.45)$$

Error analysis

The circular waveguide of length $L = 0.1226$ m and radius $a = 0.06$ m is numerically solved by the EM module and compared with the analytic solution obtained above. The normalised magnetic field pattern is shown in Figure (3.3). The analytic and numerical results show good agreement in the order of 0.7% maximum difference. The error $\epsilon$ is shown as a function of
Chapter 3. Electromagnetic model

Figure 3.4: Circular waveguide: Logarithm of the scaled absolute maximum error $\epsilon$ (equation 3.29) as a function of the logarithm of the number of grid points $N$. (1) $N$ is increased axially keeping the radial number fixed. (2) $N$ is increased radially keeping axial number of grids fixed and (3) $N$ is increased in both directions.

The number of grid points in Figure 3.4. We use the expression (3.32), which relates the number of grids to the error $\epsilon$ and find the slope $\alpha = 0.97$. The scheme is first-order accurate that is in agreement with [51]. The behaviour of the error for radial and axial directions differ (see Figure 3.4). Such an anisotropy is probably caused by the distinct governing equations in these directions and further investigation is required for a definite answer.

3.5.2 Coaxial waveguide

A schematic of the coaxial waveguide with an inner radius $a$ and outer radius $b$ is given in Figure 3.5. The waveguide is short-cut at axial position $z = L$. In the coaxial waveguide, as $a < r < b$ the plane $r = 0$ and $r = \infty$ are not part of the solution domain, therefore, the J and Y Bessel solutions are used.

$$
\tilde{H}_\phi = [AJ_1(k_r r) + BY_1(k_r r)] [C \exp(-ik_z z) + D \exp(ik_z z)].
$$

(3.46)

Using the boundary condition at $z = L$,

$$
\frac{\partial \tilde{H}_\phi}{\partial z} \bigg|_{z=L} = 0
$$

(3.47)

we obtain

$$
\tilde{H}_\phi = [AJ_1(k_r r) + BY_1(k_r r)] \cos[k_z(z - L)].
$$

(3.48)
3.5. The TM$_{01}$ mode in cylindrical coordinates

![Diagram of coaxial waveguide with inner radius $a$, outer radius $b$, and short-cut at $z = L$.]

Figure 3.5: The coaxial waveguide with an inner radius $a$, an outer radius $b$ and a short-cut at $z = L$.

From the boundary condition at $r = a$ and $r = b$

$$\frac{1}{r} \frac{\partial r \tilde{H}_\phi}{\partial r} \bigg|_{r=a,b} = 0. \quad (3.49)$$

and using the property for the derivative of the Bessel function

$$\frac{k_r \partial k_r r B_1(k_r r)}{k_r r \partial k_r r} \bigg|_{r=a} = B_0(k_r a) \quad (3.50)$$

we obtain

$$A k_r J_0(k_r a) + B k_r Y_0(k_r a) = 0, \quad (3.51)$$

$$A k_r J_0(k_r b) + B k_r Y_0(k_r b) = 0. \quad (3.52)$$

The propagation of (TM$_{0m}$) modes is given by the characteristic relation

$$J_0(k_r a)Y_0(k_r b) - J_0(k_r b)Y_0(k_r a) = 0 \quad (3.54)$$

When $k_r = 0$, a combination of TEM and TM$_{00}$ modes is obtained. In that case the boundary condition

$$\frac{1}{r} \frac{\partial r B_1(k_r r)}{\partial r} \bigg|_{r=a,b} = 0 \quad (3.55)$$

is fulfilled if $B_1(k_r r) = 1/r$. For vacuum the TM$_{00}$ mode is mostly suppressed when $b < 2.3a$.

Finally the magnetic field for the TEM mode is given by the relation

$$\tilde{H}_\phi = \frac{C}{r} \cos \left[ k_z (z - L) \right]. \quad (3.56)$$

**Error analysis**

The circular waveguide with an inner radius of $a = 0.0005$ m, an outer radius of $b = 0.045$ m and a short-cut length of $L = 0.2$ m is numerically solved and results are shown in Figure 3.6. The solution agrees with the analytic data in the order of 0.5 % at maximum. The error $\epsilon$
Figure 3.6: Numerical solution of the coaxial waveguide normalised to its maximum.

Figure 3.7: Coaxial waveguide: Logarithm of the scaled absolute maximum error $\epsilon$ as a function of logarithm of the grid cell numbers $N$.

as a function of the total number of grid cells is shown in Figure 3.7. In this case, the error data does not produce a straight line as in the circular waveguide but slightly scattered. We provide a fit line and using the expression (3.32) we find a slope of $\alpha = 1.3$. This is larger
3.6 Conclusion

We introduced the electromagnetic module of Plasimo and applied it to circular and coaxial waveguides. The numerical simulations show good agreement with the analytic results. An error is defined from these two distinct solutions and it is analysed with respect to the total grid numbers. It should be emphasised that the discretisation of a wave equation does not only cause an error in the finite difference approximations. It also alters the dispersion relation and leads to a phase difference with the exact wave. The dispersion relation is generally derived from the wave equation itself and it basically relates the wavenumber and the frequency with the phase velocity. On the other hand, the discretised wave equation causes a slight difference in the dispersion relation. This relation is called numerical dispersion [49, 29] and causes a grid length dependent phase difference between the analytic and numerical wave solutions. In this respect, as the waves propagate the error term increases.
Global (volume-averaged) model of inductively coupled chlorine plasma: Influence of Cl wall recombination and external heating on continuous and modulated power inputs
4.1 Introduction

Chlorine based inductively coupled plasmas draw attention due to their common usage for surface etching in the fabrication of microelectronics [4]. Low dissociation energy of chlorine generates significant dissociation rates in these plasmas. Combined with the large electron affinity of atomic chlorine high degrees of electronegativity are reached. Since these quantities strongly rely on the operating conditions, an optimisation is necessary to realise such a goal. These kind of plasmas reflect a wide range of diversity in the operation parameters, with an applied pressure range of $1 - 100$ mTorr and the power input variation within $100 - 1000$ W. The power is coupled either in continuous or modulated mode, in which the modulation periods are chosen in microsecond [52, 53] or millisecond time-scales [54]. The modulation is more advantageous than the continuous power due to lower energy loss and higher efficacy in time-averaged densities.

The plasma characteristics depend on various criteria and pressure, power input, chamber dimensions and mass flow rate are the most recognised among them. The atomic chlorine recombines at the chamber wall to form a molecule that is expressed by a probability. Beside all the interactions, this recombination is uniquely influential on the atomic and molecular chlorine densities. The recombination rate may depend on numerous parameters such as atomic to molecular chlorine density ratio [55], the gas temperature [56], the pressure [57], the wall material [58, 59], and even the surface coating history [59]. The role of the recombination probability is theoretically studied by Lee et al. [60] and it is further discussed by Meeks et al. [61] with experimental comparisons. However, a detailed discussion is mostly absent and an up to date analysis is necessary due to recent improvements in the chemical kinetics [62, 63]. The gas temperature is another parameter that is effective over the plasma features due to its role on the chemical reactions in the plasma volume and the interactions at the plasma boundary. The power coupling already heats the gas via electron heavy particle collisions. Apart from this self heating, the gas temperature can be externally varied via the control of the walls. The plasma sensitivity to such an external gas temperature variation is not analysed up to now. In this study, we address these issues by providing a detailed analysis of the plasma response with respect to the the recombination probability and the gas temperature.

Global (volume-averaged) models [4, 31] are strong tools to analyse these plasmas. They have less computational load and simulation results are easily accessible compared to spatially resolved hybrid (kinetic-fluid) models [64, 65]. Global models have been employed for a long time in simple [66, 67] and detailed forms of chemical kinetics [60, 68], and show quite good agreement with the experimental data. Recently, they were compared with various other models, where their validity has been discussed in detail [63, 66], while practical recommendations are also provided [67]. Time dependent global plasma models can be also used to investigate the effect of power modulation [69]. Good agreement with the measurements is reported in argon plasmas [70, 71], yet benchmarking against measurements is sparse in chlorine plasmas [71]. We also try to fill this gap by providing an extensive comparison with experimental data available in literature.

Thorsteinsson et al. recently published a series of global model studies of radio-frequency chlo-
4.2 Global (volume-averaged) model

Global models concern volume-averaged quantities under the assumption that the sheath length is negligible \cite{1}. For these quantities, particle or energy transport inside the plasma volume is irrelevant and only the net transport at the plasma-sheath boundary is influential. The transport phenomena at the boundary is effectively taken into account, based on a combination of analytic models \cite{31}. This eradicates the computational load due to the transport and allows a significantly larger number of distinct species compared to spatially resolved models. For the details of the derivation we refer to chapter \ref{sec:chap2}.

In the model, we assume that the power is distributed uniformly inside the chamber and the plasma is spatially homogeneous, i.e., the spatial particle profiles do not change significantly compared to their volume averages. We use a two-temperature description: one temperature is assigned to electrons and the other to heavy particles both with the assumption of Maxwellian distribution functions. Governing equations include particle balance equations for various species and the electron energy balance equation; all are integrated over the volume \cite{31}. Particle balance equations determine all particle densities except for the electrons. The electron density is calculated from the quasi-neutrality assumption. This assumption, however, is implemented in different ways for the continuous and modulated power inputs due to faster recombination of electrons compared to millisecond scale modulation periods. The quasi-neutrality implementation in the power modulation is explained in section \ref{sec:chap4.4}. The electron temperature is derived from the electron energy balance equation, while the heavy particle temperature is provided externally.
Chapter 4. Radio-frequency Cl plasma: Global model

4.2.1 Setup

We simulate hollow cylindrical chambers and particularly the experimental setup presented in [74]. In the setup, the plasma forms inside a (hollow) cylindrical chamber with length $L = 1.0 \times 10^{-1} \text{ m}$ and radius $R = 2.75 \times 10^{-1} \text{ m}$. The chamber wall is composed of hard anodised aluminium. Inductive power coupling is realised by an external 4-turn planar spiral coil operated at a radio-frequency of $f = 13.56 \text{MHz}$. Pure Cl$_2$ gas at $T_{in} = 300 \text{K}$ is introduced into the chamber with a mass flow rate of $Q = 50 \text{ sccm}$.

4.2.2 Particle balance equation

For a species $i$, the volume-averaged particle balance equation can be expressed by the relation

$$\frac{\partial n_i}{\partial t} = S_i, \quad (4.1)$$

where $n_i$ is the particle density and $S_i$ is the source. The source is located either inside the plasma or at its boundary. These locations distinctively characterise the nature of the source. Source terms inside the volume are defined by the chemical reactions among the species whereas, at the boundary, they are determined by the chamber wall and the particle transport. In order to denote these two source types, we use the subscripts $V$ and $W$ that symbolise the volume and the wall, respectively. The source includes the reactions in which the species $i$ is produced and destructed. The former is represented by $\{P\}$ and the latter by $\{D\}$. Based on these notations, the source is written as

$$S_i = \sum_{j \in \{P\}} R^{j}_{V,W} - \sum_{j \in \{D\}} R^{j}_{V,W}, \quad (4.2)$$

where $j$ is a particular reaction and $R^{j}_{i}$ is the rate of the reaction involving the species $i$.

Reaction rates

The volume reactions are composed of the chemical interactions between the individual plasma species, and their rates are distinctively characterised by the reactants. For a volume reaction $j$, the rate is expressed by the relation

$$R^{j}_{V} = k^{j} \prod_{i} n_{i}^{\nu_{ji}}, \quad (4.3)$$

where $k^{j}$ is the rate coefficient and $\nu_{ji}$ is the stoichiometric coefficient of reactant $i$. The rate coefficient either depends on the electron temperature $T_e$ or the gas temperature $T_h$ when all the reactants are heavy particles.

Unlike volume reactions, the wall reactions are induced by the chamber wall and effectively derived from the particle transport. These reactions are uniquely defined by the particle
4.2. Global (volume-averaged) model

charge and state. The positive ions recombine at the wall and return back to the plasma as neutrals. On the other hand, the potential drop at the sheath traps most of the negative ions, therefore, their wall losses are negligible. The neutral particles diffuse towards the boundary, where they recombine or de-excite at the chamber wall and reflect back into the volume. In addition to these processes, the convection due to mass flow carries all the species out of the plasma and feeds the chamber with the input gas.

For a positive ion labelled by $p$, the ion flux towards the boundary explicitly depends on the density located at the wall $n_p|_W$. This wall density is coupled to its volume-averaged equivalent $n_p$ by a ratio $h_p$: $n_p|_W = n_p h_p$. Furthermore, it is assumed that the ion reaches the Bohm velocity $u_{Bp} = (eT_e/m_p)$ at the wall, where $m_p$ identifies the mass. Hence, the ion flux towards the boundary is defined by the expression $n_p h_p u_{Bp}$. With the assumption that every ion that collides with the wall neutralises, the ion wall loss rate is conventionally expressed by the relation

$$R^+_p|_W = u_{Bp} n_p A_{eff,p} V,$$

(4.4)

where $V$ is the plasma volume, $A_{eff,p}$ is the effective wall area and superscript “+” denotes the positive ions. The effective wall area represents the total plasma surface and embodies the ratio $h_p$, which, in general differs in radial and axial surfaces. For a cylinder, it satisfies

$$A_{eff,p} = 2\pi (R^2 h_{L,p} + LR h_{R,p})$$

(4.5)

where $h_{L,p}$, $h_{R,p}$ are the axial and the radial edge ratios, respectively.

The ion ratios, $h_p$, are derived from analytic models of electronegative radio-frequency plasmas [75]. According to these models, they are defined by a number of spatial ion profiles, that are combined by an ansatz [37]. As a caveat; the electronegativity modifies the Bohm velocity with respect to the electropositive plasmas [76] and the modification is internally taken into account in the ratios. We adapt the ansatz $h_p = (h^2_{a,p} + h^2_{c,p})^{1/2}$ [68], which combines a low pressure electropositive edge and a flat-topped electronegative profile:

$$h_{L,a,p} \approx 0.86(3 + 2\alpha_0)$$

$$h_{R,a,p} \approx 0.8(3 + 2\alpha_0)$$

$$h_{c,p} \approx \left(\gamma^{1/2} + \gamma^{1/2} n_{ps}^{1/2} n_p n_-^{3/2}\right)^{-1}$$

(4.6)

where $\gamma = T_e/T_h$, $\alpha_0 \approx (3/2)\alpha$ is the central electronegativity [60], $n_-$ is the total negative ion density, and

$$n_{ps} = \frac{15}{56} \frac{v_p}{k_{r,p}\lambda}.$$  

(4.7)

Here $v_p = (8k_BT_h/\pi m_p)^{-1/2}$ represents its mean thermal velocity, where $k_B$ is the Boltzmann constant, and $k_{r,p}$ is the rate coefficient of mutual neutralisation with negative ions (reactions 26 and 28 in Table (4.4)). The mean free path is

$$\lambda = \frac{k_BT_h}{P\sigma}$$

(4.8)

where $P$ is the gas pressure and $\sigma$ is the effective scattering cross-section. We set an average value for the cross-section $\sigma = 7 \times 10^{-19} \text{ m}^2$ based on [68].
Chapter 4. Radio-frequency Cl plasma: Global model

The neutral particles are lost at the boundary due to the outward diffusive flux. Their collisions with the wall provoke reactions that are unique for each species and the consequent products return to the plasma. A superscript $N$ is introduced to represent their rates and for a neutral particle $i$, the wall reaction rate is given by [77, 78]

$$R_i^N |_W = n_i \left( \frac{\Lambda_0}{D_i} + \frac{2V(2 - \gamma_i)}{Av_i\gamma_i} \right)^{-1},$$

(4.9)

where $D_i$ is the diffusion coefficient [4], $v_i$ the mean neutral velocity, $m_i$ the mass, and $\gamma_i$ is the wall reaction probability. The effective diffusion length $\Lambda_0$ for a cylinder is [78]

$$\Lambda_0 = \left[ \left( \frac{\pi}{L} \right)^2 + \left( \frac{2.405}{R} \right)^2 \right]^{-1/2}.$$

(4.10)

The mass flux simply feeds the chamber with Cl$_2$ on one side and drains the plasma species on the other. In this respect, the Cl$_2$ flow-in rate is formulated as

$$R_{\text{Cl}_2}^\text{in} |_W = CQ \frac{P_{\text{atm}}}{V k_B T_{\text{in}}}$$

(4.11)

where $C = 1.6667 \times 10^{-8}$ is a conversion unit from sccm to m$^3$s$^{-1}$, $Q$ the mass flow rate in sccm, $P_{\text{atm}}$ the atmospheric pressure and $T_{\text{in}} = 300$ K is the temperature of the input gas. Similarly, a particle $i$ flows out of the chamber at the rate

$$R_i^\text{out} |_W = CQ \frac{P_{\text{atm}} T_i}{V PT_{\text{in}}} n_i.$$

(4.12)

4.2.3 Electron energy balance equation

The electron energy balance equation can be written as [31]

$$\frac{\partial p_e}{\partial t} = Q_e$$

(4.13)

where $p_e = 3/2n_e T_e$ is the energy density, the right-hand-side represents the source and the unit eV is used to describe the electron temperature. The source contains the power absorbed or released by the electronic reactions. Additionally, it includes the loss rate due to elastic electron collisions and absorption of energy, which is applied externally

$$Q_e = Q_{\text{Che}} - Q_W + Q_{\text{abs}} - Q_{\text{Ela}},$$

(4.14)

where $Q_{\text{Che}}$ is the chemical volume source, $Q_W$ is the loss at the plasma wall, $Q_{\text{abs}}$ is the absorbed input power and, $Q_{\text{Ela}}$ represents the elastic losses within the plasma.

We assume that the electrical energy provided to the chamber is mostly absorbed by the electrons and then distributed to the rest of the plasma species. The electronic reaction
4.2. Global (volume-averaged) model

Table 4.1: The power transfer efficiency $\beta$ and gas temperature $T_h$ [K] measurements at various input power $P$ [W] and pressure $P$ [mTorr].

<table>
<thead>
<tr>
<th>Par. \ P</th>
<th>2 mTorr</th>
<th>5 mTorr</th>
<th>10 mTorr</th>
<th>20 mTorr</th>
<th>50 mTorr</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta(P = 100)$</td>
<td>0.76</td>
<td>0.79</td>
<td>0.82</td>
<td>0.80</td>
<td>0.81</td>
</tr>
<tr>
<td>$\beta(P = 200)$</td>
<td>0.86</td>
<td>0.88</td>
<td>0.90</td>
<td>0.91</td>
<td>0.85</td>
</tr>
<tr>
<td>$\beta(P = 500)$</td>
<td>0.91</td>
<td>0.93</td>
<td>0.94</td>
<td>0.94</td>
<td>0.95</td>
</tr>
<tr>
<td>$T_h(P = 100)$</td>
<td>400</td>
<td>450</td>
<td>500</td>
<td>600</td>
<td>600</td>
</tr>
<tr>
<td>$T_h(P = 200)$</td>
<td>450</td>
<td>550</td>
<td>650</td>
<td>800</td>
<td>500</td>
</tr>
<tr>
<td>$T_h(P = 500)$</td>
<td>550</td>
<td>700</td>
<td>900</td>
<td>1200</td>
<td>1100</td>
</tr>
</tbody>
</table>

energies are either absorbed or released by the electrons, i.e., they are the ultimate energy reservoir in the particle interactions. In view of this, the absorption is written as

$$Q_{abs} = \beta P / V,$$

where $\beta$ is the power transfer efficiency (see Table 4.1) and $P$ is the input power. The chemical source term $Q_{Che}$ contains the electronic reactions in the following

$$Q_{Che} = \sum_j E_j R^j_e |_{V},$$

where $E_j$ is the reaction energy and $R^j_e$ is the reaction rate. The reaction rate is defined in the previous section and the reaction energy represents the net amount of energy absorbed or released by the reaction. It is the sum of internal energies of the products subtracted from those of the reactants

$$E_j = \sum_{i \in \text{reactants}} \nu_{ji} \epsilon_i - \sum_{i \in \text{products}} \nu_{ji} \epsilon_i,$$

where $\epsilon_i$ is the internal energy of the particle. The internal energies are shown in the energy diagram Figure 4.10. With the assumption that the electron temperature is much bigger than the gas temperature we define the elastic loss

$$Q_{Ela} = \sum_i n_e n_i 3T_e m_i k^{Ei}_{el},$$

where $k^{Ei}_{el}$ is the elastic rate coefficient and $m_i$ represents the mass of a particle. The elastic rate coefficient is computed from the corresponding collision cross-section and is a function of the electron temperature.

The wall energy losses are due to the positive ions lost by the transport at the plasma boundary

$$Q_W = \sum_{p \in \text{ions}} (E_e + E_s + E_P) R^+_{p} |_{W},$$

where $E_e = 2T_e$ is the mean energy loss per electron, $E_s$, $E_P$ are the sheath and the plasma potentials, respectively. We use the sheath potential expression

$$E_s \approx \ln \left( \frac{4 \tilde{u}_{Bv}}{v_e} \frac{1 + \alpha_s}{1 + \alpha_s (v_- / v_e)^2} \right) T_e,$$
Chapter 4. Radio-frequency Cl plasma: Global model

<table>
<thead>
<tr>
<th>Cl₂ plasma species</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl₂, Cl₂(v = 0, 1, 2, 3), Cl(²P3/2), Cl(²P1/2), Cl(¹P5/2), Cl⁺, Cl⁻, e</td>
</tr>
</tbody>
</table>

Table 4.2: The distinct plasma species included in the model. Cl(²P3/2) is often referred as Cl in this work.

where \( v_e \) and \( v_- \) are the electron and negative ion mean thermal velocities, respectively, \( \alpha_s = n_-/n_e \), is the degree of electronegativity at the sheath edge and \( \bar{u}_{B'} = \sum_p n_p u_{B'} p / \sum_p n_p \) is the density weighted positive ion Bohm velocity. The electronegativity changes the Bohm velocity by a factor that is provided by Braithwaite et al. [76]. Conventionally, this factor is included in the effective area for the ion wall loss rate (see equation 4.4). In the sheath potential we explicitly express the factor within the relation

\[
\bar{u}_{B',p} = \left[ \frac{eT_e (1 + \alpha_s)}{m_p (1 + \alpha_s \gamma)} \right]^{1/2}.
\]  

The plasma potential for an electronegative plasma is given by [4]

\[
\mathcal{E}_P = \frac{1}{2} \frac{1 + \alpha_s}{1 + \alpha_s \gamma} T_e.
\]  

The sheath electronegativity \( \alpha_s \) is related with the presheath electronegativity \( \alpha_b \) by [31]

\[
\alpha_s = \alpha_b \exp \left[ \frac{(1 + \alpha_s)(1 - \gamma)}{2(1 + \alpha_s) \gamma} \right].
\]  

We employ a fit function for \( \gamma > 10 \), presented in [68], with the assumption that \( \alpha_b \) is equal to the central degree of electronegativity.

4.2.4 Numerical approach

We introduce a vector notation for the sake of simplicity in the numerical implementation. Let \( \mathbf{n} = \{ n_i, p_e \} \) be the density vector, that includes the particle densities complemented with the electron energy density. Similarly, we define the source vector \( \mathbf{S} = \{ S_i, Q_e \} \). By definition the source vector explicitly depends on the density vector and the system of equations takes the form

\[
\frac{\partial \mathbf{n}}{\partial t} = \mathbf{S}(\mathbf{n}).
\]  

Providing an initial value at time \( t_0, \mathbf{n}(t_0) \), the set is solved iteratively for a variable time-step \( \Delta t \) until time \( T \). We set \( T \) large enough for steady state solutions, i.e., after \( T \) the solution does not change anymore. We refer to chapter [4] for details of the numerical solver.

4.3 Chemical model

The set of species, that are contained in the model, are shown in Table 4.2 and the energy diagram is depicted in Figure 4.10 together with the internal energies. Compared to sim-
4.3. Chemical model

Table 4.3: Neutral wall reactions and their probabilities.

<table>
<thead>
<tr>
<th>#</th>
<th>Reaction</th>
<th>Probability($\gamma$)</th>
<th>Ref.</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$\text{Cl} + \text{wall} \rightarrow 1/2\text{Cl}_2$</td>
<td>$\gamma_{[A,S]}$</td>
<td></td>
<td>See text</td>
</tr>
<tr>
<td>2-4</td>
<td>$\text{Cl}_2(v) + \text{wall} \rightarrow \text{Cl}_2(v - 1)$</td>
<td>1.0</td>
<td>72</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>$\text{Cl}(^2P_1/2) + \text{wall} \rightarrow \text{Cl}$</td>
<td>1.0</td>
<td></td>
<td>See text</td>
</tr>
<tr>
<td>6</td>
<td>$\text{Cl}(^1P_5/2) + \text{wall} \rightarrow \text{Cl}$</td>
<td>1.0</td>
<td></td>
<td>See text</td>
</tr>
</tbody>
</table>

Similar chlorine studies \[60, 68\], we explicitly include the atomic excited levels $\text{Cl}(^2P_1/2)$ and $\text{Cl}(^1P_5/2)$. The reactions and the rate coefficients are listed in Table 4.3. The rate coefficients of the electronic reactions are numerically calculated from the corresponding cross-sections with the assumption that the electron energy distribution function is Maxwellian. This numerical data is parametrically fit to functions of the electron temperature.

Most of the fit functions are adapted from a paper by Thorsteinsen et al. \[72\], whereas certain rate coefficients are directly computed from the cross-sections (reactions 11, 18, 19, 21, 22 in Table 4.4). A recently updated vibrational excitation cross-section (reaction 11) by Gregório et al. \[62\] is preferred over the one used in the paper \[72\], since it results in a significantly higher rate coefficient. The electronic excitation cross-section to level $\text{Cl}(^2P_1/2)$ (reaction 18) is calculated by Wang et al. \[63\] and to level $\text{Cl}(^1P_5/2)$ (reaction 19) by Griffin et al. \[80\]. We estimate an ionisation rate coefficient from level $\text{Cl}(^2P_1/2)$ (reaction 21) based on the electronic Cl ionisation (reaction 20). The ionisation cross-section from atomic level $\text{Cl}(^1P_5/2)$ (reaction 22) and the radiative decay coefficient are taken from \[81\].

Backward reactions of the excitations are also included in the model by detailed balancing \[82, 4\]. Additionally, the heavy particle quenching reactions (36 – 38) are incorporated. The elastic momentum transfer cross-sections are provided by \[80\].

The neutral wall reactions are shown in Table 4.3. The Cl recombination probability at a hard anodised aluminium wall has been experimentally determined by Booth et al. \[57\]. It depends on the gas pressure and we use an average value for the parameter range in this study

$$\gamma_{A1} = 2.5 \times 10^{-1},$$

(4.25)

where subscript $A1$ stands for this anodised aluminium measurement. It is also measured by Guha et al. \[55\], and lower values are reported that also depend on the $n_{\text{Cl}}/n_{\text{Cl}_2}$ density ratio. Additionally, such a dependency is also observed for a stainless steel wall by Stafford et al. \[58\]. We define these variable recombination probabilities by parametric fits \[68\]

$$\gamma_{A2} = 10^{-0.82 - 1.59 \text{exp}(-1.81 n_{\text{Cl}}/n_{\text{Cl}_2})},$$

$$\gamma_{S} = 10^{-1.22 - 1.34 \text{exp}(-1.48 n_{\text{Cl}}/n_{\text{Cl}_2})},$$

(4.26)

where $A2$ denotes the aluminium wall measurement by Guha et al. \[55\], and $\gamma_{S}$ is the measurement for the stainless steel by Stafford et al. \[58\]. We observe that the plasma is not sensitive to the variations of $\text{Cl}(^2P_1/2)$ and $\text{Cl}(^1P_5/2)$ de-excitation probabilities at the wall; consequently, they are estimated by unity in the simulations.
Table 4.4: The chemical reactions included in the plasma volume (see text). All rate coefficients are in m$^3$/s$^{-1}$, $T_h$ is in K and $T_e$ is in eV unless stated otherwise. The parametric fit range is $T_e = 0.5 - 10$ eV. The backward reactions of the electronic excitations are also included in the model via detailed balancing. These excitations are indicated by a letter "**" next to the reaction number. The electronic ionisation from Cl(2P1/2), which is symbolised by "***", is estimated from the electronic ionisation of the ground state. The symbol "****" denotes the elastic collisions.

<table>
<thead>
<tr>
<th>#</th>
<th>Reaction</th>
<th>Rate Coefficient</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$e + Cl_2(v = 0) \rightarrow Cl + Cl + e$</td>
<td>$1.04 \times 10^{-13} T_e^{-0.29} e^{-8.84/T_e}$</td>
<td>S3</td>
</tr>
<tr>
<td>2</td>
<td>$e + Cl_2(v = 0) \rightarrow Cl_2^+ + 2e$</td>
<td>$5.12 \times 10^{-14} T_e^{0.48} e^{-12.34/T_e}$</td>
<td>S4</td>
</tr>
<tr>
<td>3</td>
<td>$e + Cl_2(v = 0) \rightarrow Cl + Cl^+ + 2e$</td>
<td>$2.14 \times 10^{-13} T_e^{-0.07} e^{-25.26/T_e}$</td>
<td>S4</td>
</tr>
<tr>
<td>4</td>
<td>$e + Cl_2(v = 0) \rightarrow Cl^+ + Cl^+ + 3e$</td>
<td>$2.27 \times 10^{-16} T_e^{1.92} e^{-21.26/T_e}$</td>
<td>S4</td>
</tr>
<tr>
<td>5</td>
<td>$e + Cl_2(v = 0) \rightarrow Cl + Cl^-$</td>
<td>$3.43 \times 10^{-15} T_e^{-1.18} e^{-3.98/T_e}$</td>
<td>S5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$3.05 \times 10^{-16} T_e^{-1.33} e^{-0.11/(T_e + 0.014)}$</td>
<td>S5</td>
</tr>
<tr>
<td>6</td>
<td>$e + Cl_2(v = 1) \rightarrow Cl + Cl^-$</td>
<td>$14.06 \times 10^{-15} T_e^{-1.18} e^{-3.98/T_e}$</td>
<td>S7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$12.51 \times 10^{-16} T_e^{-1.33} e^{-0.11/(T_e + 0.014)}$</td>
<td>S7</td>
</tr>
<tr>
<td>7</td>
<td>$e + Cl_2(v = 2) \rightarrow Cl + Cl^-$</td>
<td>$30.18 \times 10^{-15} T_e^{-1.18} e^{-3.98/T_e}$</td>
<td>S7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$26.84 \times 10^{-16} T_e^{-1.33} e^{-0.11/(T_e + 0.014)}$</td>
<td>S7</td>
</tr>
<tr>
<td>8</td>
<td>$e + Cl_2(v = 3) \rightarrow Cl + Cl^-$</td>
<td>$46.31 \times 10^{-15} T_e^{-1.18} e^{-3.98/T_e}$</td>
<td>S7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$41.18 \times 10^{-16} T_e^{-1.33} e^{-0.11/(T_e + 0.014)}$</td>
<td>S7</td>
</tr>
<tr>
<td>9</td>
<td>$e + Cl_2(v = 0) \rightarrow Cl^+ + Cl^- + e$</td>
<td>$2.94 \times 10^{-16} T_e^{0.19} e^{-18.79/T_e}$</td>
<td>S9</td>
</tr>
<tr>
<td>11*</td>
<td>$e + Cl_2(v = 0) \rightarrow Cl_2(v = 1) + e$</td>
<td>$3.99 \times 10^{-12} T_e^{-1.5} e^{-7.51/T_e - 0.0001/T_e^2}$</td>
<td>S9</td>
</tr>
<tr>
<td>12*</td>
<td>$e + Cl_2(v = 0) \rightarrow Cl_2(v = 2) + e$</td>
<td>$3.28 \times 10^{-17} T_e^{-1.12} e^{-0.37/T_e}$</td>
<td>S9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$2.86 \times 10^{-17} e^{-ln(T_e) + 0.993}/(2 \times 1.06^2)$</td>
<td>S9</td>
</tr>
<tr>
<td>13*</td>
<td>$e + Cl_2(v = 0) \rightarrow Cl_2(v = 3) + e$</td>
<td>$1.30 \times 10^{-17} T_e^{-1.24} e^{-0.41/T_e}$</td>
<td>S9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$6.08 \times 10^{-18} e^{-ln(T_e) + 0.943}/(2 \times 1.02^2)$</td>
<td>S9</td>
</tr>
<tr>
<td>14*</td>
<td>$e + Cl_2(v = 1) \rightarrow Cl_2(v = 2) + e$</td>
<td>$3.00 \times 10^{-16} T_e^{-1.00} e^{-0.37/T_e}$</td>
<td>S9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$4.61 \times 10^{-16} e^{-ln(T_e) + 1.043}/(2 \times 1.10^2)$</td>
<td>S9</td>
</tr>
<tr>
<td>15*</td>
<td>$e + Cl_2(v = 2) \rightarrow Cl_2(v = 3) + e$</td>
<td>$3.00 \times 10^{-16} T_e^{-1.00} e^{-0.37/T_e}$</td>
<td>S9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$4.61 \times 10^{-16} e^{-ln(T_e) + 1.043}/(2 \times 1.10^2)$</td>
<td>S9</td>
</tr>
<tr>
<td>16*</td>
<td>$e + Cl_2(v = 1) \rightarrow Cl_2(v = 3) + e$</td>
<td>$1.25 \times 10^{-16} T_e^{-1.13} e^{-0.36/T_e}$</td>
<td>S9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$1.06 \times 10^{-16} e^{-ln(T_e) + 0.1013}/(2 \times 1.06^2)$</td>
<td>S9</td>
</tr>
<tr>
<td>17</td>
<td>$e + Cl_2^+ \rightarrow Cl + Cl$</td>
<td>$9.00 \times 10^{-14} T_e^0.50$</td>
<td>S9</td>
</tr>
<tr>
<td>18*</td>
<td>$e + Cl \rightarrow Cl(2P1/2) + 2e$</td>
<td>$4.55 \times 10^{-14} T_e^{-0.46} e^{-2.01/T_e - 0.001/T_e^2}$</td>
<td>S9</td>
</tr>
<tr>
<td>19</td>
<td>$e + Cl \rightarrow Cl(1P5/2) + 2e$</td>
<td>$7.03 \times 10^{-17} T_e^{0.55} e^{-2.15/T_e - 1.5/T_e^2 - 2.05/T_e^3}$</td>
<td>S9</td>
</tr>
<tr>
<td>20</td>
<td>$e + Cl \rightarrow Cl^+ + 2e$</td>
<td>$3.17 \times 10^{-14} T_e^{0.53} e^{-13.29/T_e}$</td>
<td>S9</td>
</tr>
<tr>
<td>21**</td>
<td>$e + Cl^2 P1/2) \rightarrow Cl^+ + 2e$</td>
<td>$3.17 \times 10^{-14} T_e^{0.53} e^{-13.19/T_e}$</td>
<td>S9</td>
</tr>
<tr>
<td>22</td>
<td>$e + Cl(1P5/2) \rightarrow Cl^+ + 2e$</td>
<td>$4.33 \times 10^{-14} T_e^{0.55} e^{-0.15/T_e - 0.85/T_e^2}$</td>
<td>S9</td>
</tr>
<tr>
<td>23</td>
<td>Cl(1P5/2) / Cl</td>
<td>$1.0 \times 10^5$ s$^{-1}$</td>
<td>S1</td>
</tr>
<tr>
<td>24</td>
<td>$e + Cl^- \rightarrow Cl + 2e$</td>
<td>$9.02 \times 10^{-15} T_e^{0.92} e^{-4.88/T_e}$</td>
<td>S9</td>
</tr>
<tr>
<td>25</td>
<td>$e + Cl^- \rightarrow Cl^+ + 3e$</td>
<td>$3.62 \times 10^{-15} T_e^{0.72} e^{-25.38/T_e}$</td>
<td>S9</td>
</tr>
<tr>
<td>26</td>
<td>Cl$^2_2 + Cl^- \rightarrow 3Cl$</td>
<td>$5.00 \times 10^{-14}(300/T_h)^{0.50}$</td>
<td>S11</td>
</tr>
<tr>
<td>27</td>
<td>Cl$^2_2 + Cl^- \rightarrow Cl + Cl_2$</td>
<td>$5.00 \times 10^{-14}$</td>
<td>S11</td>
</tr>
<tr>
<td>28</td>
<td>Cl$^+ + Cl^- \rightarrow Cl + Cl$</td>
<td>$5.00 \times 10^{-14}(300/T_h)^{0.50}$</td>
<td>S11</td>
</tr>
<tr>
<td>29-33</td>
<td>Cl$_2(v = 0 - 3) + Cl^+ \rightarrow Cl + Cl^+_2$</td>
<td>$5.40 \times 10^{-16}$</td>
<td>S11</td>
</tr>
<tr>
<td>34</td>
<td>2Cl + Cl$_2 \rightarrow Cl_2(v = 0) + Cl_2$</td>
<td>$3.50 \times 10^{-45} e^{810/T_h}$ m$^6$s$^{-1}$</td>
<td>S11</td>
</tr>
<tr>
<td>35</td>
<td>2Cl + Cl $\rightarrow Cl_2(v = 0) + Cl$</td>
<td>$8.75 \times 10^{-46} e^{810/T_h}$ m$^6$s$^{-1}$</td>
<td>S11</td>
</tr>
<tr>
<td>36-38</td>
<td>Cl + Cl$_2(v &gt; 0) \rightarrow Cl_2(v = 1) + Cl$</td>
<td>$1.3 \times 10^{-17}(T_h/300)^{1/2}$ m$^6$s$^{-1}$</td>
<td>S9</td>
</tr>
<tr>
<td>1***</td>
<td>$e + Cl_2(v = 0) \rightarrow Cl_2(v = 0) + e$</td>
<td></td>
<td>S9</td>
</tr>
<tr>
<td>2***</td>
<td>$e + Cl \rightarrow Cl + e$</td>
<td></td>
<td>S9</td>
</tr>
</tbody>
</table>
4.4. Quasi-neutrality implementations

The wall recombination together with the volume reactions identify the degree of dissociation
\[ \kappa_d = \frac{n_{Cl}}{n_{Cl} + 2n_{Cl_2}}. \]
The gas temperature determines the mutual recombination coefficients between the positive and the negative ions. It is also influential on the interactions at the boundary such as ion recombination, neutral reaction rates at the wall and the flow out rates.

4.4 Quasi-neutrality implementations

For a continuous power input, the electron density is computed from the quasi-neutrality assumption
\[ n_e = \sum_i n_i q_i / e, \quad (4.27) \]
where \( i \) represents an ion and \( q_i \) is its charge. The global models also provide time dependent behaviour in the modulated power inputs [100, 69, 71]. These papers deal with the modulation periods in the microsecond scale, and the electron density is calculated from the same quasi-neutrality implementation. In this case, the power modulation periods overlap with the electron recombination time-scale and electrons are still present even at the end of the period.

For larger modulation periods, like milliseconds, the electrons quickly recombine and vanish in the power-off region. Afterwards, the quasi-neutrality implementation induces non-physical negative electron densities due to the electronegativity. In order to prevent this a different approach is employed to impose the quasi-neutrality. We multiply the particle balance equation of each species with its charge \( q_i \), and their summation defines a volume-averaged charge continuity equation:
\[ \frac{\partial \rho}{\partial t} + \sum_i q_i R_i |W| = 0, \quad (4.28) \]
where \( \rho \) represents the total charge density. The net volume source vanishes due to the charge conservation in the reactions and only the wall flux remains. According to this expression, if initially quasi-neutrality is satisfied, it is further conserved in time, when the total flux - or the net current - to the wall vanishes
\[ \sum_i q_i R_i |W| = 0. \quad (4.29) \]

A caveat about the approach: the numerical integration schemes that use large time-steps can produce deviations. Accordingly, we explicitly solve the electron particle balance equation but impose a constraint on its wall flux
\[ R_e |W| = \sum_{i \neq e} q_i e R_i |W|. \quad (4.30) \]

As the power is switched off, the electron temperature steeply drops in microseconds, together with the plasma and sheath potential. A minimum value for the electron temperature is identified by the gas temperature with the assumption that electrons and background gas are in thermal equilibrium. Afterwards, all the electrons recombine, which is defined by a
minimal density condition in the model. The ion wall rates $R^+_p|_W$, that are derived in the presence of the electrons and a power input, are no longer valid and they are switched-off. The chemical kinetics, mass flow and the wall flux define an ion recombination time-scale. In case this time-scale is larger than that of electrons, the ions remain in the chamber and they form a quasi-neutral ion-ion plasma.

In the chlorine plasma, the ion recombination time-scales are relatively large and a quasi-neutral ion-ion plasma appears after the electrons disappear. In this respect, we define two separate regions with respect to time: (1) the plasma, (2) the ion-ion plasma (afterglow). The transition between these regions is defined by a minimal electron density condition. After the electrons disappear, the electron and the ion wall flux rates $R^+_p|_W$ are switched off and only the flow rates and the neutral wall reactions are kept. Similarly, the quasi-neutrality is imposed with negative ion wall flux

$$R_{Cl^-}|_W = \sum_{i \neq e, Cl^-} q_i/eR_i|_W.$$  \hfill (4.31)

4.5 Results

In this section, we firstly compare the simulation data with various experimental results obtained from literature. The comparison covers both continuous and modulated power inputs. Secondly, the simulation results for the recombination probabilities $\gamma_{A1}$, $\gamma_{A2}$ and $\gamma_S$ are compared with each other in the continuous mode. The recombination probability and the gas temperature are varied within a large spectrum to observe their role on the plasma. Finally, their influence on the power modulation is provided at the end of the section.

4.5.1 Experimental comparison

For steady power input we compare the simulation results with the measurements realised by Efremov et al. 101 and Hebner et al. 102. The former are carried out on a setup with a radius of $R = 1.5 \times 10^{-1}$ m, a length of $L = 1.4 \times 10^{-1}$ m at a flow rate of $Q = 20$ sccm and a power input of 400 W. We assume that 300 W is absorbed by the plasma and the gas temperature is $T_h = 500$ K adapted from 68. The second setup is a cylinder with $R = 5.5 \times 10^{-2}$ m and $L = 3.8 \times 10^{-2}$ m. The mass flow rate is 30 sccm and the power input is fixed at 240 W. For this case, we estimate the $\beta$ factors and the gas temperatures from the measurements listed in Table 4.1 by interpolation. The chamber walls in both setups are composed of stainless steel and the corresponding wall recombination probability, $\gamma_S$, is used in the simulations. The comparisons of the electron, negative ion densities and the electron temperature with respect to the pressure are shown in Figures 4.1(a) and 4.1(b). The simulation results mostly show good agreement with the experimental measurements for these cases. The agreement is fair for the electron density profile at 1.5 mTorr pressure and for the electron temperature profile at 1 mTorr and 25 mTorr.
4.5. Results

(a) $e$ ($\bigcirc$) and $\text{Cl}^-$ ($\triangle$) densities ($\text{m}^{-3}$) by Efremov et al. and Hebner et al.

(b) Electron temperature, $T_e$ (eV), by Efremov et al.

(c) $e$ ($\bigcirc$), Cl ($\square$) and Cl$(^2P_{1/2})$ ($\triangle$) densities ($\text{m}^{-3}$) by Sirse et al.

Figure 4.1: Various experimental data (points) measured by Efremov et al. [101] Hebner et al. [102] and Sirse et al. [103] together with corresponding simulation results (lines or line-points). A distinct colour is assigned to each data set. See text for the operation conditions.
Figure 4.2: Various experimental data (points) by Ahn et al. [104] and by Bodart et al. [54] together with the simulation results (lines) in the power modulation. In both graphs the experimental and the numerical results are linked with their colours. See text for the operation conditions.
4.5. Results

Sirse et al. [103] recently measured the $e$, Cl and Cl$(^2P_{1/2})$ densities in a setup identical to the one described in section 4.2.1. We also compare the calculated $e$, Cl and Cl$(^2P_{1/2})$ densities at 50 mTorr with these measurements. The comparison is shown with respect to the power input in Figure 4.1(c). In general, the results agree well with the experimental data, though the agreement is fair for the excited state density and deviates most at 100 W.

In pulsed mode we compare the simulation results with the experimental data obtained by Ahn et al. [104]. The plasma is formed inside a glass Pyrex tube with $R = 1.6 \times 10^{-1} \text{ m}$ and $L = 1.6 \times 10^{-1} \text{ m}$. The power input is 400 W and the pressure is fixed at 8 mTorr. The period of the modulation is 100 $\mu$s with a 50 % duty ratio. For the glass wall, we assume a chlorine wall recombination constant of $\gamma_G = 0.15$ proposed by Ashida et al. [69]. The absorbed power is estimated by a factor of $\beta = 0.9$ based on Table 4.1. The setup is connected to a diffusion chamber with identical gas pressure. Ramamurthi et al. [53] showed in a similar setup that the plasma does not diffuse into this chamber for the same modulation parameters. Since the period is too small compared to the flow time-scale, we also observed that a mass flow rate of 30 sccm and 0 sccm does not change the calculations. Hence, the plasma expansion into the downstream region directed towards the diffusion chamber is neglected. The electron, negative ion densities and the electron temperature data in one modulation period are shown in Figure 4.2(a). Generally, a good agreement is observed between the calculations and the measurements. The agreement for the electron density and temperature is valid throughout the modulation period, however, the model proposes a fairly smaller time-scale for the electron temperature decay. The negative ion density measurements deviate from the simulation mostly between 50 – 55 $\mu$s. Since the experimental data is inconsistent by rapid fluctuations at this interval, it is possible that the disagreement is due to the experimental errors.

Bodart et al. [54] recently measured the atomic and the molecular chlorine densities with a completely different modulation period compared to the previous case. The measurements are carried out for a period of 0.66 ms with a 15 % duty ratio. The setup dimensions are identical to the one described in the section 4.2.1. It is operated at 800 W input power, 20 mTorr pressure, 100 sccm mass flow rate, and gas temperature of 800 K. Considering the increment of the factor $\beta$ with the power input (see Table 4.1), we assume that all of the power is absorbed within the plasma. The gas temperature identifies the flow-out rate. If it is not properly defined in the pulse off region, the mass flow drains excessive amount of species from the chamber with the pulse on value of 800 K. Regarding this, we estimate a cooling time-scale about 20 ms that is based on the observations by Cunge et al. [105, 106]. In this respect, we assume that the gas temperature drops to the ambient temperature in 20 ms. The calculated and the measured data are given in Figure 4.2(b) that show good agreement with each other throughout the modulation period. However, the model predicts a fairly smaller decay time-scale in chlorine density compared to the experimental observation.

### 4.5.2 Wall recombination probability and gas temperature variations

In this section, we fix the power input at 200 W and use the setup described in section 4.2.1 for the analysis. In the simulations we employ the $\beta$ and gas temperature measurements of the setup (see Table 4.1), whenever necessary. We firstly compare the different recombination
Figure 4.3: Comparison of the electron, chlorine atom and the excited chlorine atom densities and the electron temperature for various recombination probability measurements at 200 W power input. The type of line correspond to each probability: anodised aluminium $\gamma_{A1}$ by [57] (—), anodised aluminium $\gamma_{A2}$ by [55] (— - -) and stainless steel $\gamma_{S}$ by [58] (···). The experimental data for the densities and the temperature are provided by Sirse et al. [103] for the setup described in section 4.2.1.
probability measurements $\gamma_{A1}$, $\gamma_{A2}$ and $\gamma_S$ discussed in section 4.3. The pressure resolved densities of electron, Cl and Cl$(^2P1/2)$ species and the electron temperature for these probabilities are shown in Figure 4.3 together with the experimental data [103]. The measurement, $\gamma_{A1}$, is the largest among the wall recombination probabilities and it is a constant number. However, $\gamma_{A2}$ and $\gamma_S$ vary with the pressure due to different $n_{Cl}/n_{Cl_2}$ ratio. They satisfy $0.006 < \gamma_{A2} < 0.1$, $0.003 < \gamma_S < 0.04$ and peak at 2 mTorr where the $n_{Cl}/n_{Cl_2}$ is relatively larger. Their difference with $\gamma_{A1}$ rises with the pressure. The highest difference is at 50 mTorr, consequently, the corresponding profiles disagree most at this value. This disagreement is more obvious for the Cl and Cl$(^2P1/2)$ densities, compared to electron density and temperature. Their profiles for these recombination probabilities fairly agree with each other in the presented pressure range.

In order to observe its influence on the plasma, the Cl wall recombination probability is hypothetically varied within the range $0.001 - 1$. In the investigation, we denote this hypothetical probability by $\gamma_{rec}$ covering a pressure range $5 - 50$ mTorr. The particle densities are shown as a function of $\gamma_{rec}$ at 5 mTorr and 50 mTorr pressure in Figure 4.4: (a) charged particles at 5 mTorr, (b) charged particles at 50 mTorr, (c) neutral particles at 5 mTorr and (d) neutral particles at 50 mTorr. According to these figures, there are two distinct chemical partitions and corresponding reaction channels with respect to $\gamma_{rec}$ variation. The first partition is composed of excited atomic states and Cl$^+$ that are mainly produced from Cl. The second partition consists of vibrational excited states, Cl$^+_2$ and Cl$^-$ that are dominantly produced from Cl$_2$. Since the wall recombination probability determines the dominant neutral in the plasma: either Cl or Cl$_2$, these two channels respond oppositely to the wall recombination probability.

Generally, the electron density depends on the species from both chemical partitions described above. It directly relies on all the ions in the plasma by the quasi-neutrality requirement and is indirectly determined by the neutrals as the source of the charged particle production. However, the electron density behaves similar to the first partition in the studied parameter range. This is mostly caused by the larger negative ion density that limits the electron density via the quasi-neutrality. Otherwise (for example at 500 W), we observe that the electrons behave proportional to the dominant positive ion. The pressure plays a significant role on the densities and their aforementioned variations. As a consequence, it defines a distinctive behaviour for the electron density together with the wall recombination probability. At a low pressure of 5 mTorr, Cl$^+$ is the dominant positive ion for small $\gamma_{rec}$, whereas the dominant ion switches to Cl$^+_2$ abruptly as $\gamma_{rec}$ increases. At the transition, the electron density shows a slight bump and then decreases with the wall recombination probability. At 50 mTorr, the positive ions are dominated by Cl$^+_2$ in the whole $\gamma_{rec}$ range. Since the negative ions are equally important as the dominant ion, the electron density behaviour is mostly identified by Cl$^+$ at this pressure due to the quasi-neutrality.

The degree of dissociation $\kappa_d = n_{Cl}/(n_{Cl} + 2n_{Cl_2})$, the degree of electronegativity $\alpha = n_{Cl^-}/n_e$ and the electron temperature $T_e$ variations with respect to $\gamma_{rec}$ are shown in Figure 4.5: (a) $\kappa_d$ and (b) $T_e$. The wall recombination probability dramatically reduces the degree of dissociation with a steeper drop at lower pressure. On the other hand, it increases the degree of electronegativity with a similar profile. The electron temperature is almost linearly proportional to $\gamma_{rec}$ for $\gamma_{rec} > 0.02$. Below this point, the relation depends on the pressure.
Chapter 4. Radio-frequency Cl plasma: Global model

Figure 4.4: The charged and neutral particle densities with respect to the wall recombination probability $\gamma_{\text{rec}}$ variation at 200 W power input for the pressure at 5 mTorr and 50 mTorr.

Figure 4.5: The degree of electronegativity $\alpha$, dissociation $\kappa_d$ and the electron temperature $T_e$ with respect to the wall recombination probability $\gamma_{\text{rec}}$ variation at 200 W power input.

At 5 mTorr and 10 mTorr, the temperature slightly decreases with increasing $\gamma_{\text{rec}}$, while at 50 mTorr and 20 mTorr the temperature shows an increasing trend. The transition between these two trends corresponds to the dominant ion transition, and the electron density shows a slight bump (see Figure 4.4(a)) that causes such an electron temperature behaviour. We
4.5. Results

Figure 4.6: The charged and neutral densities at 200 W power input with respect to the gas temperature.

Figure 4.7: The degree of electronegativity $\alpha$, the degree of dissociation $\kappa_d$, the electron temperature at 200 W power input at 5 mTorr and 50 mTorr with respect to the gas temperature.

observe that the well in the electron temperature for $\gamma_{\text{rec}} < 0.002$ deepens for a higher electron density bump (for example at 500 W).

Finally, the influence of the gas temperature on the plasma is investigated by externally
varying its value. This can also be physically achievable, for example, by the control of the chamber walls. The resultant particle density profiles are shown in Figure 4.6: (a) charged particles at 5 mTorr (b) charged particles at 50 mTorr (c) neutral particles at 5 mTorr and (d) neutral particles at 50 mTorr. The gas temperature variation barely alters the molecular and the negative ion densities. The largest effect on the charged particles is the increase of the electron and Cl\(^+\) densities. These behaviours agree with the observations by Thorsteinsson et al. [68]. The magnitude of the increase at 50 mTorr is significantly larger than the one at 5 mTorr. All the neutral densities are inversely proportional to the gas temperature which is more apparent at 5 mTorr.

The degree of electronegativity \(\alpha\), the degree of dissociation \(\kappa_d\) and the electron temperature \(T_e\), profiles at different pressure values are shown in Figure 4.6: (a) \(\alpha\), \(\kappa_d\) and (b) \(T_e\). The gas temperature does not affect the degree of dissociation, however it decreases the degree of electronegativity with an identical trend for all the pressure values. The electron temperature is almost linearly proportional with the gas temperature regardless of the pressure.

### Power modulation

In this section, we investigate the role of the wall recombination probability and the gas temperature on the plasma for a modulated power input. In the investigation, a square wave power modulation is applied with a period of 100 ms and a duty ratio of 50% at a 200 W peak power input and pressure 50 mTorr. We use the gas temperature and \(\beta\) measurements given in Table 4.1 whenever necessary.

Firstly, we compare four different wall recombination probabilities: \(\gamma_{A1}\), \(\gamma_{A2}\), \(\gamma_{rec} = 0.001\) and \(\gamma_{rec} = 1.0\). The corresponding time resolved charged particles and the electron temperature profiles are shown in Figure 4.8: (a) \(\gamma_{A1}\), (b) \(\gamma_{A2}\), (c) \(\gamma_{rec} = 0.001\) and (d) \(\gamma_{rec} = 1.0\). Similar Cl\(^+_2\) and Cl\(^-\) profiles are observed for the wall recombination probabilities \(\gamma_{A1}\) and \(\gamma_{A2}\). However, \(\gamma_{A2}\) produces larger electron and atomic positive ion densities and slightly lower electron temperatures. The difference is more obvious for the cases of \(\gamma_{rec} = 0.001\) and \(\gamma_{rec} = 1.0\). For \(\gamma_{rec} = 1.0\), the electron temperature and the Cl\(^+\) densities are smaller, while the electron temperature is higher. The Cl\(^+_2\) and Cl\(^-\) profiles do not alter for these two wall recombination probabilities.

Secondly, the comparison of two extreme cases of the gas temperature is shown that are \(T_h = 300\) K and \(T_h = 1500\) K, respectively. The charged particles and the electron temperature are shown with respect to time in Figure 4.9: (a) \(T_h = 300\) K and (b) \(T_h = 1500\) K. The molecular and negative ion profiles are invariant with respect to the gas temperature variation. On the other hand, the electron and Cl\(^+\) densities and the electron temperature increase.

In all of the power modulation cases, the electron temperature initially shows a very steep peak due to the low electron density, which is also measured by Ahn et al. [104]. The quantities during the pulse on are slightly larger than those for the continuous power input. However, the role of the wall recombination probability is identical for the modulated and continuous power inputs that is also observed for the gas temperature. As shown in the
4.5. Results

Figure 4.8: Power modulation with period 100 ms and 50 % duty ratio at 200 W power input and at 50 mTorr pressure. Each figure shows a different recombination probability $\gamma_{A1}$, $\gamma_{A2}$, $\gamma_{\text{rec}} = 0.001$ and $\gamma_{\text{rec}} = 1$.

Figure 4.9: Power modulation with period 100 ms and 50 % duty ratio at 200 W peak power input 50 mTorr. The figures shows 300 K and 1500 K cases.

continuous case (see Figure 4.4(a)), we also observe that at 5 mTorr Cl$^+$ is the dominant ion at most of the pulse on time for $\gamma_{\text{rec}} = 0.001$. As the power is cut-off, the electron temperature and the plasma potential immediately drop within 50 $\mu$s, and shortly after the
electrons vanish in the chamber. Cl$^+$ follows the electrons within 200 µs, which is in an agreement with the observations \cite{52}. Afterwards, an ion-ion plasma that is composed of Cl$^+$ and Cl$^-$ appears in the chamber. These ions mutually recombine, as well as they slowly flow out due to the net mass flow rate. The dominant loss mechanism of the ions is initially the mutual recombination then the dominance switches to the flow out rate. In the model we do not set any wall diffusion for these ions, which may lower the ion-ion plasma life-time.

4.6 Conclusion and discussion

We analysed a chlorine inductively coupled-radio frequency plasma both for continuous and modulated power input modes with a global model. The model shows good agreement with the various experimental data from literature for power input modes. In the model a novel quasi-neutrality implementation is employed for the power modulation and we observed an agreement with the conventional approach in the pulse on mode. In the pulse off mode an ion-ion plasma composed of Cl$^-$ and Cl$_2^+$ appears in the chamber and the quasi-neutrality is imposed by a similar condition on the negative ion. For an ion-ion plasma composed of multiple dominant negative ions the quasi-neutrality condition is to be applied to all negative ions, for example, by a density weighted flux.

In the analysis, a comparison of the plasma for distinct measurements of the Cl wall recombination probability is provided. Furthermore, the roles of the wall recombination and the gas temperature variations on the plasma are investigated and it is shown that they have a significant influence. The wall recombination releases energy at the wall and this reaction may directly alter the gas temperature, or indirectly by changing the plasma features. In the model we do not calculate the gas temperature but it is provided externally from measurements. Further analysis with a consistent gas heating requires a model self-consistently coupled to a volume-averaged heavy particle energy balance equation. Additionally, we assume that all the heavy particles are in thermal equilibrium and deviation from this, for example large ion temperature, may alter the influence of the gas temperature.

We observe that the updated vibrational excitation cross-section \cite{62} produces significantly larger Cl$_2$(v = 1) density compared to the one provided in \cite{90}. On the other hand, the rest of the vibrational excited levels, Cl$_2$(v = 2, 3) do not change and updated excitation cross-sections are necessary for these levels. Furthermore, the updated cross-section comparably increases the electron temperature and reduces the electron density; hence, it improves the agreement with the experimental data. The quenching reactions of the vibrational levels also play similar role; however, these reactions barely affects the plasma. The influence of the atomic excited chlorine is negligible within the parameter range. It is also observed that stepwise ionisation from the considered atomic and molecular excited levels are insignificant. Additionally, the plasma is not sensitive to variation of the wall de-excitation probabilities of these excited levels.
Figure 4.10: Energy diagram of the Cl & Cl₂ system. We use the symbol Cl instead of Cl($^{2}P_{3/2}$).
Global model of a microwave reactor plasma for optical fibre production: Continuous and modulated power for the feeding gas of O₂/SiCl₄ admixture
Chapter 5. Microwave O$_2$/SiCl$_4$ plasma: Global model

5.1 Introduction

Microwave induced plasmas are widely applied for surface treatment, such as etching \cite{107} and deposition \cite{108}. They lack the chemical pollutant due to the sputtering of the electrode surface and the wave transmission often expands the plasma to treat large area. These features make them advantageous compared to other means of energy coupling. The process purpose covers a large scale from microelectronics \cite{4} to solar cell production \cite{11}. One such application that forms the topic of this study is SiO$_2$ deposition on a silica substrate in the fabrication of optical glass fibres \cite{109}. The setup employed for this purpose is schematically depicted in Figure 5.1. The inner wall of a hollow cylindrical tube forms the deposition surface while the tube is covered by a reactor that injects microwave radiation to ignite and sustain a plasma. The reactor operates either in a continuous or a modulated power mode as it is known that the latter qualifies with higher efficiency \cite{100, 69}. An O$_2$/SiCl$_4$ admixture is introduced to the reactor with a net mass flow rate and the deposition neutral is created within the plasma.

Effective utilisation and optimisation demands a better understanding of the plasma dynamics. In this respect, we construct a model for a detailed investigation that often provides the quantities otherwise not available by experimental techniques. This approach also offers the plasma response with respect to hypothetical parameter variations or a sensitivity analysis. However, the plasma creates a wide variety of species with a complex chemical kinetics. Beside the difficulties in constructing an intact chemical set, this variety complicates the transport description due to the mutual interaction between the multiple ions and the ambipolar electric field. Additionally, it imposes enormous computational load with a long simulation time. Even if a convergent model is constructed, the simulation time causes rare data accessibility; therefore, it makes the optimisation and validation of the model laborious.

A global (volume-averaged) model overcomes the aforementioned challenges with a spatial integration over the plasma volume \cite{31}. In the description, only the volume-averaged quantities are available and the transport is relevant at the plasma boundary. As a result, the corresponding complexity in the description and the resultant computational load is alleviated to an eligible degree with a cost of spatial resolution. These models are commonly used to investigate radio-frequency plasmas both in continuous \cite{60, 110, 68} and modulated power inputs \cite{111}. The model is recently applied in a microwave induced plasma \cite{112}, however, the transport at the boundary is not self-consistently defined due to the much more complex sheath phenomena.

In this study, we analyse the plasma in both pure O$_2$ and O$_2$/SiCl$_4$ admixtures, based on a global model in the continuous as well as the modulated power input. Moreover, the study forms a first step for spatially resolved models (see chapter \ref{chapter:6}), where the transport is treated in detail and the spatial distributions are available. It helps to analyse the plasma sensitivity with respect to the species involved. As a result, the number of actively solved species and the regarding computational cost can be reduced in a spatially resolved model. In return the transport coefficients at the boundary are fine-tuned self-consistently and the global model provides more reliable results. Since the pure oxygen plasma is commonly studied in literature, the chemical kinetics is mostly up to date in the O$_2$ model. Moreover, the O$_2$/Cl$_2$ or Cl$_2$...
mixtures are widely analysed and the relevant reactions are also available. However, the O$_2$/SiCl$_4$ plasma is rarely investigated and the chemical reactions are sparse. In this respect, it should be emphasised that the SiCl$_4$ dilution is a first step in constructing a numerically stable chemical set and improvements may be required for a better reliability. Both models are implemented in the modular plasma simulation environment Plasimo [14, 113].

The contents are organised as follows. In section 5.2 we present the relevant setup parameters and in section 5.3 we explain the model coefficients that involve the chemical kinetics. The results are given in section 5.4 and the conclusions are provided in section 5.5. The particle set and the chemical reactions included in the model are listed in appendix 5.A together with the parametrically fit rate coefficients.

### 5.2 Setup

The deposition setup is shown in Figure 5.1. It is composed of a hollow cylindrical quartz tube surrounded by a metal reactor and fed by microwave radiation with a frequency of 2.45 GHz. The gas composition is a mixture of O$_2$ and SiCl$_4$ with a net mass flow rate of $Q = 33.2$ sccm at 1000 Pa pressure. The refractive index of the deposition layer is controlled by the feeding gas mixture that generally contains less than 10% of SiCl$_4$. The reactor is placed in a furnace that fixes the quartz temperature at 1500 K and the whole structure moves axially along the tube in order to produce a homogeneous deposition pattern.

In order to axially confine the plasma, chokes are placed on the reactor that short-cut the microwave propagation at the reactor boundaries. An optimum choke depth perfectly restrains the microwaves and the plasma. We refer to chapter 6 for details of the chokes and their optimisation. Therefore, the plasma is bound within the inner tube radius $R = 7.5$ mm and a total axial length $L = 144$ mm. The gas in the reactor (heavy particles of the plasma) is further heated up due to the microwave radiation. A volume-averaged gas temperature is

![Figure 5.1: The setup employed in the deposition of SiO$_2$ for optical fibre production.](image-url)
fixed at $T_h = 2000$ K for the input power of 250 W and at $T_h = 2200$ K for 400 W that are computed by a spatially resolved model (see chapter 6).

## 5.3 Global model

Global models calculate the volume-averaged plasma quantities such as the particle densities and the electron temperature. They intrinsically incorporate wall interactions as well as the chemical reactions occurring in the bulk volume [31]. One of these interactions that plays a key role in shaping the plasma behaviour is the ion recombination at the wall. These rates for a radio-frequency energy coupling are determined by combinations of sheath phenomena [76, 114] and analytically estimated spatial profiles in the volume [75]. However, in the case of microwave energy coupling, the spatial profile estimation is not straightforward and the sheath phenomena is much more complex. Hence, a wall recombination description in microwave induced plasmas is absent and this to be approximated as realised by Yanguas-Gil et al. [112] at a relatively lower pressure. It is also shown that the recombination rates rely on the power and the pressure by Chung et al. [110]; hence, directly adapting them is not an option. We estimate the ion wall recombination rates based on the spatially resolved models of the setup, such as chapter 6 and 115.

The global model includes particle balance equations and an electron energy balance equation that are integrated over the plasma volume. The particle balance equations determine the volume-averaged densities except for the electrons, the density of which is computed from the quasi-neutrality requirement. The electron energy balance equation provides the electron temperature. We assume that the plasma is homogeneous, i.e., its quantities do not significantly differ spatially compared to their volume average. Additionally, it is assumed that the electron energy distribution is Maxwellian. In the rest of this section, we explicitly provide the flow-in, flow-out and the ion wall recombination rates at the wall. For further details of the equations and the rates we refer to chapters 2 and 4.

The species that are included in the model are given in Table 5.A.1 together with their energies [110, 72]. The chemical reactions are divided into two parts: (1) those inside the plasma volume and (2) those at the boundary. The reactions inside the volume occur among the species and their rates are expressed by equation 4.3. The rate coefficients are either taken from the literature [72, 117] or numerically computed from corresponding cross-sections. The numerical data are parametrically fit to the electron temperature for electronic reactions and to the gas temperature otherwise. The boundary reactions are induced by the wall and they consist of de-excitations and associations. Each one is expressed by a probability that is listed in Table 5.A.10 and their rates are given by equation 4.9. The complete reaction sets are provided in appendix 5.A.

The mass flow introduces the $\text{O}_2/\text{SiCl}_4$ mixture to the plasma volume. We define individual flow-in rates for the components that depend on the relative percentages and are expressed
by the relations

\[ R_{\text{O}_2}|_W = C(100 - p)Q \frac{P_{\text{atm}}}{V_k B T_{\text{in}}}, \]  \hfill (5.1)

\[ R_{\text{SiCl}_4}|_W = C_R Q \frac{P_{\text{atm}}}{V_k B T_{\text{in}}}, \]  \hfill (5.2)

where \( p \) represents the SiCl\(_4\) percentage, \( Q \) is the net mass flow rate (see section 5.2), \( C = 1.6667 \times 10^{-8} \) represents a unit conversion factor from sccm to m\(^3\)s\(^{-1}\), \( P_{\text{atm}} \) is the atmospheric pressure, \( V \) is the plasma volume, \( k_B \) is the Boltzmann constant and \( T_{\text{in}} = 300 \) K is the input gas temperature. All of the plasma species, except negative ions, are drained from the reactor due to the net mass flow. The flow-out rate of a species \( i \) is given by the expression

\[ R_{\text{out}}^i|_W = C_Q \frac{P_{\text{atm}} T_h}{V P T_{\text{in}}} n_i, \]  \hfill (5.3)

where \( n_i \) is the particle density.

The positive ions recombine at the plasma boundary and return back to the volume as neutrals. The recombination rate of a positive ion \( p \) is

\[ R_p^+|_W = u_B p A_{\text{eff}, p} V, \]  \hfill (5.4)

where \( u_B \) is the ion Bohm velocity for electropositive plasmas, \( n_p \) is the density, \( V \) is the plasma volume, \( A_{\text{eff}, p} \) is the effective wall area and superscript “+” denotes the positive ions. The effective area depends on the total plasma surface multiplied by a unitless number \( h \)

\[ A_{\text{eff}} = 2\pi h (R^2 + LR). \]  \hfill (5.5)

The number, \( h \), represents a ratio of the ion density at the sheath edge and its volume-averaged density. In general, the ratio may vary from the radial to the axial surfaces, however, in this work we assume that it is invariant. Furthermore, in an electronegative plasma the Bohm velocity alters with a factor \[76\]

\[ \left( \frac{1 + \alpha_s}{1 + \alpha_s T_e/T_h} \right)^{1/2}, \]  \hfill (5.6)

where \( \alpha_s = n_{-s}/n_{e,S} \) is the degree of electronegativity at the sheath edge and \( T_e \) is the electron temperature. This factor is often included within the ratio, \( h \), in global models \[75\].

We define the ratio from a spatially resolved model (chapter \ref{chap6}) with the assumption that the dominant ion \( \text{O}_2^+ \) characterises it

\[ h \approx \left( \frac{1 + \alpha_s}{1 + \alpha_s T_e/T_h} \right)^{1/2} \frac{n_{S,\text{O}_2^+}}{n_{\text{O}_2^+}}, \]  \hfill (5.7)

where \( n_{S,\text{O}_2^+} \) is the ion density at the sheath edge and \( n_{\text{O}_2^+} \) is the volume-averaged ion density. The ratios computed for two different power inputs are shown in Table \ref{tab:5.1}

The electron energy source terms are also determined by the volume and wall interactions. We assume that the power input is totally absorbed by the plasma electrons (see Figure \ref{fig:6.6})
Table 5.1: Global model parameters that are determined from chapter 6 for two distinct power inputs (see text for details).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>250 W</th>
<th>400 W</th>
</tr>
</thead>
<tbody>
<tr>
<td>$h$</td>
<td>0.03</td>
<td>0.021</td>
</tr>
<tr>
<td>$T_h$</td>
<td>2000 K</td>
<td>2200 K</td>
</tr>
<tr>
<td>$E_p + E_s$</td>
<td>9 eV</td>
<td>9 eV</td>
</tr>
</tbody>
</table>

and uniformly distributed within the volume. In any electronic reactions the energy difference between reactants and products are either absorbed or provided by the electrons. The elastic energy losses inside the plasma volume are also included in the model and they are listed in Table 5.1. The sheath potential $E_S$ [68] and the plasma potential $E_P$ [4] that determine the amount of energy loss due to the ion recombination at the wall are estimated in a similar way as $h$

$$E_P \approx \frac{1 + \alpha_s}{2} \frac{T_e}{T_h} T_e,$$

$$E_S \approx \ln \left( 4 \frac{u_{B, O_2}}{v_e} \frac{1 + \alpha_s}{1 + \alpha_s (v_-/v_e)^2} \right) T_e,$$

where $v_e$ and $v_-$ are the electron and negative ion mean thermal velocities, respectively. Their sum is the relevant quantity in the global model and it is provided in Table 5.1.

5.4 Results

The simulations are carried out for two types of input gas: (1) for pure oxygen O$_2$, (i.e., $p = 0$) and (2) O$_2$/SiCl$_4$ with up to 10 % of SiCl$_4$ both in the continuous and the modulated power inputs of either 250 W or 400 W peak values. Firstly, we present the data for pure O$_2$ with a comparison to a spatially resolved model in section 6, where the number of species is reduced to decrease the computational load. In the content we also discuss a global model analysis that leads to this reduced set of species. Furthermore, the plasma sensitivity to the gas temperature, $T_h$, and the sheath volume ion density ratio, $h$, is investigated. Additionally, the role of the SiCl$_4$ dilution is discussed, assuming equal global model parameters with the pure O$_2$ case (listed in Table 5.1). We concentrate on the Si based neutral species that directly play an important role in the deposition process, namely Si, SiO and SiO$_2$. Afterwards, the plasma response to variation of $h$ and $T_h$ is discussed and the influence of the power modulation is also presented.

5.4.1 O$_2$ plasma

The volume-averaged particle densities and the electron temperature of the oxygen plasma at power inputs of 250 W and 400 W are shown in Figure 5.2 with a label “Global Model”.
5.4. Results

Figure 5.2: The volume-averaged densities and electron temperature of the global (Global), reduced global ([R]Global) and 2-D model (2-D) at (a) 250 W and (b) 400 W fed by O$_2$.

The molecular ion dominates the charged particles, whereas O$^-$ is the dominant negative ion. When the power input increases from 250 W to 400 W, the ionic and the atomic species densities increase, which is more apparent for O$^+$ and O($^1D$). The electron temperature also

\begin{align*}
\text{Densities (m}^{-3}\text{)} & \quad \text{Te (eV)} \\
\text{Particles} & \\
O_2 & O_2^+ & O(^1D) & O_2(b^1 \Sigma_g^+) & O_3^- & O_2(A^3 \Sigma_u^+),.. & \text{Te (eV)} \\
\text{Global Model} & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\
\text{[R]Global Model} & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\
\text{2-D Model} & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\
\end{align*}
Figure 5.3: The charged particle densities and the electron temperature for a peak power input at 250 W modulated with a period of 100 ms and 50% duty ratio for pure $\text{O}_2$.  

slightly increases with the power.

An analysis of the global model shows that the absence of certain species does not affect all the plasma features, consequently, they can be ignored in a simulation. Such a measure can be used to reduce the number of equations in a calculation to lower the computational load. The global model is also constructed by ignoring the species $\text{O}_3$, $\text{O}_2^-$, and $\text{O}_3^-$. The simulation data is also shown in Figure 5.2 with a label “[R]Global Model” that agrees with the previous results for the full set of particles. Such a reduced set is used in a spatially resolved model in chapter 6. For comparison, the volume-averaged quantities of this model are also presented in Figure 5.2 with a label “2-D Model”. It shows an agreement for both power inputs for the common densities and the electron temperature. The agreement is good for most of the species and fair for $\text{O}^1(D)$ and $\text{O}^+$ densities. The spatial inhomogeneity is relatively stronger for these two species (see Figures 6.8 and 6.10), and it is possible that the inhomogeneity causes the fair agreement.

Furthermore, a plasma sensitivity study with respect to $h$ and $T_h$ is realised and the corresponding ratios of the plasma quantities are shown in Table 5.2. The plasma is sensitive to the former with a maximum ratio of 0.61 in the dominant charged species. A higher electron temperature is acquired with $h$ due to the decrease in the electron density. As the gas temperature increases, the charged particle densities increase with a slight boost in the electron temperature, though the effect is less profound compared to $h$. In both cases, $\text{O}^+$ density shows the highest sensitivity as it constitutes less than 10% of all the positive ions. This is similar to the $\text{Cl}^+$ behaviour in the radio-frequency chlorine plasma studied in chapter 4.
5.4. Results

<table>
<thead>
<tr>
<th>Quantity</th>
<th>$h[0.0008 : 0.08]$</th>
<th>$T_h[1500 : 2500]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$e$</td>
<td>1 : 0.61</td>
<td>1 : 1.38</td>
</tr>
<tr>
<td>$O_2^+$</td>
<td>1 : 0.64</td>
<td>1 : 1.27</td>
</tr>
<tr>
<td>$O^+$</td>
<td>1 : 3.33</td>
<td>1 : 3.93</td>
</tr>
<tr>
<td>$O^-$</td>
<td>1 : 0.85</td>
<td>1 : 1.28</td>
</tr>
<tr>
<td>$T_e$</td>
<td>1 : 1.23</td>
<td>1 : 1.06</td>
</tr>
</tbody>
</table>

Table 5.2: The sensitivity analysis of the $O_2$ plasma with respect to $h$ and $T_h$. The symbol ":" represents the ratio of the quantities.

The time resolved charged particle densities and the electron temperature for a modulated peak power of 250W with a 100ms period and a 50\% duty ratio is shown in Figure 5.3. Initially, the electron temperature increases steeply above 5 eV due to the low electron density, then quickly settles around 1.8 eV. All the charged particle densities and the electron temperature sharply decrease, when the power is turned off. The electron temperature drops to the gas temperature in $0.3 \times 10^{-3}$ ms and the electrons vanish in 1 ms together with the dominant ion $O_2^+$. The rest of the charged species recombine before the dominant ion does. We also observed that the atomic oxygen completely recombines and the molecular oxygen almost reaches its initial value in about 50 ms.

5.4.2 $O_2$/SiCl$_4$ plasma

The charged particle densities, the neutral densities of Si, SiO, SiO$_2$ and the electron temperature are shown in Figure 5.4 for SiCl$_4$ percentages in the range of 0.01 \% and 10 \% with 250 W input power. We used the same global model parameters, $h$, $E_p$, $E_a$ and $T_h$ as for the $O_2$ model. Compared to pure $O_2$, a small amount of SiCl$_4$ dilution significantly reduces the electron density. This leads to lower energy losses and causes a higher electron temperature. Moreover, as the percentage of SiCl$_4$ increases, the temperature significantly decreases. The dominant ion is SiCl$_4^+$ among the positively charged species and this dominance changes from $O_2$ based ions to those created from SiCl$_4$ around $p = 1$. Among the negative ions, $O_3^-$ is the dominant at low dilution, whereas Cl$^-$ takes over at about $p = 8$. The small amount of dilution significantly reduces the atomic oxygen density: $(5.46 \times 10^{19} \text{ m}^{-3}$ at $p = 0.01)$ and the amount proportionally decreases its density. All silicon based deposition neutrals Si, SiO and SiO$_2$ increase with the percentage.

The dominant charged particles at $p = 5$ \% SiCl$_4$ dilution for variable $h$ and $T_h$ values are shown in Figure 5.5. The charged particles decrease with higher $h$, whereas ClO$_2^+$ and Cl$^-$ increase. The decrease in the electron density is smaller compared to the other charged species. We observe that the electron temperature linearly changes from 1.20 eV to 1.95 eV. The sensitivity to the gas temperature is less significant as it mainly effects the negative ions. As the $O_3^-$ density decreases the densities of the electrons and Cl$^-$ increase. Furthermore, it is observed that both $h$ and $T_h$ variations negligibly effect the SiO$_2$ density.
Chapter 5. Microwave $O_2$/$SiCl_4$ plasma: Global model

(a) The charged particle profiles with respect to the $SiCl_4$ percentage. A unique colour is assigned to each type: the electrons (black), the negative ions (blue), the Si based ions (red), O based positive ions (magenta), Cl based positive ions (green) and $ClO^+$ (brown).

(b) $Si$, $SiO$, $SiO_2$

Figure 5.4: The (volume-averaged) densities and the electron temperature at 250 W. The reactor is fed by a $O_2$/$SiCl_4$ mixture at various percentages: (a) The charged particles. (b) Silicon based deposition neutrals.
Figure 5.5: Behaviour of the dominant charged species with respect to $h$ and $T_h$ at 250 W power input for the $O_2/\text{SiCl}_4$ mixture with $\text{SiCl}_4$ fraction of $p = 5\%$.
Figure 5.6: The (volume-averaged) particle densities and the electron temperature at 250 W with a power modulation period of 100 ms and 50% duty ratio. The reactor is fed by O$_2$/SiCl$_4$ at $p = 5\%$: (a) Charged particles (b) deposition neutrals and electron temperature.
5.5 Conclusion

Figure 5.6 shows the dominant charged species, deposition neutrals and the electron temperature for 5% SiCl\textsubscript{4} dilution, during a power modulation at a 250W power input with a 100ms period and a 50% duty ratio. During the pulse on mode, the ion dominance does not change compared to the continuous power input. The electron density gradually decreases, whereas the electron temperature increases within the pulse on time. As the power is turned off, the electron temperature drops to the gas temperature in $0.1 \times 10^{-3}$ ms. The electrons completely recombine in about $5 \times 10^{-3}$ ms and afterwards a quasi-neutral ion-ion plasma appears in the reactor. The dominant ions are SiCl\textsuperscript{+} in positively and O\textsuperscript{−} in negatively charged species. In about $3 \times 10^{-3}$ ms the ion-ion plasma produces electrons mostly via reaction 48 with an electron density satisfying $n_{O^−}/n_e > 10^4$. For this plasma we impose the quasi-neutrality by applying the zero wall flux condition (equation 4.29) on these electrons (see equation 4.30). It should be emphasised that the ion wall recombination is ignored in the afterglow since their rates are defined for an electronic plasma with a power input. The plasma slowly vanishes by the recombination and the net mass flow rates. Si is created via electronic dissociation of SiCl and mutual recombination of Si\textsuperscript{+} with Cl\textsuperscript{−} and lost by ionisation and SiO creation. Its creation suddenly drops when the power is turned-off and it diminishes together with SiO due to SiO\textsubscript{2} production.

5.5 Conclusion

A microwave induced plasma that is confined inside a cylindrical reactor is simulated via a global (volume-averaged) model in both continuous and modulated power inputs. The plasma is fed by either pure O\textsubscript{2} or a O\textsubscript{2}/SiCl\textsubscript{4} mixture and the model parameters are determined from a 2-D model in chapter 6. Additionally, sensitivity analyses with respect to the sheath volume ion density ratio, $h$, and the gas temperature, $T_h$, are provided. In pure O\textsubscript{2} plasma, the model is initially used to reduce the chemical set to lower the computational load in the spatially resolved model. It is observed that excluding the species O\textsubscript{3}, O\textsubscript{3} and O\textsubscript{2} does not pose any significant difference in the rest of the quantities and a reduced set of species is proposed for the simulations. In return, the spatially resolved model improves the global model parameters and a comparison of their volume-averaged plasma quantities shows good agreement. The charged particles are sensitive with respect to the $h \in [0.0008:0.08]$ with a maximum ratio of 0.61, whereas the sensitivity to the $T_h$ is less pronounced. It should be emphasised that relatively smaller variations in these quantities do not significantly effect the dominant charged particles and the electron temperature. We observe that the pulse on time-averaged plasma quantities in the power modulation are comparable to those in the continuous mode. This suggests that smaller periods are necessary for a better time-averaged plasma efficiency. The O\textsubscript{2}/SiCl\textsubscript{4} mixture study forms a first step to construct a numerically stable chemical set in the studied parameter range and to define a pathway for a detailed investigation. The chemical set still requires further improvements or updates until an agreement of the particle densities are confirmed.

We observe that the electron energy losses due to the ion wall recombination at the wall is negligible compared to the volume energy losses. On the other hand, the ion wall recombination plays an essential role in the plasma quantities. As a consequence, a consistent
simulation requires a model which self-consistently determines the sheath to volume ion ratio, $h$. Furthermore, the wall reactions are, in general, strongly influential on the plasma, on the other hand their probabilities for a quartz wall are mostly absent or poorly approximated. Additionally, we do not include the essential reaction, SiO$_2$ deposition at the wall, which is far more complex than de-excitation and recombination processes.
5.A. Chemical kinetics

Appendix

5.A Chemical kinetics

The species that are included in the model are given in Table 5.A.1. All rates are in m³s⁻¹ unless stated otherwise. \( T_h \) in K and \( T_e \) in eV. They are mostly taken from [72], otherwise they are calculated from the cross-sections. The calculations are parametrically fit to a function and they are represented by the symbol “wire”. The reaction rate coefficients for electron impact collisions are calculated assuming a Maxwellian electron energy distribution function for a fit range of \( T_e = 0.01 - 10 \) eV. The rate coefficients for backward reactions are also calculated using detailed balancing [82, 72], these are denoted by the symbol “*”.

Table 5.A.1: Species included in the model with their energies [72, 116]

<table>
<thead>
<tr>
<th>Particle</th>
<th>( \mathcal{E} ) (eV)</th>
<th>Particle</th>
<th>( \mathcal{E} ) (eV)</th>
<th>Particle</th>
<th>( \mathcal{E} ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( O^- )</td>
<td>-0.64</td>
<td>Si</td>
<td>0</td>
<td>Cl⁻</td>
<td>-2.36</td>
</tr>
<tr>
<td>( O_2 )</td>
<td>-0.45</td>
<td>SiO</td>
<td>1.45</td>
<td>Cl₂</td>
<td>0</td>
</tr>
<tr>
<td>( O_2(a^1\Delta_g) )</td>
<td>0.98</td>
<td>SiO₂</td>
<td>3.32</td>
<td>Cl₂(v = 2)</td>
<td>0.14</td>
</tr>
<tr>
<td>( O^- )</td>
<td>1.1</td>
<td>SiCl₂</td>
<td>4.42</td>
<td>Cl₂(v = 3)</td>
<td>0.21</td>
</tr>
<tr>
<td>( O_2(b^3\Sigma^+_g) )</td>
<td>1.63</td>
<td>SiCl₄</td>
<td>4.78</td>
<td>Cl</td>
<td>1.25</td>
</tr>
<tr>
<td>( O_3(X^1\Sigma_g) )</td>
<td>1.46</td>
<td>SiCl₄</td>
<td>6.17</td>
<td>Cl₂⁺</td>
<td>11.50</td>
</tr>
<tr>
<td>( O(P) )</td>
<td>2.56</td>
<td>Si⁺</td>
<td>8.11</td>
<td>Cl⁺</td>
<td>14.25</td>
</tr>
<tr>
<td>( O_2(A^3\Sigma^+_g, A^3\Delta_u, c^1\Sigma^-_u) )</td>
<td>4.2</td>
<td>SiCl₂⁺</td>
<td>8.23</td>
<td>ClO⁻</td>
<td>6.51</td>
</tr>
<tr>
<td>( O(D) )</td>
<td>4.52</td>
<td>SiCl⁺</td>
<td>9.41</td>
<td>ClO⁺</td>
<td>17.41</td>
</tr>
<tr>
<td>( O_2^+ )</td>
<td>12.1</td>
<td>SiO⁺</td>
<td>12.88</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( O^+ )</td>
<td>16.16</td>
<td>SiO₂⁺</td>
<td>15.45</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cl₂⁺</td>
<td>17.40</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>SiCl₂⁺</td>
<td>18.78</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 5.A.2: Electron - Oxygen reactions

<table>
<thead>
<tr>
<th>#</th>
<th>Reaction</th>
<th>Rate Coefficient</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$e + O_2 \rightarrow O_2^+ + 2e$</td>
<td>$2.01 \times 10^{-15} T_e^{1.09} e^{12.41/T_e}$</td>
<td>[118]</td>
</tr>
<tr>
<td>2</td>
<td>$e + O_2 \rightarrow O(3P) + O^+ + 2e$</td>
<td>$1.04 \times 10^{-14} T_e^{-1.11} e^{-21.27/T_e}$</td>
<td>[118]</td>
</tr>
<tr>
<td>3</td>
<td>$e + O_2 \rightarrow O(3P) + O^-$</td>
<td>$1.12 \times 10^{-15} T_e^{-1.41} e^{-6.16/T_e}$</td>
<td>[119]</td>
</tr>
<tr>
<td>4</td>
<td>$e + O_2(a^1 \Delta_g) \rightarrow O(3P) + O^-$</td>
<td>$4.33 \times 10^{-15} T_e^{-1.39} e^{-5.17/T_e}$</td>
<td>[119]</td>
</tr>
<tr>
<td>5</td>
<td>$e + O_2(a^1 \Delta_g) \rightarrow O(1D) + O^-$</td>
<td>$1.01 \times 10^{-15} T_e^{-1.46} e^{-7.36/T_e}$</td>
<td>[119]</td>
</tr>
<tr>
<td>6</td>
<td>$e + O_2(A^3 \Sigma_g^+ \ldots) \rightarrow O(3P) + O^-$</td>
<td>$5.77 \times 10^{-16} T_e^{-0.90} e^{-0.12/T_e}$</td>
<td>[120]</td>
</tr>
<tr>
<td>7</td>
<td>$e + O(3P) \rightarrow O^+ + 2e$</td>
<td>$4.75 \times 10^{-15} T_e^{0.78} e^{-14.27/T_e}$</td>
<td>[121]</td>
</tr>
<tr>
<td>8</td>
<td>$e + O^- \rightarrow O(3P) + 2e$</td>
<td>$4.64 \times 10^{-14} T_e^{0.50} e^{-3.44/T_e}$</td>
<td>[122]</td>
</tr>
<tr>
<td>9</td>
<td>$e + O_2 \rightarrow O(3P) + O(1D) + e$</td>
<td>$8.45 \times 10^{-15} T_e^{0.38} e^{-11.84/T_e}$</td>
<td>[123]</td>
</tr>
<tr>
<td>10</td>
<td>$e + O_2 \rightarrow O(3P) + O(3P) + e$</td>
<td>$9.49 \times 10^{-16} T_e^{0.38} e^{-11.84/T_e}$</td>
<td>[124]</td>
</tr>
<tr>
<td>11</td>
<td>$e + O_2 \rightarrow O(1D) + O(1D) + e$</td>
<td>$9.49 \times 10^{-17} T_e^{0.38} e^{-11.84/T_e}$</td>
<td>[125]</td>
</tr>
<tr>
<td>12</td>
<td>$e + O_2 \rightarrow O^+ + O^- + e$</td>
<td>$4.12 \times 10^{-14} T_e^{-0.25} e^{-20.80/T_e}$</td>
<td>[126]</td>
</tr>
<tr>
<td>13</td>
<td>$e + O(3P) \rightarrow O(1D) + e$</td>
<td>$2.19 \times 10^{-14} T_e^{-0.57} e^{-4.10/T_e}$</td>
<td>[127]</td>
</tr>
<tr>
<td>14</td>
<td>$e + O_2 \rightarrow O_2(a^1 \Delta_g) + e$</td>
<td>$1.25 \times 10^{-14} T_e^{-0.97} e^{-5.51/T_e}$</td>
<td>[128]</td>
</tr>
<tr>
<td>15</td>
<td>$e + O_2 \rightarrow O_2(b^1 \Sigma_g^+ \ldots) + e$</td>
<td>$3.84 \times 10^{-15} T_e^{-1.05} e^{-5.71/T_e}$</td>
<td>[129]</td>
</tr>
<tr>
<td>16</td>
<td>$e + O_2 \rightarrow O_2(A^3 \Sigma_u^+ \ldots) + e$</td>
<td>$2.39 \times 10^{-14} T_e^{-1.00} e^{-9.52/T_e}$</td>
<td>[129]</td>
</tr>
<tr>
<td>17</td>
<td>$e + O_2(a^1 \Delta_g) \rightarrow O_2(b^1 \Sigma_g^+ \ldots) + e$</td>
<td>$6.69 \times 10^{-15} T_e^{-0.56} e^{-1.73/T_e}$</td>
<td>[129]</td>
</tr>
<tr>
<td>18</td>
<td>$e + O_2(a^1 \Delta_g) \rightarrow O_2(A^3 \Sigma_u^+ \ldots) + e$</td>
<td>$7.23 \times 10^{-14} T_e^{-1.25} e^{-7.63/T_e}$</td>
<td>[129]</td>
</tr>
<tr>
<td>19</td>
<td>$e + O_2(b^1 \Sigma_g^+ \ldots) \rightarrow O_2(A^3 \Sigma_u^+ \ldots) + e$</td>
<td>$8.47 \times 10^{-14} T_e^{-1.23} e^{-7.12/T_e}$</td>
<td>[129]</td>
</tr>
<tr>
<td>20</td>
<td>$e + O_3 \rightarrow O_2 + O^- $</td>
<td>$3.24 \times 10^{-15} T_e^{-0.94} e^{-0.91/T_e}$</td>
<td>[129]</td>
</tr>
<tr>
<td>21</td>
<td>$e + O_3 \rightarrow O(3P) + O_2^-$</td>
<td>$9.56 \times 10^{-16} T_e^{-1.26} e^{-0.95/T_e}$</td>
<td>[129]</td>
</tr>
<tr>
<td>22</td>
<td>$e + O_3 \rightarrow O_2 + O(3P) + e$</td>
<td>$1.42 \times 10^{-14} T_e^{-0.68} e^{-2.60/T_e}$</td>
<td>[130]</td>
</tr>
<tr>
<td>23</td>
<td>$e + O_3 \rightarrow O_2(a^1 \Delta_g) + O(3P) + e$</td>
<td>$4.16 \times 10^{-15} T_e^{-0.73} e^{-3.15/T_e}$</td>
<td>[130]</td>
</tr>
<tr>
<td>24</td>
<td>$e + O_3 \rightarrow O_2(a^1 \Delta_g) + O(1D) + e$</td>
<td>$6.68 \times 10^{-15} T_e^{-0.82} e^{-4.07/T_e}$</td>
<td>[130]</td>
</tr>
<tr>
<td>25</td>
<td>$e + O_3 \rightarrow O_2(b^1 \Sigma_g^+ \ldots) + O(1D) + e$</td>
<td>$1.34 \times 10^{-13} T_e^{-0.87} e^{-6.63/T_e}$</td>
<td>[130]</td>
</tr>
<tr>
<td>26</td>
<td>$e + O_2^+ \rightarrow O_2 + 2e$</td>
<td>$5.74 \times 10^{-14} T_e^{0.58} e^{-4.68/T_e}$</td>
<td>[131]</td>
</tr>
<tr>
<td>27</td>
<td>$e + O_3^- \rightarrow O_2 + 2e$</td>
<td>$3.43 \times 10^{-14} T_e^{0.22} e^{-8.81/T_e}$</td>
<td>[132]</td>
</tr>
<tr>
<td>28</td>
<td>$e + O_3^- \rightarrow O_2 + O(3P) + 2e$</td>
<td>$2.69 \times 10^{-14} T_e^{0.06} e^{-20.10/T_e}$</td>
<td>[132]</td>
</tr>
<tr>
<td>29</td>
<td>$e + O_3^- \rightarrow O_2 + O^- + e$</td>
<td>$3.67 \times 10^{-14} T_e^{-8.26/T_e}$</td>
<td>[132]</td>
</tr>
<tr>
<td>30</td>
<td>$e + O_2^+ \rightarrow O(3P) + O(1D)$</td>
<td>$2.20 \times 10^{-14} T_e^{-0.50}$</td>
<td>[133]</td>
</tr>
</tbody>
</table>
### 5.A. Chemical kinetics

#### Table 5.A.3: Oxygen - Oxygen reactions

<table>
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<th>#</th>
<th>Reaction</th>
<th>Rate Coefficient</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>31</td>
<td>$O_2^+ + O^- \rightarrow O_2 + O(^3P)$</td>
<td>$2.60 \times 10^{-14} (300/T_h)^{0.44}$</td>
<td>135</td>
</tr>
<tr>
<td>32</td>
<td>$O^+ + O^- \rightarrow 2O(^3P)$</td>
<td>$4.00 \times 10^{-14} (300/T_h)^{0.43}$</td>
<td>133</td>
</tr>
<tr>
<td>33</td>
<td>$O(^3P) + O^- \rightarrow O_2 + e$</td>
<td>$2.30 \times 10^{-16}$</td>
<td>134</td>
</tr>
<tr>
<td>34</td>
<td>$O_2 + O^+ \rightarrow O(^3P) + O_2^-$</td>
<td>$2.10 \times 10^{-17} (300/T_h)^{0.50}$</td>
<td>135</td>
</tr>
<tr>
<td>35</td>
<td>$O_2 + O(^1D) \rightarrow O_2 + O(^3P)$</td>
<td>$2.56 \times 10^{-17} e^{67/T_h}$</td>
<td>135</td>
</tr>
<tr>
<td>36</td>
<td>$O(^1P) + O(^1D) \rightarrow 2O(^3P)$</td>
<td>$8.00 \times 10^{-18}$</td>
<td>135</td>
</tr>
<tr>
<td>37</td>
<td>$O_2(a^1\Delta_g) + O^- \rightarrow O(^3P) + O_2^-$</td>
<td>$4.75 \times 10^{-17}$</td>
<td>134</td>
</tr>
<tr>
<td>38</td>
<td>$O_2^+ + O_2^- \rightarrow 2O_2$</td>
<td>$2.01 \times 10^{-13} (300/T_h)^{0.50}$</td>
<td>135</td>
</tr>
<tr>
<td>39</td>
<td>$O^+ + O_2^- \rightarrow O_2 + O(^3P)$</td>
<td>$2.70 \times 10^{-13} (300/T_h)^{0.50}$</td>
<td>135</td>
</tr>
<tr>
<td>40</td>
<td>$O(^3P) + O_2^- \rightarrow O_2 + O^-$</td>
<td>$3.31 \times 10^{-16}$</td>
<td>135</td>
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<tr>
<td>41</td>
<td>$O_2(a^1\Delta_g) + O_2^- \rightarrow 2O_2 + e$</td>
<td>$2.00 \times 10^{-16}$</td>
<td>134</td>
</tr>
<tr>
<td>42</td>
<td>$O_2 + O^- \rightarrow O_3 + e$</td>
<td>$5.00 \times 10^{-21}$</td>
<td>135</td>
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<tr>
<td>43</td>
<td>$O_2(a^1\Delta_g) + O^- \rightarrow O_3 + e$</td>
<td>$1.42 \times 10^{-16}$</td>
<td>134</td>
</tr>
<tr>
<td>44</td>
<td>$O_3 + O^+ \rightarrow O_2 + O^+_2$</td>
<td>$1.00 \times 10^{-16}$</td>
<td>135</td>
</tr>
<tr>
<td>45</td>
<td>$O(^1P) + O_3 \rightarrow 2O_2$</td>
<td>$1.81 \times 10^{-17} e^{-2300/T_h}$</td>
<td>135</td>
</tr>
<tr>
<td>46</td>
<td>$O_3 + O^- \rightarrow O(^3P) + O_3^-$</td>
<td>$5.30 \times 10^{-16}$</td>
<td>135</td>
</tr>
<tr>
<td>47</td>
<td>$O(^3P) + O_3^- \rightarrow O_2 + O_3^-$</td>
<td>$1.00 \times 10^{-16}$</td>
<td>135</td>
</tr>
<tr>
<td>48</td>
<td>$O(^3P) + O^-_3 \rightarrow 2O_2 + e$</td>
<td>$3.00 \times 10^{-16}$</td>
<td>135</td>
</tr>
<tr>
<td>49</td>
<td>$O_2^+ + O_3^- \rightarrow O_2 + O_3$</td>
<td>$2.00 \times 10^{-13} (300/T_h)^{0.50}$</td>
<td>135</td>
</tr>
<tr>
<td>50</td>
<td>$O_2^+ + O_3^- \rightarrow 2O(^3P) + O_3^-$</td>
<td>$1.01 \times 10^{-13} (300/T_h)^{0.50}$</td>
<td>135</td>
</tr>
<tr>
<td>51</td>
<td>$O_3 + O_2^- \rightarrow O_2 + O_3$</td>
<td>$4.00 \times 10^{-16}$</td>
<td>135</td>
</tr>
<tr>
<td>52</td>
<td>$O(^1P) + O_3^- \rightarrow O_3 + e$</td>
<td>$3.30 \times 10^{-16}$</td>
<td>135</td>
</tr>
<tr>
<td>53</td>
<td>$O_2 + O(^1D) \rightarrow O_2(a^1\Delta_g) + O(^3P)$</td>
<td>$1.00 \times 10^{-18}$</td>
<td>135</td>
</tr>
<tr>
<td>54</td>
<td>$O_2(b^1\Sigma_g^+ + O^- \rightarrow O_2 + O(^3P) + e$</td>
<td>$6.90 \times 10^{-16}$</td>
<td>135</td>
</tr>
<tr>
<td>55</td>
<td>$O_2(b^1\Sigma_g^+ + O(^3P) \rightarrow O_2(a^1\Delta_g) + O(^3P)$</td>
<td>$8.10 \times 10^{-20}$</td>
<td>135</td>
</tr>
<tr>
<td>56</td>
<td>$O_2 + O_2(a^1\Delta_g) \rightarrow 2O_2 + O(^3P)$</td>
<td>$3.79 \times 10^{-22} (300/T_h)^{-2.40} e^{-281/T_h}$</td>
<td>135</td>
</tr>
<tr>
<td>57</td>
<td>$O_2(a^1\Delta_g) + O(^3P) \rightarrow O_2 + O(^3P)$</td>
<td>$1.30 \times 10^{-22}$</td>
<td>135</td>
</tr>
<tr>
<td>58</td>
<td>$O_2^+ + O^- \rightarrow 3O(^3P)$</td>
<td>$2.60 \times 10^{-14} (300/T_h)^{0.44}$</td>
<td>133</td>
</tr>
<tr>
<td>59</td>
<td>$O_2 + O_2(a^1\Delta_g)$ \rightarrow 2O_2</td>
<td>$2.20 \times 10^{-24} (300/T_h)^{-0.80}$</td>
<td>135</td>
</tr>
<tr>
<td>60</td>
<td>$O_2(b^1\Sigma_g^+ \rightarrow O_2 + O(^3P) + O(^1D)$ \rightarrow O_2(b^1\Sigma_g^+ + O(^3P)$ \rightarrow O_2 + O(^3P)$</td>
<td>$1.35 \times 10^{-18}$</td>
<td>135</td>
</tr>
<tr>
<td>61</td>
<td>$O_2 + O_3 \rightarrow 2O_2 + O(^3P)$</td>
<td>$7.26 \times 10^{-16} e^{-1400/T_h}$</td>
<td>135</td>
</tr>
<tr>
<td>62</td>
<td>$O_2(a^1\Delta_g) + O_2(a^1\Delta_g) \rightarrow O_2 + O_2(b^1\Sigma_g^+)$</td>
<td>$1.80 \times 10^{-24} (300/T_h)^{3.80} e^{-700/T_h}$</td>
<td>135</td>
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<tr>
<td>63</td>
<td>$O_2(a^1\Delta_g) + O_2(a^1\Delta_g) \rightarrow 2O_2$</td>
<td>$5.50 \times 10^{-29} (300/T_h)^{-0.50}$</td>
<td>131</td>
</tr>
<tr>
<td>64</td>
<td>$O_2(b^1\Sigma_g^+ + O_3 \rightarrow 2O_2 + O(^3P)$</td>
<td>$1.50 \times 10^{-17}$</td>
<td>135</td>
</tr>
<tr>
<td>65</td>
<td>$O_2(a^1\Delta_g) + O_3 \rightarrow 2O_2 + O(^3P)$</td>
<td>$6.01 \times 10^{-17} e^{-2853/T_h}$</td>
<td>135</td>
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<tr>
<td>66</td>
<td>$O_2 + O_2(A^3\Sigma_g^+ \rightarrow 2O_2(b^1\Sigma_g^+)$</td>
<td>$2.90 \times 10^{-19}$</td>
<td>135</td>
</tr>
<tr>
<td>67</td>
<td>$O_2^+ + O_2^- \rightarrow 2O_2 + O(^3P)$</td>
<td>$1.01 \times 10^{-13} (300/T_h)^{0.50}$</td>
<td>135</td>
</tr>
<tr>
<td>68</td>
<td>$O_2(b^1\Sigma_g^+ \rightarrow O_2 + h\nu$</td>
<td>$6.251/s$</td>
<td>137</td>
</tr>
<tr>
<td>69</td>
<td>$O_2(A^3\Sigma_g^+ \rightarrow 2O_2 + O(^3P)$ \rightarrow O_2 + O(^3P)$</td>
<td>$4.95 \times 10^{-18}$</td>
<td>142</td>
</tr>
<tr>
<td>70</td>
<td>$O_2(A^3\Sigma_g^+ \rightarrow 2O_2 + O(^3P)$ \rightarrow O_2(a^1\Delta_g) + O(^1D)$</td>
<td>$2.70 \times 10^{-18}$</td>
<td>142</td>
</tr>
<tr>
<td>71</td>
<td>$2O_2(b^1\Sigma_g^+ \rightarrow O_2 + O_2(a^1\Delta_g)$</td>
<td>$3.60 \times 10^{-23} (300/T_h)^{0.50}$</td>
<td>135</td>
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</tbody>
</table>
Table 5.A.4: Three body reactions of oxygen in units of m^6s^{-1}

<table>
<thead>
<tr>
<th>#</th>
<th>Reaction</th>
<th>Rate Coefficient</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>72</td>
<td>$e + e + O^+ \rightarrow O(3P) + e$</td>
<td>$7.89 \times 10^{-39} T_e^{-4.50}$</td>
<td>[135]</td>
</tr>
<tr>
<td>73</td>
<td>$e + O_2 + O_2 \rightarrow O_2 + O^-$</td>
<td>$2.26 \times 10^{-42} T_e^{0.50}$</td>
<td>[139]</td>
</tr>
<tr>
<td>75</td>
<td>$O_2 + O(3P) + O(3P) \rightarrow O(3P) + O_3$</td>
<td>$2.15 \times 10^{-40} e^{345/T_h}$</td>
<td>[135]</td>
</tr>
<tr>
<td>76</td>
<td>$e + O_2 + O(3P) \rightarrow O(3P) + O_2^-$</td>
<td>$1.00 \times 10^{-43}$</td>
<td>[135]</td>
</tr>
<tr>
<td>77</td>
<td>$e + O_2 + O(3P) \rightarrow O_2 + O^-$</td>
<td>$1.00 \times 10^{-43}$</td>
<td>[135]</td>
</tr>
<tr>
<td>78</td>
<td>$e + O_2 + O^+ \rightarrow O_2 + O(3P)$</td>
<td>$1.00 \times 10^{-38}$</td>
<td>[135]</td>
</tr>
<tr>
<td>79</td>
<td>$O_2 + O_2 + O^- \rightarrow O_2 + O_3^-$</td>
<td>$1.00 \times 10^{-42} (300/T_h)$</td>
<td>[135]</td>
</tr>
<tr>
<td>80</td>
<td>$O_2 + O^+ + O^- \rightarrow O_2 + O_2$</td>
<td>$2.10 \times 10^{-37} (300/T_h)^{2.50}$</td>
<td>[135]</td>
</tr>
<tr>
<td>81</td>
<td>$O_2 + O_2^+ + O^- \rightarrow O_2 + O_3$</td>
<td>$2.01 \times 10^{-37} (300/T_h)^{2.50}$</td>
<td>[135]</td>
</tr>
<tr>
<td>82</td>
<td>$O_2 + O_2 + O(3P) \rightarrow O_2 + O_3$</td>
<td>$6.90 \times 10^{-46} (300/T_h)^{1.25}$</td>
<td>[135]</td>
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<tr>
<td>83</td>
<td>$O_2 + O(3P) + O(3P) \rightarrow O_2 + O_2 (A^3 \sum_u^+ ...)$</td>
<td>$1.20 \times 10^{-46}$</td>
<td>[140]</td>
</tr>
<tr>
<td>84</td>
<td>$O_2 + O_2 (a^1 \Delta_u) + O(3P) \rightarrow O_2 + O_2 + O(3P)$</td>
<td>$1.00 \times 10^{-44}$</td>
<td>[142]</td>
</tr>
<tr>
<td>85</td>
<td>$3O(3P) \rightarrow O_2 (a^1 \Delta_u) + O(3P)$</td>
<td>$1.93 \times 10^{-47} (300/T_h)^{0.63}$</td>
<td>[140]</td>
</tr>
<tr>
<td>86</td>
<td>$O_2 + O(3P) + O(3P) \rightarrow O_2 + O_2 (a^1 \Delta_u)$</td>
<td>$6.93 \times 10^{-47} (300/T_h)^{0.63}$</td>
<td>[140]</td>
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</table>
## 5.A. Chemical kinetics

### Table 5.A.5: Electron - Chlorine reactions

<table>
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<th>#</th>
<th>Reaction</th>
<th>Rate Coefficient</th>
<th>Ref</th>
</tr>
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<tbody>
<tr>
<td>87</td>
<td>$e + Cl_2(v = 0) \rightarrow Cl + Cl + e$</td>
<td>$1.04 \times 10^{-13} T_e^{-0.29} e^{-8.84/T_e}$</td>
<td>[93]</td>
</tr>
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<td>88</td>
<td>$e + Cl_2(v = 0) \rightarrow Cl^+_2 + 2e$</td>
<td>$5.12 \times 10^{-14} T_e^{-0.48} e^{-12.34/T_e}$</td>
<td>[84]</td>
</tr>
<tr>
<td>89</td>
<td>$e + Cl_2(v = 0) \rightarrow Cl + Cl^+ + 2e$</td>
<td>$2.14 \times 10^{-13} T_e^{-0.07} e^{-25.26/T_e}$</td>
<td>[84, 85]</td>
</tr>
<tr>
<td>90</td>
<td>$e + Cl_2(v = 0) \rightarrow Cl^+ + Cl^+ + 3e$</td>
<td>$2.27 \times 10^{-16} T_e^{-1.92} e^{-21.26/T_e}$</td>
<td>[84, 85]</td>
</tr>
<tr>
<td>91</td>
<td>$e + Cl_2(v = 0) \rightarrow Cl + Cl^-$</td>
<td>$3.43 \times 10^{-15} T_e^{-1.18} e^{-3.98/T_e}$</td>
<td>[86, 87]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$3.05 \times 10^{-16} T_e^{-1.33} e^{-0.11/(T_e+0.014)}$</td>
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</tr>
<tr>
<td>92</td>
<td>$e + Cl_2(v = 1) \rightarrow Cl + Cl^-$</td>
<td>$14.06 \times 10^{-15} T_e^{-1.18} e^{-3.98/T_e}$</td>
<td>[86, 87]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$12.51 \times 10^{-16} T_e^{-1.33} e^{-0.11/(T_e+0.014)}$</td>
<td></td>
</tr>
<tr>
<td>93</td>
<td>$e + Cl_2(v = 2) \rightarrow Cl + Cl^-$</td>
<td>$30.18 \times 10^{-15} T_e^{-1.18} e^{-3.98/T_e}$</td>
<td>[86, 87]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$26.84 \times 10^{-16} T_e^{-1.33} e^{-0.11/(T_e+0.014)}$</td>
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<tr>
<td>94</td>
<td>$e + Cl_2(v = 3) \rightarrow Cl + Cl^-$</td>
<td>$46.31 \times 10^{-15} T_e^{-1.18} e^{-3.98/T_e}$</td>
<td>[86, 87]</td>
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<tr>
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<td></td>
<td>$41.18 \times 10^{-16} T_e^{-1.33} e^{-0.11/(T_e+0.014)}$</td>
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<tr>
<td>95</td>
<td>$e + Cl_2(v = 0) \rightarrow Cl^+ + Cl^- + e$</td>
<td>$2.94 \times 10^{-16} T_e^{-0.19} e^{-18.79/T_e}$</td>
<td>[88, 89]</td>
</tr>
<tr>
<td>96</td>
<td>$e + Cl_2(v = 0) \rightarrow Cl_2(v = 1) + e$</td>
<td>$1.22 \times 10^{-16} T_e^{-0.99} e^{-0.49/T_e}$</td>
<td>[90] *</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$1.88 \times 10^{-16} e^{-((ln(T_e)+0.01)T_e)/1.10^2}$</td>
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</tr>
<tr>
<td>97</td>
<td>$e + Cl_2(v = 0) \rightarrow Cl_2(v = 2) + e$</td>
<td>$3.28 \times 10^{-17} T_e^{-1.12} e^{-0.37/T_e}$</td>
<td>[90] *</td>
</tr>
<tr>
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<td>$2.86 \times 10^{-17} e^{-((ln(T_e)+0.09)T_e)/1.06^2}$</td>
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<tr>
<td>98</td>
<td>$e + Cl_2(v = 0) \rightarrow Cl_2(v = 3) + e$</td>
<td>$1.30 \times 10^{-17} T_e^{-1.24} e^{-0.41/T_e}$</td>
<td>[90] *</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$6.08 \times 10^{-18} e^{-((ln(T_e)+0.94)T_e)/1.02^2}$</td>
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<tr>
<td>99</td>
<td>$e + Cl_2(v = 1) \rightarrow Cl_2(v = 2) + e$</td>
<td>$3.00 \times 10^{-16} T_e^{-1.00} e^{-0.37/T_e}$</td>
<td>[90] *</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$4.61 \times 10^{-16} e^{-((ln(T_e)+0.04)T_e)/1.02^2}$</td>
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<tr>
<td>100</td>
<td>$e + Cl_2(v = 2) \rightarrow Cl_2(v = 3) + e$</td>
<td>$3.00 \times 10^{-16} T_e^{-1.00} e^{-0.37/T_e}$</td>
<td>[90] *</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$4.61 \times 10^{-16} e^{-((ln(T_e)+0.04)T_e)/1.02^2}$</td>
<td></td>
</tr>
<tr>
<td>101</td>
<td>$e + Cl_2(v = 1) \rightarrow Cl_2(v = 3) + e$</td>
<td>$1.25 \times 10^{-16} T_e^{-1.13} e^{-0.36/T_e}$</td>
<td>[90] *</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$1.06 \times 10^{-16} e^{-((ln(T_e)+0.01)T_e)/1.06^2}$</td>
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<tr>
<td>102</td>
<td>$e + Cl_2^+ \rightarrow Cl + Cl$</td>
<td>$9.00 \times 10^{-14} T_e^{-0.50}$</td>
<td>[95]</td>
</tr>
<tr>
<td>103</td>
<td>$e + Cl \rightarrow Cl^+ + 2e$</td>
<td>$3.17 \times 10^{-14} T_e^{-0.53} e^{-13.29/T_e}$</td>
<td>[91, 92]</td>
</tr>
<tr>
<td>104</td>
<td>$e + Cl^- \rightarrow Cl + 2e$</td>
<td>$9.02 \times 10^{-15} T_e^{-0.92} e^{-4.88/T_e}$</td>
<td>[93]</td>
</tr>
<tr>
<td>105</td>
<td>$e + Cl^- \rightarrow Cl^+ + 3e$</td>
<td>$3.62 \times 10^{-15} T_e^{-0.72} e^{-25.38/T_e}$</td>
<td>[93]</td>
</tr>
<tr>
<td>106</td>
<td>$Cl^+_2 + Cl^- \rightarrow 3Cl$</td>
<td>$5.00 \times 10^{-14} (300/T_h)^{0.50}$</td>
<td>[94, 95]</td>
</tr>
<tr>
<td>107</td>
<td>$Cl^+ + Cl^- \rightarrow Cl + Cl$</td>
<td>$5.00 \times 10^{-14} (300/T_h)^{0.50}$</td>
<td>[94, 95]</td>
</tr>
<tr>
<td>108</td>
<td>$Cl_2(v = 0) + Cl^+ \rightarrow Cl + Cl^+_2$</td>
<td>$5.40 \times 10^{-16}$</td>
<td>[96]</td>
</tr>
<tr>
<td>109</td>
<td>$Cl_2(v = 1) + Cl^+ \rightarrow Cl + Cl^+_2$</td>
<td>$5.40 \times 10^{-16}$</td>
<td>[96]</td>
</tr>
<tr>
<td>110</td>
<td>$Cl_2(v = 2) + Cl^+ \rightarrow Cl + Cl^+_2$</td>
<td>$5.40 \times 10^{-16}$</td>
<td>[96]</td>
</tr>
<tr>
<td>111</td>
<td>$Cl_2(v = 3) + Cl^+ \rightarrow Cl + Cl^+_2$</td>
<td>$5.40 \times 10^{-16}$</td>
<td>[96]</td>
</tr>
<tr>
<td>112</td>
<td>$2Cl + Cl_2 \rightarrow Cl_2(v = 0) + Cl_2$</td>
<td>$3.50 \times 10^{-45} e^{-810/T_h}$</td>
<td>[97]</td>
</tr>
<tr>
<td>113</td>
<td>$2Cl + Cl \rightarrow Cl_2(v = 0) + Cl$</td>
<td>$8.75 \times 10^{-46} e^{-810/T_h}$</td>
<td>[95]</td>
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Table 5.A.6: Oxygen-Chlorine reactions

<table>
<thead>
<tr>
<th>#</th>
<th>Reaction</th>
<th>Rate Coefficient</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>114</td>
<td>( \text{Cl}^+ + { \text{O}_2, \text{O} } \rightarrow \text{Cl} + \text{O}_2^+ )</td>
<td>( 4.90 \times 10^{-16} )</td>
<td>[50]</td>
</tr>
<tr>
<td>115</td>
<td>( \text{Cl}_2 + \text{O}_2^+ \rightarrow \text{Cl}_2^+ + \text{O}_2 )</td>
<td>( 4.90 \times 10^{-16} )</td>
<td>[72]</td>
</tr>
<tr>
<td>116</td>
<td>( \text{Cl}_2 + \text{O}^+ \rightarrow \text{Cl}_2^+ + \text{O}(^3\text{P}) )</td>
<td>( 4.90 \times 10^{-16} )</td>
<td>[72]</td>
</tr>
<tr>
<td>117</td>
<td>( \text{Cl} + \text{O}^+ \rightarrow \text{Cl}^+ + \text{O}(^3\text{P}) )</td>
<td>( 4.90 \times 10^{-16} )</td>
<td>[72]</td>
</tr>
<tr>
<td>118</td>
<td>( \text{Cl}^- + \text{O}_2^+ \rightarrow \text{Cl} + \text{O}_2 )</td>
<td>( 5.00 \times 10^{-14}(300/T_h)^{0.50} )</td>
<td>[72]</td>
</tr>
<tr>
<td>119</td>
<td>( \text{Cl}^- + \text{O}^+ \rightarrow \text{Cl} + \text{O}(^3\text{P}) )</td>
<td>( 5.00 \times 10^{-14}(300/T_h)^{0.50} )</td>
<td>[72]</td>
</tr>
<tr>
<td>120</td>
<td>( \text{Cl}_2^+ + \text{O}^- \rightarrow 2\text{Cl} + \text{O}(^3\text{P}) )</td>
<td>( 2.60 \times 10^{-14}(300/T_h)^{0.44} )</td>
<td>[72]</td>
</tr>
<tr>
<td>121</td>
<td>( \text{Cl}^+ + \text{O}^- \rightarrow \text{Cl} + \text{O}(^3\text{P}) )</td>
<td>( 4.00 \times 10^{-14}(300/T_h)^{0.43} )</td>
<td>[72]</td>
</tr>
<tr>
<td>122</td>
<td>( \text{Cl}_2^+ + \text{O}_2^- \rightarrow 2\text{Cl} + \text{O}_2 )</td>
<td>( 2.01 \times 10^{-13}(300/T_h)^{0.50} )</td>
<td>[72]</td>
</tr>
<tr>
<td>123</td>
<td>( \text{Cl}^+ + \text{O}_2^- \rightarrow \text{Cl} + \text{O}_2 )</td>
<td>( 2.70 \times 10^{-13}(300/T_h)^{0.50} )</td>
<td>[72]</td>
</tr>
<tr>
<td>124</td>
<td>( \text{Cl}_2^+ + \text{O}^- \rightarrow 2\text{Cl} + \text{O}_3 )</td>
<td>( 2.00 \times 10^{-13}(300/T_h)^{0.50} )</td>
<td>[72]</td>
</tr>
<tr>
<td>125</td>
<td>( \text{Cl}^+ + \text{O}_2^- \rightarrow \text{Cl} + \text{O}_3 )</td>
<td>( 2.70 \times 10^{-13}(300/T_h)^{0.50} )</td>
<td>[72]</td>
</tr>
<tr>
<td>126</td>
<td>( \text{Cl}_2 + \text{O}_2(a^1\Delta_g) \rightarrow \text{Cl}_2 + \text{O}_2 )</td>
<td>( 2.20 \times 10^{-24}(300/T_h)^{-0.80} )</td>
<td>[72]</td>
</tr>
<tr>
<td>127</td>
<td>( \text{Cl}_2 + \text{O}_2(b^1\sum_g^+) \rightarrow \text{Cl}_2 + \text{O}_2(a^1\Delta_g) )</td>
<td>( 3.79 \times 10^{-22}(300/T_h)^{-2.40} e^{-281/T_h} )</td>
<td>[72]</td>
</tr>
<tr>
<td>128</td>
<td>( \text{Cl}_2 + \text{O}_2(A^3\sum_u^+, \ldots) \rightarrow 2\text{Cl} + \text{O}_2 )</td>
<td>( 2.00 \times 10^{-18} )</td>
<td>[151]</td>
</tr>
<tr>
<td>129</td>
<td>( \text{Cl}_2 + \text{O}(^1\text{D}) \rightarrow \text{Cl}_2 + \text{O}(^3\text{P}) )</td>
<td>( 7.00 \times 10^{-17} )</td>
<td>[152]</td>
</tr>
<tr>
<td>130</td>
<td>( \text{Cl} + \text{O}_2(a^1\Delta_g) \rightarrow \text{Cl} + \text{O}_2 )</td>
<td>( 1.30 \times 10^{-22} )</td>
<td>[72]</td>
</tr>
<tr>
<td>131</td>
<td>( \text{Cl} + \text{O}_2(b^1\sum_g^+) \rightarrow \text{Cl} + \text{O}_2(a^1\Delta_g) )</td>
<td>( 8.10 \times 10^{-20} )</td>
<td>[72]</td>
</tr>
<tr>
<td>132</td>
<td>( \text{Cl} + \text{O}_2(A^3\sum_u^+, \ldots) \rightarrow \text{Cl} + \text{O}_2 )</td>
<td>( 4.95 \times 10^{-18} )</td>
<td>[72]</td>
</tr>
<tr>
<td>133</td>
<td>( \text{Cl} + \text{O}(^1\text{D}) \rightarrow \text{Cl} + \text{O}(^3\text{P}) )</td>
<td>( 8.00 \times 10^{-18} )</td>
<td>[72]</td>
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</table>

Table 5.A.7: Chlorine monoxide based reactions

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<th>#</th>
<th>Reaction</th>
<th>Rate Coefficient</th>
<th>Ref</th>
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</thead>
<tbody>
<tr>
<td>134</td>
<td>( \text{e} + \text{ClO} \rightarrow \text{ClO}^+ + 2\text{e} )</td>
<td>( 9.48 \times 10^{-15}T_e^{0.85}e^{-12.24/T_h} )</td>
<td>[153]</td>
</tr>
<tr>
<td>135</td>
<td>( \text{e} + \text{ClO} \rightarrow \text{Cl} + \text{O}(^3\text{P}) + e^- )</td>
<td>( 1.27 \times 10^{-13}T_e^{-1.36} e^{-6.84/T_h} )</td>
<td>[154]</td>
</tr>
<tr>
<td>136</td>
<td>( \text{O}^+ + \text{ClO} \rightarrow \text{O}(^3\text{P}) + \text{ClO}^+ )</td>
<td>( 4.90 \times 10^{-16} )</td>
<td>[72]</td>
</tr>
<tr>
<td>137</td>
<td>( \text{O}_2^+ + \text{ClO} \rightarrow \text{O}_2 + \text{ClO}^+ )</td>
<td>( 4.90 \times 10^{-16} )</td>
<td>[72]</td>
</tr>
<tr>
<td>138</td>
<td>( \text{Cl}^+ + \text{ClO} \rightarrow \text{Cl} + \text{ClO}^+ )</td>
<td>( 4.90 \times 10^{-16} )</td>
<td>[72]</td>
</tr>
<tr>
<td>139</td>
<td>( \text{Cl}_2^+ + \text{ClO} \rightarrow \text{Cl}_2 + \text{ClO}^+ )</td>
<td>( 4.90 \times 10^{-16} )</td>
<td>[72]</td>
</tr>
<tr>
<td>140</td>
<td>( \text{Cl}^- + \text{ClO}^+ \rightarrow \text{Cl} + \text{ClO} )</td>
<td>( 5.00 \times 10^{-14}(300/T_h)^{0.50} )</td>
<td>[72]</td>
</tr>
<tr>
<td>141</td>
<td>( \text{O}^- + \text{ClO}^+ \rightarrow \text{O}(^3\text{P}) + \text{ClO}^- )</td>
<td>( 2.60 \times 10^{-14}(300/T_h)^{0.44} )</td>
<td>[72]</td>
</tr>
<tr>
<td>142</td>
<td>( \text{O}_2^- + \text{ClO}^+ \rightarrow \text{O}_2 + \text{ClO}^- )</td>
<td>( 2.01 \times 10^{-13}(300/T_h)^{0.50} )</td>
<td>[72]</td>
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<tr>
<td>143</td>
<td>( \text{O}_2^- + \text{ClO}^+ \rightarrow \text{O}_3 + \text{ClO}^- )</td>
<td>( 2.01 \times 10^{-13}(300/T_h)^{0.50} )</td>
<td>[72]</td>
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<tr>
<td>144</td>
<td>( \text{O}(^3\text{P}^1\text{D}) + \text{ClO} \rightarrow \text{Cl} + \text{O}_2 )</td>
<td>( 4.11 \times 10^{-17} e^{-42/T_h} )</td>
<td>[155]</td>
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<tr>
<td>145</td>
<td>( \text{Cl}_2 + \text{O}(^3\text{P}) \rightarrow \text{Cl} + \text{ClO} )</td>
<td>( 7.40 \times 10^{-18} e^{-1650/T_h} )</td>
<td>[152]</td>
</tr>
<tr>
<td>146</td>
<td>( \text{Cl}_2 + \text{O}(^1\text{D}) \rightarrow \text{Cl} + \text{ClO} )</td>
<td>( 2.11 \times 10^{-16} )</td>
<td>[152]</td>
</tr>
<tr>
<td>147</td>
<td>( \text{Cl} + \text{O}_2 \rightarrow \text{O}_2 + \text{Cl} )</td>
<td>( 2.49 \times 10^{-17} e^{-233/T_h} )</td>
<td>[155]</td>
</tr>
<tr>
<td>148</td>
<td>( 2\text{ClO} \rightarrow \text{Cl}_2 + \text{O}_2 )</td>
<td>( 6.38 \times 10^{-21} )</td>
<td>[156]</td>
</tr>
<tr>
<td>149</td>
<td>( 2\text{ClO} \rightarrow \text{Cl}_2 + 2\text{Cl} )</td>
<td>( 1.56 \times 10^{-20} )</td>
<td>[156]</td>
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Table 5.A.8: Silicon based reactions

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<th>Reaction</th>
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<th>Ref</th>
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<tbody>
<tr>
<td>150</td>
<td>$e + \text{SiCl}_4 \rightarrow \text{SiCl}_4^+ + 2e$</td>
<td>$5.913 \times 10^{-6} \frac{T_e}{e}^0.6324 \exp(-2.5/T_e) \cdot 1.8/T_e^2 \cdot 2.11/T_e^3$</td>
<td>157</td>
</tr>
<tr>
<td>151</td>
<td>$e + \text{SiCl}_4 \rightarrow \text{SiCl}_3 + \text{Cl} + e$</td>
<td>$7.27 \times 10^{-15} \exp(-4.73/T_e)$</td>
<td>95</td>
</tr>
<tr>
<td>152</td>
<td>$e + \text{SiCl}_4 \rightarrow \text{SiCl}_3^+ + \text{Cl} + 2e$</td>
<td>$2.0 \times 10^{-3} \exp(-12.44/T_e)$</td>
<td>95</td>
</tr>
<tr>
<td>153</td>
<td>$e + \text{SiCl}_3 \rightarrow \text{SiCl}_3^+ + 2e$</td>
<td>$2.427 \times 10^{-14} \exp(0.8603/T_e) \cdot 2.15/T_e - 1.8/T_e^2 - 0.9157/T_e^3$</td>
<td>157</td>
</tr>
<tr>
<td>154</td>
<td>$e + \text{SiCl}_3 \rightarrow \text{SiCl}_2 + \text{Cl} + e$</td>
<td>$7.27 \times 10^{-15} \exp(-2.91/T_e)$</td>
<td>95</td>
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<tr>
<td>155</td>
<td>$e + \text{SiCl}_3 \rightarrow \text{SiCl}_2^+ + \text{Cl} + 2e$</td>
<td>$4.90 \times 10^{-14} \exp(-13.9/T_e + 6.89/T_e - 1.45/T_e)$</td>
<td>95</td>
</tr>
<tr>
<td>156</td>
<td>$e + \text{SiCl}_2 \rightarrow \text{SiCl} + \text{Cl} + e$</td>
<td>$7.27 \times 10^{-15} \exp(-4.99/T_e)$</td>
<td>95</td>
</tr>
<tr>
<td>157</td>
<td>$e + \text{SiCl}_2 \rightarrow \text{SiCl}_2^+ + 2e$</td>
<td>$1.783 \times 10^{-14} \exp(0.85/T_e) \cdot 3.48/T_e - 0.15/T_e^2 - 0.35/T_e^3$</td>
<td>157</td>
</tr>
<tr>
<td>158</td>
<td>$e + \text{SiCl}_2 \rightarrow \text{SiCl}^+ \text{Cl} + 2e$</td>
<td>$8.93 \times 10^{-9.81/T_e}$</td>
<td>95</td>
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<tr>
<td>159</td>
<td>$e + \text{SiCl} \rightarrow \text{SiCl}^+ 2e$</td>
<td>$4.149 \times 10^{-14} \exp(0.506/T_e) \cdot 0.6991/T_e - 0.8909/T_e^2 - 0.9593/T_e^3$</td>
<td>157</td>
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<tr>
<td>160</td>
<td>$e + \text{SiCl} \rightarrow \text{Si} + \text{Cl} + e$</td>
<td>$7.27 \times 10^{-15} \exp(-3.95/T_e)$</td>
<td>95</td>
</tr>
<tr>
<td>161</td>
<td>$e + \text{SiCl} \rightarrow \text{Si}^+ + \text{Cl} + 2e$</td>
<td>$8.85 \times 10^{-14} \exp(-12.1/T_e)$</td>
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<tr>
<td>162</td>
<td>$e + \text{Si} \rightarrow \text{Si}^+ + 2e$</td>
<td>$1.089 \times 10^{-14} \exp(0.5385/T_e) \cdot 1.0/T_e - 3.0/T_e^2 - 2.0/T_e^3$</td>
<td>158</td>
</tr>
<tr>
<td>163</td>
<td>$e + \text{SiO} \rightarrow \text{SiO}^+ + 2e$</td>
<td>$1.145 \times 10^{-14} \exp(0.75/T_e) \cdot 10.5/T_e - 8.4/T_e^2 - 9.5/T_e^3$</td>
<td>158</td>
</tr>
<tr>
<td>164</td>
<td>$e + \text{SiO}_2 \rightarrow \text{SiO}_2^+ + 2e$</td>
<td>$1.116 \times 10^{-14} \exp(0.7943/T_e) \cdot 15.4/T_e - 5.8/T_e^2 - 7.6/T_e^3$</td>
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<tr>
<td>165</td>
<td>$\text{SiCl}_4^+ + \text{Cl}^- \rightarrow \text{SiCl}_4 + \text{Cl}$</td>
<td>$5.0 \times 10^{-14}$</td>
<td>95</td>
</tr>
<tr>
<td>166</td>
<td>$\text{SiCl}_3^+ + \text{Cl}^- \rightarrow \text{SiCl}_3 + \text{Cl}$</td>
<td>$5.0 \times 10^{-14}$</td>
<td>95</td>
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<tr>
<td>167</td>
<td>$\text{SiCl}_2^+ + \text{Cl}^- \rightarrow \text{SiCl}_2 + \text{Cl}$</td>
<td>$5.0 \times 10^{-14}$</td>
<td>95</td>
</tr>
<tr>
<td>168</td>
<td>$\text{SiCl}^+ + \text{Cl}^- \rightarrow \text{SiCl} + \text{Cl}$</td>
<td>$5.0 \times 10^{-14}$</td>
<td>95</td>
</tr>
<tr>
<td>169</td>
<td>$\text{Si}^+ + \text{Cl}^- \rightarrow \text{Si} + \text{Cl}$</td>
<td>$5.0 \times 10^{-14}$</td>
<td>95</td>
</tr>
<tr>
<td>170</td>
<td>$\text{Si}^+ + \text{SiCl}_4 \rightarrow \text{SiCl}_4^+ + \text{SiCl}_2$</td>
<td>$2.378 \times 10^{-17} \exp(1.71/T_e)$</td>
<td>159</td>
</tr>
<tr>
<td>171</td>
<td>$\text{Si}^+ + \text{SiCl}_4 \rightarrow \text{SiCl}_3^+ + \text{SiCl}_3$</td>
<td>$3.362 \times 10^{-17} \exp(1.71/T_e)$</td>
<td>159</td>
</tr>
<tr>
<td>172</td>
<td>$\text{Si}^+ + \text{SiCl}_4 \rightarrow \text{SiCl}_3^+ + \text{SiCl}$</td>
<td>$2.67 \times 10^{-17} \exp(1.71/T_e)$</td>
<td>159</td>
</tr>
<tr>
<td>173</td>
<td>$\text{Si} + \text{O}_2 \rightarrow \text{SiO} + \text{O}$</td>
<td>$3.964 \times 10^{-16} \exp(1.71/T_e)$</td>
<td>160</td>
</tr>
<tr>
<td>174</td>
<td>$\text{SiO} + \text{O}_2 \rightarrow \text{SiO}_2 + \text{O}$</td>
<td>$1.66 \times 10^{-17} \exp(-3271/T_e)$</td>
<td>117</td>
</tr>
<tr>
<td>175</td>
<td>$\text{SiCl}_4 \rightarrow \text{SiCl}_3 + \text{Cl}$</td>
<td>$1.7 \times 10^{11} \exp(-3.5764 \times 10^{-04}/T_h)$</td>
<td>161</td>
</tr>
</tbody>
</table>

Table 5.A.9: Elastic electronic collisions

<table>
<thead>
<tr>
<th>#</th>
<th>Collision</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$e + \text{O}_2$</td>
<td>162</td>
</tr>
<tr>
<td>2</td>
<td>$e + \text{O}$</td>
<td>163</td>
</tr>
<tr>
<td>3</td>
<td>$e + \text{O}_3$</td>
<td>139</td>
</tr>
<tr>
<td>4</td>
<td>$e + \text{Cl}$</td>
<td>80</td>
</tr>
<tr>
<td>5</td>
<td>$e + \text{Cl}_2$</td>
<td>164</td>
</tr>
<tr>
<td>6</td>
<td>$e + \text{SiCl}_4$</td>
<td>157</td>
</tr>
</tbody>
</table>
## Table 5.A.10: Neutral wall reactions

<table>
<thead>
<tr>
<th>#</th>
<th>Reaction</th>
<th>probability(γ)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cl + wall → $1/2\text{Cl}_2$</td>
<td>$1.5 \times 10^{-2}$</td>
<td>[69]</td>
</tr>
<tr>
<td>2</td>
<td>$\text{Cl}_2(v) + \text{wall} \rightarrow \text{Cl}_2(v - 1)$</td>
<td>1</td>
<td>[72]</td>
</tr>
<tr>
<td>3</td>
<td>$\text{O}^{(3P,1)}D + \text{wall} \rightarrow 1/2\text{O}_2$</td>
<td>0.09</td>
<td>[165]</td>
</tr>
<tr>
<td>4</td>
<td>$\text{O}^{(1D)} + \text{wall} \rightarrow \text{O}^{(3P)}$</td>
<td>0.1</td>
<td>[72]</td>
</tr>
<tr>
<td>5</td>
<td>$\text{O}_2(a^1\Delta_g) + \text{wall} \rightarrow \text{O}_2$</td>
<td>0.007</td>
<td>[165]</td>
</tr>
<tr>
<td>6</td>
<td>$\text{O}_2(b^1\Sigma_u^+) + \text{wall} \rightarrow \text{O}_2$</td>
<td>0.1</td>
<td>[72]</td>
</tr>
<tr>
<td>7</td>
<td>$\text{O}_2(A^3\Sigma_u^+,...) + \text{wall} \rightarrow \text{O}_2$</td>
<td>0.1</td>
<td>[72]</td>
</tr>
</tbody>
</table>
2-D model of a microwave reactor for optical fibre production: Plasma and confinement for the feeding gas of O$_2$
6.1 Introduction

Microwave (MW) induced plasmas attract attention due to their large scale applicability and electrode-less nature. The wave propagation allows broad power distribution that enlarges the plasma, whereas the absence of electrodes prevents any kind of pollution led by them. Such a feature also enhances their durability by avoiding limited electrode life time. Hence, they are commonly employed in scientific investigations as well as industrial applications, such as ion or radical formation [167, 168] and surface treatment [169]. In this work, we investigate such an industrial MW induced plasma application for the purpose of optical fibre production [115].

The optical fibre manufacturing process is composed of three successive steps: deposition, collapsing and drawing. The first step incorporates a microwave induced plasma for the purpose of deposition that is the main topic of this study and the last two transform the fibre to its final form. The deposition setup is schematically shown in Figure 6.1. The plasma actively creates a proper environment to deposit SiO$_2$ with the so called plasma activated chemical vapour deposition (PCVD) process [115]. The plasma is located inside a hollow quartz tube and deposition takes place on the inner surface. The tube is covered by a MW reactor that delivers the electromagnetic power in order to sustain the plasma. A furnace is placed over the setup to keep the ambient gas temperature fixed at 1500 K. This structure moves back and forth along the tube for a homogeneous deposition profile. It is fed by a O$_2$/SiCl$_4$ admixture with a net mass flow rate and the deposition product SiO$_2$ is formed inside the plasma.

Figure 6.1: Setup employed in PCVD process of SiO$_2$ for optical fibre production.

The setup allows surface wave propagation along the glass-plasma interface and the microwave power can be transmitted farther to the axial edge. In this respect, the plasma creates a proper boundary for the axial wave propagation as the wave mutually increases the plasma length. This is a crucial characteristic of a surface wave discharge [45] that enables it to expand...
6.1. Introduction

Figure 6.2: Power absorption percentage in Ar at 50 W power input with respect to the choke depth $d_c$. $P_{pl}$ represents the power percentage absorbed by the plasma, while $P_{tu}$ is absorbed by the tube. $P_t$ is the percentage transmitted to the setup and it is the sum of the radially ($P_r$) and axially transmitted power percentages ($P_{z,-}, P_{z,+}$). The power absorbed by the plasma peaks at $d_c = 38.5$ mm.

Axially to cover a larger deposition area. On the other hand, such an expansion is not desired in the setup since it disrupts the process by an inhomogeneous deposition pattern. In order to confine the plasma and to reach a higher power density, chokes are placed within the reactor (see Figure 6.3). In this chapter an optimum value of the choke depth is obtained that perfectly confines the discharge in the reactor and maximises the power absorption.

The deposition setup was first studied by Kuppers with a focus on the deposition process. The role of transport on the deposition layers is investigated analytically by Weling, where the chemical kinetics is reduced to one reaction. The first electromagnetic model is constructed by Rau et al., where the plasma transport and the chemical descriptions are absent. The first study that contain a self-consistent electromagnetic and an argon plasma model is carried out by van den Donker et al. This model is later improved by Jimenez-Diaz et al. and used for the choke depth optimisation in argon plasma, which is found to be $d_c = 38.5$ mm (see Figure 6.2).

The oxygen plasma significantly differs with that of argon due to its distinct chemical features. The former is a molecular gas as its dissociation produces a different neutral in the medium: Atomic oxygen. Depending on the operation parameters, one of these neutrals dominates the plasma and defines its characteristics. Furthermore, they produce multiple ions as well as excited atoms and molecules. These ions may be negatively charged due to the electronegative nature of oxygen. The chemical diversity in an oxygen plasma leads to larger energy absorption and reduces the degree of ionisation compared to an argon plasma,
Table 6.1: The operation parameters, where $\omega$ is the microwave frequency, $p$ is the total pressure, $P$ is the power input and $T^a$ is the ambient temperature.

<table>
<thead>
<tr>
<th>Par.</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\omega$</td>
<td>2.45 GHz</td>
</tr>
<tr>
<td>$p$</td>
<td>1000 Pa</td>
</tr>
<tr>
<td>$P$</td>
<td>250 – 400 W</td>
</tr>
<tr>
<td>$T^a$</td>
<td>1500 K</td>
</tr>
</tbody>
</table>

as a consequence, it may also alter the confinement. The diversity also complicates the ion transport via the ambipolar electric field as well as the chemical kinetics. Regarding these, we investigate pure O$_2$ plasma properties and its confinement in this work. This forms a first study to further analyse the actual deposition chemistry. The investigation is carried out by using a 2-D numerical model with a self-consistent electromagnetic description. We use a modular platform Plasimo [14] for the simulations.

This chapter is organised as follows. In section 6.2, we describe the physical model together with the boundary conditions and the computational domain, whereas the numerical approach is briefly discussed in section 6.3. The results are presented in section 6.4 and the conclusions are given in the last section.

### 6.2 Physical model

We use the first three moments of the Boltzmann equation [18] with a multi-fluid description of the plasma (see chapter 2). The description consists of stationary particle, momentum and energy balance equations for various species and it assumes that certain types of particles behave collectively as a single fluid. The chemical model incorporates oxygen species with a reaction set and it defines the source parameters in the balance equations. Additionally, the electromagnetic (EM) waves are coupled to the plasma by a self-consistent model of the Maxwell curl equations.

#### 6.2.1 Plasma fluid model

Each particle density with label $i$ is determined by a steady-state particle balance equation

$$\nabla \cdot (n_i v_b - D_i \nabla n_i) = S_i,$$  \hspace{1cm} (6.1)

where $n_i$ is the density, $v_b$ is the bulk velocity due to barycentric motion and $S_i$ is the net local source of all the chemical reactions. The calculation of the bulk velocity is explained below in the plasma bulk description. The second part at left-hand-side is the Fick expression for diffusive velocity and $D_i$ is the diffusion coefficient. For most of the particles, an effective
6.2. Physical model

diffusion coefficient $D_i^E$ applies [24]

$$D_i^E = p \left( \sum_{j \neq i} \frac{p_i}{D_{ij}} \right)^{-1}$$

(6.2)

where $p_i$ is the partial pressure, $p$ is the total pressure and $D_{ij}$ is the binary diffusion coefficient [3]. On the other hand, for charged particles the ambipolar electric field alters this coefficient and we use the multiple-ion Fick like diffusion coefficient $D_i^A$ [23] instead. Together with the assumption $\nabla n_i/n_i \approx \nabla n_e/n_e$ [26, 27]; the coefficient is written as

$$D_i^A = D_i \left( 1 + \frac{q_i e T_e}{T_i} \right)$$

(6.3)

where $q_i$ represents the particle charge, $e$ is the absolute electron charge and $T_i$ is the temperature. We refer to chapter [2] for the details of the derivation and the assumption. In this respect, the diffusion coefficient is defined with respect to the charge:

$$D_i = \begin{cases} D_i^E & \text{if } i \text{ represents a neutral or a negative ion} \\ D_i^A & \text{if } i \text{ represents a positive ion} \end{cases}$$

(6.4)

where we ignored ambipolar diffusion for negative ions. The electron density is not derived from the particle balance equation but from the charged particle densities via the quasi-neutrality assumption

$$n_e = \frac{1}{e} \sum_{j \neq e} q_j n_j.$$ 

(6.5)

We employ a two-temperature plasma description, one of which is assigned to electrons $T_e$ and the other to heavy particles $T_h$. It is based on the assumption that all the heavy particles are in thermal equilibrium, $T_{i\neq e} = T_h$. Within this formalism the electron temperature is governed by a steady-state electron energy balance equation

$$\nabla \cdot \left( \frac{3}{2} k_B n_e T_e \mathbf{v}_b \right) + p_e \nabla \cdot \mathbf{v}_b + \nabla \cdot \mathbf{q}_e = Q_e,$$

(6.6)

where $n_e$ is the electron density, $k_B$ is the Boltzmann constant, $p_e$ the partial electron pressure and $\mathbf{q}_e$ is the conductive heat flux. Here, the viscous dissipation of electrons [3] is neglected. As a caveat, this term can play a significant role on the energy balance at low pressure [172, 173], hence, its effect should be analysed priorly. The flux is defined via Fourier’s law [24]

$$\mathbf{q}_e = -\lambda_e \nabla T_e,$$

(6.7)

where $\lambda_e$ is the electron thermal conductivity. The conductivity is derived from the Frost mixture rules [174, 79].

The right hand side of equation (6.6) represents the local energy source and it features three distinct parts

$$Q_e = Q_{\text{Ohm}} - Q_{\text{inel}}^e - Q_{\text{elas}}^e.$$ 

(6.8)

The first term represents the ohmic power absorption and associates with the coupling between the plasma and the MW field. The second term is the energy sink that is induced by the
chemical interactions whereas the third term is the energy loss due to elastic collisions. We assume that all electrical power is coupled to the plasma via the electrons, therefore, the ohmic absorption is given by the relation \[ Q_{\text{Ohm}} = \frac{1}{2} \text{Re}(|\sigma|) |E|^2 \] (6.9)

where \( \sigma \) is a complex conductivity. The conductivity is obtained from the electron momentum balance equation with a cold plasma assumption \[ \sigma = \frac{\epsilon_0 \omega_p^2}{\nu_{eh} + i \omega} \] (6.10)

where \( \omega_p \) is the plasma and \( \omega \) is the wave frequency and \( \nu_{eh} \) is the total electron heavy particle momentum transfer frequency. The latter is the sum of the individual elastic momentum transfer frequencies \( \nu_{eh} = \sum_{e \neq j} \nu_{ej} \), where \( j \) labels the particle \[ Q_{\text{elas}}^e = \sum_r R_r \epsilon_r, \] (6.11)

where a reaction is represented by the subscript \( r \), with a rate \( R_r \) and an energy loss \( \epsilon_r \). Similarly, the elastic sink is the sum of energy losses over each electron heavy particle elastic collision \[ Q_{\text{elas}}^h = \sum_{j \neq e} \frac{3}{2} \nu_{ej} \left( \frac{m_e}{m_j} \right) k_B (T_e - T_h), \] (6.12)

where \( m \) is mass of the corresponding species.

The heavy particle particle temperature \( T_h \) is governed by a collective energy balance equation, which is acquired by summing each heavy particle energy balance equation

\[ \nabla \cdot \left( \sum_{j \neq e} \frac{3}{2} k_B T_h n_j v_b \right) + \sum_{j \neq e} p_j \nabla \cdot \mathbf{v}_b + \nabla \cdot \mathbf{q}_h = \tau : \nabla \mathbf{v}_b + Q_{\text{elas}}^e + Q_{\text{elas}}^h. \] (6.13)
6.2. Physical model

<table>
<thead>
<tr>
<th>O₂ plasma species</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂, O₂(a¹Δg), O₂(b¹⁰∑⁺⁺), O₂(A³∑⁺⁺, A³Δu, c³∑⁻⁻), O³(P), O(¹D), O⁺, O⁺₂, O⁻, e</td>
</tr>
</tbody>
</table>

Table 6.2: The distinct plasma species included in the model.

The conductive heat flux is

$$ \mathbf{q}_h = -\lambda_h \nabla T_h, \quad (6.14) $$

where $\lambda_h$ is the heavy particle thermal conductivity [79]. The viscous dissipation is represented by $\tau : \nabla \mathbf{v}_b$, where $\tau$ is the viscous stress tensor. Assuming a Newtonian fluid it is described by the equation [24]

$$ \tau : \nabla \mathbf{v}_b = 2\mu \left( \sum_{ij} \Gamma_{ij} \Gamma_{ij} - \frac{1}{3} (\nabla \cdot \mathbf{v}_b)^2 \right) \quad (6.15) $$

where $\Gamma_{ij}$ is the stress tensor and $\mu$ is the dynamic viscosity. Here, $Q^\text{elas}_h$ is the elastic losses, which is mentioned above, whereas $Q^\text{incl}_h$ represents the energy source due to the chemical reactions.

The collective behaviour of all species determines the plasma bulk properties. The total mass density is expressed by the relation $\rho = \sum_j m_j n_j$ and it is governed by the bulk mass balance equation. It is obtained by adding all individual mass weighted particle balances

$$ \nabla \cdot (\rho \mathbf{v}_b) = 0, \quad (6.16) $$

where the right hand side vanishes due to the mass conservation in the chemical reactions.

The plasma bulk velocity $\mathbf{v}_b$ and the total pressure $p$ are determined by the corresponding momentum balance equation with the assumption of laminar flow [25]:

$$ \nabla \cdot (\rho \mathbf{v}_b \mathbf{v}_b) = -\nabla p + \nabla \cdot \tau, \quad (6.17) $$

where the friction loss is absent due to the momentum conservation in the collisional processes. The gravitational force is neglected while a background static magnetic field is absent in the medium. Moreover, the electrical force vanishes because of the quasi-neutrality assumption. The viscous stress tensor for a Newtonian fluid is

$$ \tau_{ij} = 2\mu \left( \Gamma_{ij} - \frac{1}{3} (\nabla \mathbf{v}_b) \right), \quad (6.18) $$

The particle balance equations assign a unique partial pressure to each species via Dalton’s law for ideal gas $p_i = n_i k_B T_h$. Their sum also determines a total pressure $p_{PBE} = \sum_i p_i$, which may conflict with the one assessed by the bulk equation. In order to solve their disagreement, the most abundant particle density, which is O₂ in the setup, is adjusted so that both values are equal.
6.2.2 Chemical model

The plasma species included in the model are given in Table 6.2 and the energy diagram is depicted in Figure 6.A.1. We limited their number for an eligible simulation with a prior sensitivity analysis (see chapter 5). The excited species are also incorporated for chemical and thermal integrity as well as the charged particles, molecular and atomic oxygen. The corresponding reaction set is adapted from [72, 117], and the rate coefficients are provided in Tables 6.A.1, 6.A.2 and 6.A.3.

The electron induced reactions are shown in Table 6.A.1. The rate coefficients are numerically computed from the cross-sections for a Maxwellian electron energy distribution function. Their expressions are obtained through the parametric fitting to the numerical data with a range $T_e = 0.01 - 10$ eV. Among these, certain backward reactions are also included by imposing detailed balancing [117, 23]. The elastic electron heavy particle collision cross-sections frequencies are also presented in this table. These are computed differently compared to the chemical reactions [79]. The oxygen-oxygen reactions are given in the Table 6.A.2 while three body reactions are presented in the Table 6.A.3. The reactions induced by the quartz wall are also taken into account (see Table 6.A.4). They are implemented as a flux boundary condition in the model, and the details are discussed in section 6.2.4.
6.2. Physical model

<table>
<thead>
<tr>
<th>Par.</th>
<th>Inlet</th>
<th>Outlet</th>
<th>$r = R_p$</th>
<th>$z = 0$</th>
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<tbody>
<tr>
<td>$T_e$</td>
<td>$\frac{\partial T_e}{\partial z} = 0$</td>
<td>$\frac{\partial T_e}{\partial z} = 0$</td>
<td>$\frac{\partial T_e}{\partial r} = 0$</td>
<td>$\frac{\partial T_e}{\partial r} = 0$</td>
</tr>
<tr>
<td>$T_h$</td>
<td>$T_h = 1500K$</td>
<td>$\frac{\partial T_h}{\partial z} = 0$</td>
<td>$T_h = 1500K$</td>
<td>$\frac{\partial T_h}{\partial r} = 0$</td>
</tr>
<tr>
<td>$p$</td>
<td>1002 Pa</td>
<td>1000 Pa</td>
<td>$\frac{\partial p}{\partial r} = 0$</td>
<td>$\frac{\partial p}{\partial r} = 0$</td>
</tr>
<tr>
<td>$v_{b,z}$</td>
<td>$\frac{\partial v_{b,z}}{\partial z} = 0$</td>
<td>$\frac{\partial v_{b,z}}{\partial z} = 0$</td>
<td>$\frac{\partial v_{b,z}}{\partial r} = 0$</td>
<td>$\frac{\partial v_{b,z}}{\partial r} = 0$</td>
</tr>
<tr>
<td>$v_{b,r}$</td>
<td>$v_{b,r} = 0$</td>
<td>$\frac{\partial v_{b,r}}{\partial z} = 0$</td>
<td>$v_{b,r} = 0$</td>
<td>$\frac{\partial v_{b,r}}{\partial r} = 0$</td>
</tr>
</tbody>
</table>

Table 6.3: The boundary conditions.

6.2.3 Electromagnetic model

The electromagnetic model is composed of the Maxwell curl equations \[15\] in a complex notation \[43\]. With the assumption that the time dependence is harmonic $e^{i\omega t}$, they are

$$
\nabla \times \mathbf{E} + i\omega \mu_0 \mathbf{H} = 0
$$

$$
\nabla \times \mathbf{H} - i\omega \varepsilon_0 \varepsilon_r \mathbf{E} = \mathbf{J},
$$

where $\varepsilon_r$ is the relative permittivity, $\mathbf{J}$ is the charge current and $\mathbf{E}, \mathbf{H}$ are complex electric and magnetic fields respectively. The field divergences disappear due to the quasi-neutrality, hence, the rest of the Maxwell equations are not solved. Moreover, we assume that the plasma is a non-magnetic, linear and dissipative medium. Using Ohm’s law for this type of medium $\mathbf{J} = \hat{\sigma} \mathbf{E}$, we acquire

$$
\nabla \times \mathbf{E} + ik_0 \mathbf{H} = 0,
$$

$$
\nabla \times \mathbf{H} - ik_0 \varepsilon_r \mathbf{E} = 0,
$$

where $k_0 = \omega \sqrt{\varepsilon_0 \mu_0}$ is the free space wavenumber, $\mathbf{H} = i \sqrt{\mu_0 / \varepsilon_0} \mathbf{H}$ is the normalised magnetic field, and $\varepsilon_r$ is the complex relative permittivity.

$$
\varepsilon_r = \begin{cases}
1 & \text{air} \\
4 & \text{quartz (estimated)} \\
\varepsilon_r - i \frac{\hat{\sigma}}{\omega \varepsilon_0} & \text{plasma}.
\end{cases}
$$

In the discretisation we use the integral form of these equations.

6.2.4 Boundary conditions

We assume that the setup is axially symmetric and neglect the rotational variation. In this respect, the computational domain reduces to the two-dimensional cross section of the reactor as shown in Figure 6.3. The domain includes four different regions with distinct electrical properties: metal, air, quartz tube and plasma, see Figure 6.4.

The chemical and plasma models are only applied to the plasma region with four types of boundaries: quartz wall, symmetry axis, inlet and outlet. The boundary conditions are given
in Table 6.3. Among these, the quartz wall is essential for the surface wave propagation and the wall induced reactions. The cylindrical symmetry axis represents the axial symmetry with a homogeneous Neumann boundary condition (hN-BC). At the quartz plasma boundary, we fixed the O$_2^+$ density to $1.0 \times 10^{17}$ m$^{-3}$ and that of O$^-$ to $1.0 \times 10^{15}$ m$^{-3}$, in order to eliminate electromagnetic sheath-resonance [176]. Moreover, the flux towards this boundary is set according to the wall reactions [174]

$$-D_i \left( \frac{\partial n_i}{\partial r} \right) \bigg|_{r=R_p} = \gamma_i n_i v_{i,r} \bigg|_{r=R_p}$$

(6.22)

where the subscript $i$ labels the particle, $\gamma_i$ is the wall reaction probability - see Table 6.A.4 - and $v_{i,r}$ is the radial velocity. The velocity is characterised by the particle charge: it is either the thermal velocity for the neutral particles or the Bohm velocity for the ions

$$v_{i,r} \bigg|_{r=R_p} = \begin{cases} \left( \frac{8k_B T_i}{\pi m_i} \right)^{1/2} & \text{if } i \text{ is neutral} \\ \left( \frac{8k_B T_e}{\pi m_i} \right)^{1/2} & \text{if } i \text{ is ion.} \end{cases}$$

(6.23)

The electron temperature fulfils the hN-BC at the boundaries that impose the continuity. Similarly, the heavy particle temperature satisfies the hN-BC, however, it is set to 1500 K at the quartz wall and the inlet. The pressure is fixed at 1002 Pa on the inlet boundary and it is set to 1000 Pa at the outlet. The difference in the pressure boundary conditions creates a slight mass flow along the symmetry axis.

The bulk velocity components satisfy various types of BCs relying on the boundary itself. At the quartz wall, the so called no-slip BC [170] is utilised, i.e., both components are set to zero. At the other boundaries, the $z$ component $v_{b,z}$ satisfies the hN-BC, while the radial component $v_{b,r}$ vanishes except at the outlet. At the outlet, we assume that the radial bulk velocity fulfils the hN-BC.

The electromagnetic model is applied to the whole computational domain except the metal region. Its outer boundary is divided into four types: excitation, metal, propagation boundaries and the symmetry axis. The MW field is introduced to the reactor at the excitation boundary (see Figure 6.4), where we set the initial value of $E_z$ ($z$ component of the electric field). It is rescaled at each iteration according to the power input [177]. We assume that the metal is a perfect electrical conductor and electric field component parallel to its surface is set to zero. The propagation boundary is an artificial edge that limits the computational domain and its duties are to transmit the MW field and prevent any non-physical reflections. We apply the propagation BC [177] at this surface, which is also known as absorbing BC [48]. Similar to plasma boundaries, the symmetry axis imitates the axial symmetry with the hN-BC on $E_z$. The inner boundaries also exist in the domain due to the interfaces between plasma, quartz and air. The corresponding BC for such discontinuities in the media is derived from the integral form of the Maxwell divergence equations [43], with the assumption that surface charges and currents are absent.
6.3 Numerical approach

All equations are discretised via the finite difference method \cite{28} and iteratively solved until a predefined convergence criterion is met. In this section, we briefly discuss the techniques employed for these procedures.

Two distinct discretisation approaches are employed in EM and plasma models. We use the control volume approach \cite{28} to discretise the plasma model equations. This technique simply integrates the balance equation over each nodal volume, and hence, different quantities are placed at diverse positions in the nodal cell. While fluxes are positioned at the boundary, source and density are placed at the centre of the cell. We employ the Yee grid cell approach \cite{41} in the discretisation of EM equations. This scheme is also characterised by its unique placement of the vector field components in the nodal cells \cite{178}: The radial electric field $E_r$ is placed at the axial and $E_z$ is positioned at the radial boundaries, while $H_\phi$ is placed at the centre of the Yee cell. Such an arrangement significantly simplifies the implementation of the EM BCs.

The computation commences with the initialisation of the grid, boundary conditions and various dependent parameters, such as densities, temperatures and flow. At the first step, a main loop starts with calculation of the transport coefficients and the source parameters by the chemical model. Afterwards, the EM model acquires inelastic collision frequencies, calculated in the previous step. These frequencies are crucial in the coupling between plasma and EM fields, since they define the plasma conductivity. All source parameters are available when the EM model determines the ohmic source. Following this, the plasma bulk equations are solved with the SIMPLE algorithm \cite{28}. At the last step of the loop, species balance

![Flow chart of the main iterative scheme.](image-url)
6.4 Results

The deposition reactor is simulated for the operation parameters given in Table 6.1. We firstly investigate the plasma confinement at 250 W of power input and determine the optimum choke depth in oxygen. The comparison with the argon confinement is also provided in this context. Secondly, the plasma is analysed at the optimum choke depth as its chemical, electrical, thermal and transport features are revealed. The role of the power increment is also shown with a power input fixed at 400 W.

6.4.1 Confinement

We simulated the reactor at various choke depths for the power input of 250 W. They are chosen among the values, for which the power absorption percentage changes considerably in Ar plasma (see Figure 6.2). The power absorption percentage within the reactor shows a similar profile with Ar (see Figure 6.3). On the other hand, about 84% of the power is already consumed in the O₂ plasma, even without chokes. This increases up to 99% around 38 mm and peaks at the optimum choke depth \( d_c = 38.5 \) mm. Certain electron density profiles along the symmetry axis are shown in Figure 6.7. The chokes confine the plasma, which otherwise expands outside the reactor. On the other hand, at \( d_c = 51 \) mm, they have negligible effect. The confinement maximises at \( d_c = 38.5 \) mm with significant increment in the electron density.
6.4. Results

Figure 6.7: The electron density profile along the symmetry axis at 250 W for different choke depths. The red line above the figure represents the reactor dimensions in mm, while the shorter lines show the chokes and central slit. Note that the profiles for \( d_c = 38 \text{ mm} \) and \( d_c = 38.7 \text{ mm} \) are virtually identical.

Around this value, at \( d_c = 38.7 \text{ mm} \) or \( d_c = 37 \text{ mm} \) the plasma slightly enlarges outwards. The chokes also alter the spatial distribution of the plasma. In addition to the increase in electron density, the wide and dense central column is broken into three equal columns.

6.4.2 Plasma features

The spatial resolutions of the charged particle densities, the electron and the heavy particle temperatures with power input 250 W and choke depth \( d_c = 38.5 \text{ mm} \) are shown in Figure 6.8. The plasma is composed of three similar columns that connect with conic wells. Its axial boundary is defined by the chokes with a strict confinement between them. The maxima are not located on the axis but radially shifted towards the quartz wall, which is more obvious for the positive ion \( \text{O}^+ \). The plasma core is surrounded by a highly electronegative shell, with a central degree of electronegativity fixed around \( n_{O^-}/n_e = 0.32 \). The radial charged particle profiles at the axial centre (\( z = 250 \text{ mm} \)) are shown in Figure 6.9. A Bessel like radial profile associates with a diffusion controlled regime, where the particles shape with a dominant transport [4, 179]. Since these profiles do not fit a Bessel function the plasma is in a source controlled regime, where the charged particles are dominantly governed by the local source, while the diffusive velocity is negligible.

The charged particle distributions are mere imitations of each other. The dominant ion is \( \text{O}_2^+ \), while the \( \text{O}^+ \) density is the smallest with a ratio of 1/7. The electrons dominate the equivalent negative charge density, whereas the negative ions share 1/3 of this. The main creation mechanism of \( \text{O}_2^+ \) is the ionisation of molecular oxygen, while \( \text{O}^- \) is primarily
Figure 6.8: Spatial distributions of the basic plasma quantities at 250 W power input and at the optimum choke depth $d_c = 38.5$ mm: $e$, O$^+$, O$^+_2$, O$^-$ densities, electron and gas temperatures. The red line above the figures represents the reactor dimensions in mm, while the shorter lines show the chokes and central slit.
produced by the dissociative attachment of $O_2$ and $O_2(a^1\Delta_g)$, reactions 3 and 4 of Table 6.A.1, respectively. The small amount of $O^+$ is created equally by reactions 7 and 12 of Table 6.A.1. The electron temperature is quite flat within the reactor and shows a steep decline at the axial plasma boundary. It is about 2 eV at the axis and barely surpasses this at the quartz wall. The gas temperature peaks at the symmetry axis with a maximum of 2200 K and parabolically decreases towards the radial wall.

The spatially averaged plasma frequency $\omega_p \approx 15\omega$, and that of total elastic collision frequency is approximately $\nu_{eh} \approx \omega$. For these values, the average skin depth for the MW penetration is $5\text{mm}$ \textsuperscript{180}. Since it is comparable to the radial plasma dimensions, the electromagnetic fields inside the plasma do not completely vanish. Furthermore, the relative permittivity satisfies $\epsilon_r \leq -25$, i.e., the plasma behaves inductively.

The neutral particle densities at 250 W and $d_c = 38.5\text{mm}$ are shown in Figure 6.10. Molecular oxygen is the dominant background species, which constitutes about 70% of the plasma at the centre. It is inversely proportional to the electron density and increases over 90% in every direction. Atomic oxygen forms less than 10% of the plasma at the centre, with a maximum degree of dissociation $n_O/n_{O^+} + 2n_{O_2} = 0.13$. The dominant excited level density belongs to $O_2(a^1\Delta_g)$, which owns quite flat spatial distribution. Its lower probability of de-excitation at the quartz wall play significant role on the flat profile. Its density is followed by $O_2(b^1\Sigma_g^+)$, $O_2(A^3\Sigma_u^+, A^3\Delta_u, c^1\Sigma_u^-)$ and finally $O(^1D)$. 

Figure 6.9: The radial profiles of charged particles at 250 W and $z = 250\text{mm}$. Note that $e$, $O^+$ and $O^-$ densities are given by the left axis while the $O^+$ density is shown on the right.
Figure 6.10: Spatial distributions of the neutral particle densities at 250W and at the optimum choke depth $d_c = 38.5$ mm. The number of the particle is given as (1) $O_2$, (2) $O(3P)$, (3) $O_2(a^1\Delta_g)$, (4) $O(1D)$, (5) $O_2(b^1\Sigma^+_g)$, (6) $O_2(A^3\Sigma^+_u, A^3\Delta_u, c^3\Sigma_u^-)$. The red line above the figures represents the reactor dimensions in mm, while the shorter lines show the chokes and central slit.
Figure 6.11: Spatial distributions of the basic plasma quantities at 400 W at the optimum choke depth \( d_c = 38.5 \text{ mm} \): \( e \), \( \text{O}^+ \), \( \text{O}_2^+ \), \( \text{O}^- \) densities, electron and gas temperatures. The red line above the figures represents the reactor dimensions in mm, while the shorter lines show the chokes and central slit.
6.4.3 Higher power input

The reactor is also simulated at 400 W for \( d_c = 38.5 \text{ mm} \) and the resulting charged particle densities, the electron and the heavy particle temperatures are shown in figure 6.11. Most of the charged particles increase with a factor of 1.3 compared to the lower power input, while the deviation from Bessel profile is amplified. The central degree of electronegativity did not change considerably, whereas the electronegative shell has shrunk slightly. The molecular excited levels barely changes with the power and the degree of dissociation has increased up to 0.20 at the centre. This increment corresponds to a ratio of 1.8 in the atomic oxygen density. Since \( \text{O}^+ \) and \( \text{O}^1(D) \) are mainly produced from atomic oxygen, their density increased with a ratio of 2. The atomic oxygen density increases; however, molecular oxygen still dominates with a density percentage above 50%. The electron temperature did not change while the gas is heated up to 2900 K.

6.5 Conclusion

The simulations show that the optimum value of the choke depth is \( d_c = 38.5 \text{ mm} \) and otherwise the plasma expands out of the reactor. At this value, the plasma is fully confined within the chokes and its boundary is strictly defined by them. Interestingly, the optimum choke depth in an oxygen plasma is very similar to that in an argon plasma (see Figure 6.2). The reason for this is that the electromagnetic fields feel the same shielding in both cases and very similar wavelength has appeared for their axial propagation.

The optimised chokes further reshape the spatial plasma profiles as three equivalent columns and increase the electron density. The neutral density profiles, except that of \( \text{O}_2 \), mostly resemble that of electrons since they are mainly created by the electron induced reactions. This also means that they are mainly governed by the local source rather than the transport. Most of the power is absorbed near the quartz boundary. However, the MW power is still transmitted into the plasma due to plasma dimension that is comparable to the skin depth. The electron temperature is mainly determined by the power absorbed per electron, hence, it increases at the quartz wall mostly due to the smaller electron density. The plasma has a unique gas heating mechanism with elastic electron-heavy particle collisions and heavy particle quenching. In this application, it is obvious that the coupling of electromagnetic fields to the plasma allows further heating inside the tube, which would not be possible using a simpler burner.

In the model, we assume that any positively charged particle \( i \) satisfies \( \nabla n_i/n_i \approx \nabla n_e/n_e \). This assumption relies on the fact that their profiles shape similarly \( 26, 27 \). This simply circumvents the numerical difficulties that arise in implementing multiple ion Fick-like diffusion \( 23 \), with a cost of less consistent diffusive description. The resulting profiles agree with this assumption and they further suggest a source dominated plasma rather than diffusion. As a consequence, the effect of ambipolar diffusion can be negligible. The role of the ambipolar field on the negative ion diffusion is completely neglected (see appendix 2.B in chapter 2) and the negative ions are chemically present in the model. The profile leads the electropositive
core and electronegative shell of the plasma. This is in contrast with the glow discharge \[181\] and radio-frequency plasmas \[38\]; however, a similar electronegativity profile is also observed in MW plasmas \[182\]. In this form, the ambipolar diffusion is poorly incorporated and the validity of these charged particle profiles requires a model that self-consistently implements it for all ions \[183\].

An electromagnetic sheath resonance \[176\] occurs at \( \omega_p = \omega \), which corresponds to a critical electron density \( n_{e,c} = 7.41 \times 10^{16} \text{ m}^{-3} \). The electromagnetic model cannot cope with the resonant fields and it restrains the implementation of any flux boundary conditions for the dominant ions \[174\], \[76\], \[181\]. As a consequence, Dirichlet boundary conditions are applied for these ions, such that quasi-neutrality imposes an electron density that exceeds the critical value, \( n_{e,c} \). Within this constraint, lower O\(^-\) Dirichlet boundary conditions do not alter the plasma properties. Furthermore, in the electromagnetic model, we only included the dominant mode that is axially symmetric. The effect of the higher order modes can be discussed together with a three-dimensional EM model.

We assumed a Maxwellian electron energy distribution function while a decrease in its tail, i.e., absence of energetic electrons, can appear in MW plasmas \[184\]. In order to observe its role a kinetic model (Boltzmann solver) should be applied.
Appendix

6.A Chemical kinetics

In this section, we provide the reactions and their rates that are used in the model. They are divided into four categories: (1) the electron-oxygen, (2) oxygen-oxygen, (3) three-body and (4) wall reactions. Some of the backward reactions are included by applying the detailed balancing [82]. The electronic reactions are valid for $0.1 \text{ eV} < T_e < 10 \text{ eV}$.

Figure 6.A.1: Energy level diagram of $\text{O}_2$ plasma species.
### 6.A. Chemical kinetics

Table 6.A.1: Electron - Oxygen reactions provided from [72]. The rate units are $m^3 s^{-1}$, while the unit of eV is used for $T_e$. The rates are valid between 0.1 eV and 10 eV. The symbol \( \ast \) specifies the reactions, where the detailed balancing is used [22].

<table>
<thead>
<tr>
<th>#</th>
<th>Reaction</th>
<th>Rate</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$e + O_2 \rightarrow O_2^+ + 2e$</td>
<td>$2.01 \times 10^{-15}T_e^{1.09} \exp(-12.41/T_e)$</td>
<td>[118]</td>
</tr>
<tr>
<td>2</td>
<td>$e + O_2 \rightarrow O(3P) + O^+ + 2e$</td>
<td>$1.04 \times 10^{-14}T_e^{1.11} \exp(-21.27/T_e)$</td>
<td>[119]</td>
</tr>
<tr>
<td>3</td>
<td>$e + O_2 \rightarrow O(3P) + O^-$</td>
<td>$1.12 \times 10^{-15}T_e^{-1.41} \exp(-6.16/T_e)$</td>
<td>[119]</td>
</tr>
<tr>
<td>4</td>
<td>$e + O_2(a^1\Delta_u) \rightarrow O(3P) + O^-$</td>
<td>$4.33 \times 10^{-15}T_e^{-1.35} \exp(-5.17/T_e)$</td>
<td>[119]</td>
</tr>
<tr>
<td>5</td>
<td>$e + O_2(a^1\Delta_g) \rightarrow O(1D) + O^-$</td>
<td>$1.01 \times 10^{-15}T_e^{-1.46} \exp(-7.36/T_e)$</td>
<td>[119]</td>
</tr>
<tr>
<td>6</td>
<td>$e + O_2(A^3\sum_u^+, A^3\Delta_u, c^3\sum_u^-) \rightarrow O(3P) + O^-$</td>
<td>$5.77 \times 10^{-16}T_e^{-0.99} \exp(-0.12/T_e)$</td>
<td>[121]</td>
</tr>
<tr>
<td>7</td>
<td>$e + O(3P) \rightarrow O^+ + 2e$</td>
<td>$4.75 \times 10^{-15}T_e^{0.78} \exp(-14.27/T_e)$</td>
<td>[121]</td>
</tr>
<tr>
<td>8</td>
<td>$e + O^- \rightarrow O(3P) + 2e$</td>
<td>$4.64 \times 10^{-14}T_e^{0.50} \exp(-3.44/T_e)$</td>
<td>[122]</td>
</tr>
<tr>
<td>9</td>
<td>$e + O_2 \rightarrow O(3P) + O(1D) + e$</td>
<td>$8.45 \times 10^{-15}T_e^{0.38} \exp(-11.84/T_e)$</td>
<td>[123]</td>
</tr>
<tr>
<td>10</td>
<td>$e + O_2 \rightarrow O(3P) + O(3P) + e$</td>
<td>$9.49 \times 10^{-16}T_e^{0.38} \exp(-11.84/T_e)$</td>
<td>[123]</td>
</tr>
<tr>
<td>11</td>
<td>$e + O_2 \rightarrow O(1D) + O(1D) + e$</td>
<td>$9.49 \times 10^{-17}T_e^{0.38} \exp(-11.84/T_e)$</td>
<td>[123]</td>
</tr>
<tr>
<td>12</td>
<td>$e + O_2 \rightarrow O^+ + O^- + e$</td>
<td>$4.12 \times 10^{-14}T_e^{-0.25} \exp(-20.80/T_e)$</td>
<td>[123]</td>
</tr>
<tr>
<td>13</td>
<td>$e + O(3P) \rightarrow O(1D) + e$</td>
<td>$2.19 \times 10^{-14}T_e^{-0.57} \exp(-4.10/T_e)$</td>
<td>[125]</td>
</tr>
<tr>
<td>14</td>
<td>$e + O_2 \rightarrow O_2(a^1\Delta_u) + e$</td>
<td>$1.25 \times 10^{-14}T_e^{-0.97} \exp(-5.51/T_e)$</td>
<td>[125]</td>
</tr>
<tr>
<td>15</td>
<td>$e + O_2 \rightarrow O_2(b^1\sum_u^+ + e$</td>
<td>$3.84 \times 10^{-15}T_e^{-1.05} \exp(-5.71/T_e)$</td>
<td>[126]</td>
</tr>
<tr>
<td>16</td>
<td>$e + O_2 \rightarrow O_2(A^3\sum_u^+, A^3\Delta_u, c^3\sum_u^- + e$</td>
<td>$2.39 \times 10^{-14}T_e^{-1.06} \exp(-9.52/T_e)$</td>
<td>[127]</td>
</tr>
<tr>
<td>17</td>
<td>$e + O_2(a^1\Delta_u) \rightarrow O_2(b^1\sum_u^+ + e$</td>
<td>$6.69 \times 10^{-15}T_e^{-0.54} \exp(-1.73/T_e)$</td>
<td>[128]</td>
</tr>
<tr>
<td>18</td>
<td>$e + O_2(a^1\Delta_u) \rightarrow O_2(A^3\sum_u^+, A^3\Delta_u, c^3\sum_u^- + e$</td>
<td>$7.23 \times 10^{-14}T_e^{-1.25} \exp(-7.63/T_e)$</td>
<td>[128]</td>
</tr>
<tr>
<td>19</td>
<td>$e + O_2(b^1\sum_u^+ \rightarrow O_2(A^3\sum_u^+, A^3\Delta_u, c^3\sum_u^- + e$</td>
<td>$8.47 \times 10^{-14}T_e^{-1.23} \exp(-7.12/T_e)$</td>
<td>[128]</td>
</tr>
<tr>
<td>20</td>
<td>$e + O_2 \rightarrow O(3P) + O(1D)$</td>
<td>$2.20 \times 10^{-14}T_e^{-0.50}$</td>
<td>[133]</td>
</tr>
<tr>
<td>E1</td>
<td>$e + O_2 \rightarrow e + O_2$</td>
<td></td>
<td>[135]</td>
</tr>
<tr>
<td>E2</td>
<td>$e + O \rightarrow e + O$</td>
<td></td>
<td>[169]</td>
</tr>
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Table 6.A.2: Oxygen-Oxygen reactions provided by \[72, 117\]. The rate units are m\(^3\)s\(^{-1}\) and \(T_h\) unit is K, unless otherwise stated.

<table>
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<th>Reaction</th>
<th>Rate</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>21</td>
<td>(O_2^+ + O^- \rightarrow O_2 + O(3P))</td>
<td>(2.60 \times 10^{-14}(300/T_h)^{0.44})</td>
<td>133</td>
</tr>
<tr>
<td>22</td>
<td>(O(1D) + O_2 \rightarrow O(3P) + O_2)</td>
<td>(3.20 \times 10^{-17}\exp(-67.0/T_h))</td>
<td>117</td>
</tr>
<tr>
<td>23</td>
<td>(O(1D) + O \rightarrow O(3P))</td>
<td>(4.00 \times 10^{-17})</td>
<td>132</td>
</tr>
<tr>
<td>24</td>
<td>(O^+ + O^- \rightarrow 2O(3P))</td>
<td>(4.00 \times 10^{-14}(300/T_h)^{0.43})</td>
<td>133</td>
</tr>
<tr>
<td>25</td>
<td>(O_2^+ + O \rightarrow O(3P) + O_2)</td>
<td>(2.10 \times 10^{-17}(300/T_h)^{0.50})</td>
<td>133</td>
</tr>
<tr>
<td>26</td>
<td>(O_2 + O(1D) \rightarrow O_2 + O(3P))</td>
<td>(2.56 \times 10^{-17}\exp(67/T_h))</td>
<td>133</td>
</tr>
<tr>
<td>27</td>
<td>(O(3P) + O(1D) \rightarrow 2O(3P))</td>
<td>(8.00 \times 10^{-18})</td>
<td>133</td>
</tr>
<tr>
<td>28</td>
<td>(O_2 + O(1D) \rightarrow O_2(a^1\Delta_g) + O(3P))</td>
<td>(1.00 \times 10^{-18})</td>
<td>133</td>
</tr>
<tr>
<td>29</td>
<td>(O_2(b^1\Sigma^+_g) + O^- \rightarrow O_2 + O(3P) + e)</td>
<td>(6.90 \times 10^{-16})</td>
<td>133</td>
</tr>
<tr>
<td>30</td>
<td>(O_2(b^1\Sigma^+_g) + O(3P) \rightarrow O_2(a^1\Delta_g) + O(3P))</td>
<td>(8.10 \times 10^{-20})</td>
<td>133</td>
</tr>
<tr>
<td>31</td>
<td>(O_2 + O_2(b^1\Sigma^+_g) \rightarrow O_2 + O_2(a^1\Delta_g))</td>
<td>(3.79 \times 10^{-22}(300/T_h)^{-2.40}\exp(-281/T_h))</td>
<td>133</td>
</tr>
<tr>
<td>32</td>
<td>(O_2(a^1\Delta_g) + O(3P) \rightarrow O_2 + O(3P))</td>
<td>(1.30 \times 10^{-22})</td>
<td>133</td>
</tr>
<tr>
<td>33</td>
<td>(O_2^+ + O^- \rightarrow 3O(3P))</td>
<td>(2.60 \times 10^{-14}(300/T_h)^{0.44})</td>
<td>133</td>
</tr>
<tr>
<td>34</td>
<td>(O_2 + O_2(a^1\Delta_g) \rightarrow 2O_2)</td>
<td>(2.20 \times 10^{-24}(300/T_h)^{-0.80})</td>
<td>133</td>
</tr>
<tr>
<td>35</td>
<td>(O_2(A^3\Sigma^+_u, A^3\Delta_u, c^1\Sigma^-_u) + O(3P) \rightarrow O_2(b^1\Sigma^+_g) + O(1D))</td>
<td>(1.35 \times 10^{-18})</td>
<td>133</td>
</tr>
<tr>
<td>36</td>
<td>(O_2(a^1\Delta_g) + O_2(a^1\Delta_g) \rightarrow O_2 + O_2(b^1\Sigma^+_g))</td>
<td>(1.80 \times 10^{-24}(300/T_h)^{3.40}\exp(700/T_h))</td>
<td>133</td>
</tr>
<tr>
<td>37</td>
<td>(O_2(a^1\Delta_g) + O_2(a^1\Delta_g) \rightarrow 2O_2)</td>
<td>(5.50 \times 10^{-29}(300/T_h)^{-0.50})</td>
<td>133</td>
</tr>
<tr>
<td>38</td>
<td>(O_2 + O_2(A^3\Sigma^+_u, A^3\Delta_u, c^1\Sigma^-_u) \rightarrow O_2(b^1\Sigma^+_g))</td>
<td>(2.90 \times 10^{-19})</td>
<td>133</td>
</tr>
<tr>
<td>39</td>
<td>(O_2(A^3\Sigma^+_u, A^3\Delta_u, c^1\Sigma^-_u) \rightarrow O_2 + \hbar\nu)</td>
<td>(6.251/s)</td>
<td>133</td>
</tr>
<tr>
<td>40</td>
<td>(O_2(A^3\Sigma^+_u, A^3\Delta_u, c^1\Sigma^-_u) + O(3P) \rightarrow O_2 + O(0P))</td>
<td>(4.95 \times 10^{-18})</td>
<td>133</td>
</tr>
<tr>
<td>41</td>
<td>(O_2(A^3\Sigma^+_u, A^3\Delta_u, c^1\Sigma^-_u) + O(3P) \rightarrow O_2(a^1\Delta_g) + O(1D))</td>
<td>(2.70 \times 10^{-18})</td>
<td>133</td>
</tr>
<tr>
<td>42</td>
<td>(2O_2(b^1\Sigma^+_g) \rightarrow O_2 + O_2(a^1\Delta_g))</td>
<td>(3.60 \times 10^{-23}(300/T_h)^{0.50})</td>
<td>133</td>
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</table>

Table 6.A.3: Three body reactions given in \[72\]. The rate units are m\(^6\)s\(^{-1}\) and \(T_h\) unit is K.

<table>
<thead>
<tr>
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<th>Rate</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>43</td>
<td>(e + e + O^+ \rightarrow O(3P) + e)</td>
<td>(7.89 \times 10^{-39}T_h^{-4.50})</td>
<td>133</td>
</tr>
<tr>
<td>44</td>
<td>(e + O_2 + O(3P) \rightarrow O_2 + O^-)</td>
<td>(1.00 \times 10^{-43})</td>
<td>133</td>
</tr>
<tr>
<td>45</td>
<td>(e + O_2 + O^+ \rightarrow O_2 + O(3P))</td>
<td>(1.00 \times 10^{-38})</td>
<td>133</td>
</tr>
<tr>
<td>46</td>
<td>(O_2 + O^+ + O^- \rightarrow O_2 + O_2)</td>
<td>(2.10 \times 10^{-37}(300/T_h)^{2.50})</td>
<td>133</td>
</tr>
<tr>
<td>47</td>
<td>(O_2 + 2O(3P) \rightarrow O_2 + O_2(A^3\Sigma^+_u, A^3\Delta_u, c^1\Sigma^-_u))</td>
<td>(1.20 \times 10^{-46})</td>
<td>133</td>
</tr>
<tr>
<td>48</td>
<td>(O_2 + O_2(a^1\Delta_g) + O(3P) \rightarrow O_2 + O_2 + O(3P))</td>
<td>(1.00 \times 10^{-44})</td>
<td>133</td>
</tr>
<tr>
<td>49</td>
<td>(3O(3P) \rightarrow O_2(a^1\Delta_g) + O(3P))</td>
<td>(1.93 \times 10^{-47}(300/T_h)^{0.63})</td>
<td>133</td>
</tr>
<tr>
<td>50</td>
<td>(O_2 + 2O(3P) \rightarrow O_2 + O_2(a^1\Delta_g))</td>
<td>(6.93 \times 10^{-47}(300/T_h)^{0.63})</td>
<td>133</td>
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Table 6.A.4: The wall reactions which is provided from [72].

<table>
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<th>Ref</th>
</tr>
</thead>
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<tr>
<td>W1</td>
<td>$O(^3P,^1D) + \text{wall} \rightarrow 1/2O_2$</td>
<td>0.09</td>
<td>[165]</td>
</tr>
<tr>
<td>W2</td>
<td>$O_2(a^1\Delta_u) + \text{wall} \rightarrow O_2$</td>
<td>0.007</td>
<td>[166]</td>
</tr>
<tr>
<td>W3</td>
<td>$O_2(b^1\Sigma^+_u) + \text{wall} \rightarrow O_2$</td>
<td>0.1</td>
<td>[72]</td>
</tr>
<tr>
<td>W4</td>
<td>$O_2(A^3\sum^+_u, A^3\Delta_u, c^3\sum^-_u) + \text{wall} \rightarrow O_2$</td>
<td>0.1</td>
<td>[72]</td>
</tr>
<tr>
<td>W5</td>
<td>$O^+ + \text{wall} \rightarrow O_2$</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>
Chapter 6. Microwave $O_2$ plasma: 2-D model
Low dimensional manifolds


Chapter 7. Low dimensional manifolds

7.1 Introduction

In the multi-fluid description of the plasma, behaviour of each species is described by the particle, momentum, and energy balance equations [79]. For a model that contains all these equations, even three distinct species create a significant amount of computational load in the numerical simulations; therefore, long simulation times emerge. In order to prevent this, the number of equations or their complexity are reduced wherever possible via delicate assumptions, occasionally with a cost of accuracy. For example, the momentum balances are reduced to a simpler form by physical assumptions on the collision frequencies in the drift-diffusion formulation [21, 22]. Another example is the two-temperature models that assign one temperature to the electrons and another to the heavy particles [19, 187]. In simple terms, this assignment reduces all the heavy particle heat transport to a single common expression.

Even though the energy and momentum balance equations are neglected the numerical load becomes enormous, if a large number of species is present in the model. In general, these species are also strongly coupled to each other due to entangled networks of the chemical reactions. For example, a mercury plasma that is commonly employed in lighting purposes is such a system due to the role of numerous excited mercury atoms on the light emission [188]. Any model of the plasma should include these excited levels in addition to the ground and ion states and the electrons. In order to reduce the set of balance equations, the system is treated with the so called Collisional Radiative Models (CRM) defined in [189]. The model realises the reduction by the quasi-steady state (QSS) assumption on certain excited levels.

Mathematically, the problem is not restricted to plasma science but numerous other disciplines also struggle with these issues. In these disciplines, similar approaches are also noticeable among the model implementations. For example, QSS assumptions are also employed in mathematical biology [190] and chemical physics [191]. A system that shares identical difficulties is the combustion flame, where various particles interact in numerous chemical reactions. Models in this field commonly simplify the chemical kinetics with a few types of approaches. As well as the QSS assumptions, complex mathematical techniques that are invariant of the chemical kinetics are developed in these models. The system is not evenly sensitive to all reactions, but certain reactions are not effective and can be neglected. The Principal component analysis technique systematically investigates the system sensitivity with respect to the reactions and excludes the insignificant ones [192]. If a species only interacts with these excluded reactions, it can be ignored to reduce the number of equations. A chemical system is characterised by an equilibrium density configuration and it contains invariant quantities such as the net atom number. In mathematical form these configurations and the invariant quantities describe a low dimensional manifold in density space (see Figure 7.1). The Intrinsic Low-Dimensional Manifold (ILDM) technique determines these manifolds and use them to reduce the number of equations [193].

This chapter serves as an introduction to the notions of the low dimensional manifolds, and specifically, their identification in ILDM method is the main concern. These notions are inspirational and useful tools that are employed in chapter 8. The similarities of the manifold concept with density constraints in plasma models are also shown in the context. Furthermore, we discuss the applicability of the ILDM technique on plasma models. We introduce a notation
in section 7.2 then identify and discuss the low dimensional manifolds in section 7.3. We use a simplified system to further understand and visualise the manifolds in section 7.4 and provide discussion in 7.5.

7.2 Notation

In this chapter, we consider a set of coupled particle balance equations. For a species labelled $i$, it is given by the expression

$$\frac{\partial n_i}{\partial t} + \nabla \cdot \vec{\Gamma}_i = S_i,$$  \hspace{1cm} (7.1)
Chapter 7. Low dimensional manifolds

where \( n_i \) represents the particle density, \( \vec{\Gamma}_i \) the flux density, and \( S_i \) is the net source. For the sake of simplicity, we use a matrix notation for these quantities

\[
\mathbf{n} = \begin{pmatrix} n_1 \\ n_2 \\ \vdots \\ n_N \end{pmatrix}, \quad \mathbf{S} = \begin{pmatrix} S_1 \\ S_2 \\ \vdots \\ S_N \end{pmatrix}, \quad \vec{\nabla} \cdot \vec{\Gamma} = \begin{pmatrix} \vec{\nabla} \cdot \vec{\Gamma}_1 \\ \vec{\nabla} \cdot \vec{\Gamma}_2 \\ \vdots \\ \vec{\nabla} \cdot \vec{\Gamma}_N \end{pmatrix},
\]

so a compact form of the set of equations is acquired

\[
\frac{\partial \mathbf{n}}{\partial t} + \vec{\nabla} \cdot \vec{\Gamma} = \mathbf{S}. \tag{7.2}
\]

The source term \( \mathbf{S} \), plays an important role in the following analysis, since it describes the chemical reactions between the species. In this respect, the role of the transport is neglected to identify the low dimensional manifolds in the ILDM technique. This simply converts the set of partial differential equations into the set of ordinary differential equations

\[
\frac{\partial \mathbf{n}}{\partial t} = \mathbf{S}. \tag{7.3}
\]

7.3 Low dimensional manifolds

In a closed system, a reaction equilibrates within a characteristic time-scale and conserves certain physical quantities such as the net amount of mass, the number of atoms and the total electrical charge. The equilibrium condition is characterised by a density configuration and it can be given by a mathematical expression \( f(\mathbf{n}) = 0 \), where \( f \) is a function of the density vector. The particle densities satisfy this expression whenever the reaction equilibrates. Similarly, the conserved quantities can be mathematically expressed by a function \( g(\mathbf{n}) = 0 \) and the particle densities always respect such a relation. For a set of species, reacting with numerous entangled networks, identification of the conserved quantities and the net equilibrium channels in the whole system is not always straightforward. In simple terms, the ILDM technique exposes a form of such quantities \( \{ f, g \} \) and uses the corresponding constraints \( f(\mathbf{n}) = 0 \) and \( g(\mathbf{n}) = 0 \) to reduce the number of treated differential equations. The method can be divided into two successive steps: (1) Identify these density configurations of a system and (2) use them to reduce the number of differential equations. In this chapter, we focus on the first step and refer to [194] for the second step.

In general, a source \( \mathbf{S} \), may contain nonlinear terms due to the reactions involving three or more reactants. Firstly, this is dealt with a linearisation around a density vector \( \mathbf{n}_0 \) \[28\]

\[
\mathbf{S}(\mathbf{n}) = \mathbf{S}(\mathbf{n}_0) + \mathbf{M}(\mathbf{n} - \mathbf{n}_0), \tag{7.4}
\]

where \( \mathbf{M} \) is the Jacobian matrix. Furthermore, assuming that the Jacobian is diagonalisable, it satisfies

\[
\mathbf{M} = \mathbf{VAV}^{-1}, \tag{7.5}
\]
Table 7.1: The behaviour of the pseudo densities with respect to the eigenvalues, the corresponding density configurations and types.

<table>
<thead>
<tr>
<th>Eigenvalue Behaviour</th>
<th>Density configuration</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda_i = 0$</td>
<td>$\bar{n}<em>i - \bar{n}</em>{i,0} = 0$</td>
<td>$(V^{-1}n)_i - (V^{-1}n_0)_i = 0$</td>
</tr>
<tr>
<td>$Re(\lambda_i) &lt; 0$</td>
<td>$\lim_{t \to \infty} \bar{S}_i = 0$</td>
<td>$\lim_{t \to \infty} (V^{-1}S)_i = 0$</td>
</tr>
</tbody>
</table>

where $V$ contains the left eigenvectors and $\Lambda$ is a diagonal matrix whose elements correspond to the eigenvalues $\Lambda = \text{diag}(\lambda_1, \lambda_2, \cdots \lambda_N)$.

Left multiplying the density vector $n$ with $V^{-1}$, we define a corresponding vector in the diagonal basis $\bar{n} = V^{-1}n$. This vector is a linear combination of the original densities and for the sake of clarity we call its elements pseudo densities. Similarly, the source in the diagonal basis is defined by the expression $\bar{S} = V^{-1}S$ that satisfies the linearised relation

$$\bar{S} = \bar{S}(\bar{n}_0) + \Lambda [\bar{n} - \bar{n}_0].$$

Left multiplying equation (7.6) with $V^{-1}$ and considering a time-scale in which the eigenvectors and the eigenvalues are steady we acquire the particle balance equations in the diagonal basis

$$\frac{\partial \bar{n}}{\partial t} = \bar{S}(\bar{n}_0) + \Lambda [\bar{n} - \bar{n}_0].$$

In equation (7.7), the coupling between distinct pseudo densities is absent and a pseudo density with label $i$ analytically satisfies

$$\bar{n}_i = \bar{n}_{i,0} + \frac{\bar{S}_i(\bar{n}_{i,0})}{\lambda_i} (e^{\lambda_i t} - 1),$$

where the eigenvalue $\lambda_i$ defines the time dependent behaviour. The eigenvalues that are zero relate with the conserved quantities in the system [194], for which $\bar{S}_i(\bar{n}_{i,0}) = 0$. The corresponding pseudo densities scale with the conserved quantities and define the density configurations $\bar{n}_i - \bar{n}_{i,0} = 0$. Complex eigenvalues, however, do not reflect physical reality, but may appear during the iterative calculations and the complex component creates an oscillatory behaviour. A positive real part, $Re(\lambda_i) > 0$ implies an exponential growth and a negative value $Re(\lambda_i) < 0$ represents an exponential decay. The latter possesses a characteristic decay time-scale $1/|Re(\lambda_i)|$ and its source asymptotically vanishes. This defines an equilibrium condition for a reaction network $\lim_{t \to \infty} S_i(t) = 0$ in the system. Asymptotically vanishing sources and the conserved quantities constrain the possible states of the pseudo species and determine a density configuration of the chemical equilibrium. The pseudo species that define the density configurations are shown in Table 7.1.

The density configurations $\{f, g\}$, represent a low dimensional structure in density space, e.g., a 2-D surface or a 1-D line inside a 3-D density space. In a broader sense, the structure is called a manifold [195] giving name to the method Intrinsic Low Dimensional Manifold. Such a structure is also known as slow manifold of the system of ordinary differential equations [196] or invariant manifold [197]. After obtaining a low dimensional manifold, a reduced number of partial differential equations is explicitly solved by projecting them onto the manifold.
Table 7.2: The behaviour of the pseudo densities with respect to the eigenvalues and corresponding density configurations compared to a given time-scale $\tau$.

<table>
<thead>
<tr>
<th>Eigenvalue</th>
<th>Type</th>
<th>Behaviour</th>
<th>Density configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda_i = 0$</td>
<td>Invariant</td>
<td>$\bar{n}<em>i - \bar{n}</em>{i,0} = 0$</td>
<td>$(V^{-1} n)_i - (V^{-1} n_0)_i = 0$</td>
</tr>
<tr>
<td>$Re(\lambda_i) &lt; 0$</td>
<td>Fast</td>
<td>$\lim_{t \to \tau} \bar{S}_i = 0$</td>
<td>$\lim_{t \to \tau} (V^{-1} S)_i = 0$</td>
</tr>
<tr>
<td>$Re(\lambda_i) &lt; 0$</td>
<td>Slow</td>
<td>$\lim_{t \to \infty} \bar{S}_i = 0$</td>
<td>$\lim_{t \to \infty} (V^{-1} S)_i = 0$</td>
</tr>
</tbody>
</table>

The dimension of the necessary low dimensional manifold is determined by the number of equations to be solved in the reduced system. We leave further details of these steps to [194]. Any density configuration defines a low dimensional manifold. In this respect, these manifolds are not only used in the ILDM technique but also in other reduction techniques or any model that is imposing a density configuration. For example, a set of species $l$ that is assumed to be in QSS, $S_l = 0$ defines a low dimensional manifold. Another example is one of the basic features of plasmas: quasi-neutrality that is explicitly imposed in many models [68, 177].

7.3.1 Additional classification of the pseudo densities

It is possible to classify the pseudo species with negative eigenvalues based on their equilibrium time-scales. For the sake of coherence, we firstly assign the classification Invariant to the pseudo species that have zero eigenvalues. Secondly, we identify a pseudo species $i$ whose eigenvalue satisfies $Re(\lambda_i) < 0$, with respect to an externally given time-scale $\tau$. The time-scale of the exponential decay is given by $1/|Re(\lambda_i)|$. If the eigenvalue $\lambda_i$ satisfies the condition $1/|Re(\lambda_i)| \ll \tau$, the pseudo species has already equilibrated at $\tau$ and we call it a Fast pseudo species. Otherwise, it continues to evolve in time and we call it a Slow pseudo species. The pseudo species that define the density configurations with respect to $\tau$ are shown in Table 7.2.

In other words, Invariant pseudo species represents a low dimensional manifold that the densities satisfy at all time. The Fast sources describe the manifolds that densities already settled in at time $\tau$. The Slow sources correspond to those manifolds that the density configuration occupies later than $\tau$.

7.4 Analysis case: Three-level system

In this section, we analyse the low dimensional manifolds of a simple system as an example case. We assume that the source is linear in the densities and hence it can be written in the form $S = Mn$. Furthermore, for negligible transport, the particle balance equations are

$$\frac{\partial n}{\partial t} = Mn.$$  (7.9)
7.4. Analysis case: Three-level system

Figure 7.2: Three-level system that contains three species with reactions $1 \rightarrow 2$, $1 \rightarrow 3$ and $2 \rightarrow 3$. The horizontal lines represent the species, whereas the vertical arrows represent the reactions with the corresponding forward reaction frequencies. Note that the reactions favour the excitation to the species 3.

The diagonalisation of the Jacobian $\mathbf{M}$ leads to
\[
\frac{\partial \mathbf{n}}{\partial t} = \mathbf{\Lambda} \mathbf{n},
\] (7.10)
and then the pseudo density $i$ satisfies
\[
\bar{n}_i = \bar{n}_{i,0} e^{\lambda_i t}.
\] (7.11)

We consider a system that is composed of three types of species: 1, 2 and 3. Concerning these, we define three reactions with frequencies $\nu_{12}$, $\nu_{23}$ and $\nu_{13}$, where the first subscript represents the reactant. The system densities and reactions are depicted in Figure 7.2.

The source term is given by the relation
\[
\mathbf{S} = \begin{pmatrix}
-(\nu_{12} + \nu_{13}) & 0 & 0 \\
\nu_{12} & -\nu_{23} & 0 \\
\nu_{13} & \nu_{23} & 0
\end{pmatrix}
\begin{pmatrix}
n_1 \\
n_2 \\
n_3
\end{pmatrix}.
\]

In this system, the density $n_1$, extinguishes since it is not created but only converted to other species in an excitation dominant system. Similarly, $n_2$ vanishes and all species are asymptotically converted to $n_3$. The eigenvalues of the Jacobian matrix $\mathbf{M}$ are
\[
\lambda_1 = 0, \quad \lambda_2 = -\nu_{12} - \nu_{13}, \quad \lambda_3 = -\nu_{23}.
\]

The pseudo species are defined by the relation $\mathbf{n} = \mathbf{V}^{-1} \mathbf{\bar{n}}$ and they satisfy
\[
\begin{pmatrix}
\bar{n}_1 \\
\bar{n}_2 \\
\bar{n}_3
\end{pmatrix} = \begin{pmatrix}
n_1 + n_2 + n_3 \\
n_1 \\
n_1 + C n_2
\end{pmatrix}.
\]
Chapter 7. Low dimensional manifolds

Figure 7.3: The intrinsic low dimensional manifolds of the three-level system. The surface represents a 2-D manifold described by \( n_1 + n_2 + n_3 = 1 \), where we assume that the total particle density is \( n_{tot} = 1 \). The thin line corresponds to a 1-D manifold given by \( n_1 = 0 \) and \( n_1 + n_2 + n_3 = 1 \). The dot represents complete chemical equilibrium (0-D manifold).

where \( C = 1 + \frac{\nu_{13}}{\nu_{12}} \). The first pseudo density \( \bar{n}_1 \), represents the total particle density \( n_{tot} = n_1 + n_2 + n_3 \). The second pseudo density \( \bar{n}_2 \), corresponds to the density of the first species \( n_1 \). The third pseudo density \( \bar{n}_3 \), is a combination of the first and the second species.

According to equation (7.11) \( \bar{n} \) is expressed by the relation

\[
\begin{pmatrix}
\bar{n}_1 \\
\bar{n}_2 \\
\bar{n}_3
\end{pmatrix} = \begin{pmatrix}
\bar{n}_1(0) \\
\bar{n}_2(0) exp[-(\nu_{12} + \nu_{13})t] \\
\bar{n}_3(0) exp[-\nu_{23}t]
\end{pmatrix},
\]

and the pseudo species with zero eigenvalue, \( \bar{n}_1 \), represents the total particle density is a conserved quantity of the system. The second pseudo species \( \bar{n}_2 \), is characterised by a real negative eigenvalue and asymptotically vanishes. The time-scale of the extinction is given by the eigenvalue in the form \( 1/(\nu_{12} + \nu_{13}) \). The third pseudo species , \( \bar{n}_3 \), also has a real negative value and it vanishes with a time-scale of \( 1/\nu_{23} \).

A few low dimensional manifolds of the system are shown in Figure (7.3). The first pseudo species sets a 2-D low dimensional manifold in the density space via the plane density configuration \( n_1 + n_2 + n_3 = n_{tot} \). The second and the third pseudo species have real negative
### 7.4. Analysis case: Three-level system

<table>
<thead>
<tr>
<th>Plasma Parameters</th>
<th>Frequencies (1/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma_{pq} = 10^{-19}$ m$^2$</td>
<td>$\nu_{12} = 9.0023 \times 10^8$</td>
</tr>
<tr>
<td>$T_e = 1$ eV</td>
<td>$\nu_{13} = 2.6975 \times 10^{10}$</td>
</tr>
<tr>
<td>$n_e = 5 \times 10^{17}$ m$^{-3}$</td>
<td>$\nu_{23} = 1.0027 \times 10^6$</td>
</tr>
</tbody>
</table>

Table 7.3: The description of the hypothetical hydrogen plasma together with the reaction frequencies.

The eigenvalues, and each one defines a distinct surface, on which the densities asymptotically settle. The second surface is given by the plane $n_1 = 0$, and its intersection with the first one $n_1 + n_2 + n_3 = n_{tot}$ forms a line. This line corresponds to a 1-D low dimensional manifold of the system. Moreover, the intersection of this line with the third surface $n_1 + Cn_2 = 0$ sets a point that describes the complete equilibrium (0-D manifold). Note that the densities can have negative values which is physically meaningless. Regarding this, the physical density constraint $n_i > 0$ is also included in the manifold definitions [193].

Let us assume that for a given time-scale $\tau$, the second eigenvalue satisfies $1/|−\nu_{12} − \nu_{13}| \ll \tau$, while the third one does not. This suggests that the density configuration settles on the line represented by $n_1 = 0$ and $n_1 + n_2 + n_3 = n_{tot}$ at $\tau$. Furthermore, under the assumption that species $n_2$ reaches quasi-steady state after a certain time, at that time the lower dimensional manifold $S_2 = n_1\nu_{12} − n_2\nu_{23} = 0$ is occupied by the densities.

### 7.4.1 A three-level hydrogen plasma model

In this section, we specify the frequencies based on a simple hypothetical plasma model and observe the characteristic time-scales of the system. Using the manifolds of the system a simple reduction on the number of equations is applied both analytically and numerically. We let the species 1, 2 and 3 correspond to the the hydrogen ground state, an excited level and the ion: $1 \equiv H(p = 1), 2 \equiv H^+(p = 2)$ and $3 \equiv H^+(p = \infty)$, respectively. The energy of state $p$ is given by $E_p = −E_{ion}/p^2$, where $E_{ion} = 13.6$ eV is the ion energy. We assume that excitation and ionisation are induced by electronic collisions. The excitation frequencies from species $p$ to $q$, such that $p < q$, are given in Arrhenius form

$$\nu_{pq} = n_e\sigma_{pq}v_{th}e^{−E_p/E_e}/p < q,$$

where $T_e$ is the electron temperature, $n_e$ is the electron density, $\sigma_{pq}$ is the cross-section of the transition and $v_{th} = \sqrt{8k_BT_e/\pi m_e}$ is the thermal velocity (see Table 7.4.1 for the parameter values). According to equations (7.11) and (7.3) the equilibrium time-scales of the pseudo densities are $1/\lambda_2 = 3 \times 10^{-11}$ s and $1/\lambda_3 = 1 \times 10^{-06}$ s respectively.

From this point, we define two sets of equations. The first set is equation (7.9) for the hydrogen plasma and we assume that initial densities are

$$n_1 = \frac{8}{10}n_{tot}, n_2 = \frac{1}{10}n_{tot}, n_3 = \frac{1}{10}n_{tot},$$
Chapter 7. Low dimensional manifolds

(a) Time evolution of the densities by reduced (black) and full set (red) of equations.

(b) The time dependent trajectory in density space, where arrows denote the direction of the time evolution. The red line represents the density behaviour using the full set of equations and the black line is the reduced set. The dot is the density configuration at complete chemical equilibrium. In both, the total amount of density is conserved, i.e., they are on the 2-D manifold, \( n_1 + n_2 + n_3 = n_{\text{tot}} \).

Figure 7.4: The analytic solutions of the system with respect to time and its corresponding trajectory in the density space. Both full and reduced sets are shown; the latter is shown in black. The densities settle on the 1-D manifold in \( 3 \times 10^{-9} \) s and equilibrium is reached in \( 3 \times 10^{-4} \) s.
where the total density is \( n_{\text{tot}} = 10^{23} \text{ m}^3 \). In this set, the densities are determined by solving all three differential equations. The second set of equations is called a reduced set. It contains two algebraic equations of the 1-D manifold \( n_1 + n_2 + n_3 = n_{\text{tot}} \) and \( n_1 = 0 \), and the differential equation of \( n_3 \). Note that, with the manifold the number of differential equations is reduced to one. Within this set, we only solve the time dependent differential equation for \( n_3 \) and the rest of the densities are determined by the manifold equations \( n_1 + n_2 + n_3 = n_{\text{tot}} \) and \( n_1 = 0 \). The differential equation on the 1-D manifold satisfies

\[
\frac{\partial n_3}{\partial t} = \nu_{23} n_{\text{tot}} - \nu_{23} n_3 
\]  

(7.12)

and we use the initial value for the solution

\[
n_3 = n_{\text{tot}} \frac{1}{10},
\]

In other words, using the manifold in the second set, three coupled ordinary differential equations are reduced to two algebraic equations and one ordinary differential equation that significantly lowers the computational load in a numerical approach.

The time evolution of both the reduced and full set of equations is shown in Figure 7.4 (a). The corresponding trajectories in density space are depicted in Figure 7.4 (b). The densities perfectly settle on the 1-D manifold in \( 3 \times 10^{-9} \) s, while it further takes \( 1 \times 10^{-4} \) s to reach complete chemical equilibrium.

The full and the reduced systems are also numerically integrated until steady-state solutions are reached. We apply two simple integration methods: Explicit and implicit Euler methods (see appendix 7.A) using a fixed time-step \( \delta t \). The former method is relatively faster, however it diverges for a stiff set of equations at large time-steps. Though the implicit Euler method is slower, it converges at large time-steps for a stiff set of equations. Furthermore, we define a numerical error based on the analytic solution

\[
\epsilon = \frac{n_A - n_N}{n_A},
\]

(7.13)

where \( n_A \) represents steady-state analytic solution and \( n_N \) is the steady-state numerical solution. Similar errors are observed in the reduced and full set of equations. However, the implicit and explicit methods show distinct behaviour in the convergence. The former converges with a time-step \( \delta t < 2 \times 10^{-1} \) s for both sets since it can handle stiffness. This is not the case in the explicit method: The full set of equations suffers from divergence at large time-steps \( \delta t > 7 \times 10^{-11} \) s. However, convergence is obtained for the reduced set also at these large time-steps (see Figure 7.5). In this respect, the reduction also prevents stiffness in the set of differential equations and allows usage of the explicit method.

7.5 Conclusion

Reduction techniques, which simplify the chemical kinetics are commonly used in numerous fields in order to investigate systems that incorporate various interacting species. These
Chapter 7. Low dimensional manifolds

Figure 7.5: The numerical error $\epsilon$ for the reduced (+) and full (o) set of equations (see text for details). The explicit Euler method is employed until steady state is reached. The numerical integration of the full set of equations diverges for $\delta t > 7 \times 10^{-11}$ due to stiffness of the problem.

methods share basic notions such as quasi-steady state assumptions. The Intrinsic low dimensional manifold method is such a technique that is employed in combustion flame models. It determines the conserved quantities and the collective equilibrium density configuration in a system, which simply define a low dimensional manifold in density space. The method further makes use of this configuration to reduce explicitly treated set of equations. We observed that such manifolds, by definition, are not only used in this technique but in numerous models: QSS assumptions in CRMs or even quasi-neutrality in plasmas. More generally, any physical or chemical constraint on the density configuration indicates a low dimensional manifold.

We mainly focused on these manifolds and their determination, together with their visualisation in a simple example three-level system. In addition to a decrease of the computational load, the model further eliminates the stiffness related divergence at large time-steps in the set of ordinary equations. The technique is used only in steady-state calculations but novel classification of these manifolds via the pseudo densities, is also promising in time dependent simulations.

In the manifold definitions, the role of the transport is neglected and the transport can significantly alter the manifold structure by the relation

$$\frac{\partial \bar{n}}{\partial t} = \mathbf{S}(\bar{n}_0) + \Lambda [\bar{n} - \bar{n}_0] - \mathbf{V}^{-1} \nabla \cdot \mathbf{I}.$$  \hspace{1cm} (7.14)

Generally, the transport can not be neglected in a plasma and it is a complex phenomena due to the electrical interactions of the charged particles. Additionally, a plasma can be bounded by a solid wall and wall reactions and sheath phenomena define the plasma behaviour. In this respect, any identification of the low dimensional manifolds in a plasma has to respect these features.
7.A. Euler method

Euler methods are used in the discretisation of first order ordinary differential equations, which are the most simple techniques for the purpose of numerical integration. They are based on the Taylor series expansion and have two types of implementations: (1) Implicit and (2) explicit. The implicit method is suitable for stiff sets of equations, which are featured by a broad range of characteristic time-scales. Such a range restricts the maximum time-step allowed on the method due to convergence criteria and may cause divergence if explicit methods are used with too large time-steps. On the other hand, the explicit methods are faster per time-step compared to the implicit methods.

For a set of equations, that has the form
\[ \frac{\partial n}{\partial t} = Mn, \]
the Taylor series expansion implies that
\[ n(t + \delta t) = n(t) + Mn\delta t, \]
where \( \delta t \) is a small time-step. Iteratively, it is written as
\[ n^{k+1} = \begin{cases} (I + M\delta t)n^k & \text{explicit} \\ (I - M\delta t)^{-1}n^k & \text{implicit} \end{cases}, \]
where \( k \) represents the iteration in time.

7.B Diagonalisation

The diagonalisation of a square matrix \( M \) has two convertible forms: \( M = V\Lambda V^{-1} \) and \( M = U^{-1}\Lambda U \) with \( U = V^{-1} \). Conventionally, the right eigenvectors form the columns of \( V \) and the left eigenvectors form the rows of \( V^{-1} \). These two follow the non-commutative matrix multiplication of left and right. If the first form is used, the diagonalisation procedure is given in the following. Right multiplying with an arbitrary column matrix \( a^s \) gives
\[ Ma^s = V\Lambda V^{-1}a^s. \]

In component form it is written as
\[ \sum_j M_{ij}a_j^s = \sum_k V_{ik}\lambda_k \sum_j V^{-1}_{kj}a_j^s. \]
This column matrix corresponds to a column of the eigenvector matrix, i.e.,
\[ V = (a^1 \ a^2 \ \cdots \ a^s \ \cdots), \quad a_j^s = V_{js}; \]
so that the last term is identity

\[ \sum_j M_{ij} a_j^s = \sum_k V_{ik} \lambda_k \delta_{ks}, \]

then

\[ \sum_j M_{ij} a_j^s = V_{is} \lambda_s, \]

leading to

\[ M a^s = \lambda_s a^s, \]  \hspace{1cm} (7.15)

with \( a^s \) is the \( s \)th column of \( V \).
Evaluation of a measure on the validity of quasi-steady state assumption of collisional radiative models via intrinsic low dimensional manifold technique
Chapter 8. Quasi-steady state error of collisional radiative models

8.1 Introduction

Plasmas are extensively employed for the purpose of surface treatment [199, 200] and lighting applications [201]. Their collective feature is the large number of locally interacting species such as excited atomic or molecular states and chemical reactants. This characteristic induces numerical difficulties such as heavy computational load and stiffness; therefore, long-lasting simulations and troublesome convergences appear. Although models that contain large number of species are still viable, these difficulties persuade reduction of this number.

Naive approach in reducing the number of species is to ignore low-valued particle densities. Although it decreases the computational load and relieve the stiffness, it may lock essential reaction channels in the physical system. Hence, reduction techniques respecting all the local interactions are obligatory. Collisional Radiative Model (CRM) is such a reduction method, which is widely used in low-temperature atomic plasmas. It focuses on the interplay between collisional and radiative processes. The technique was commenced by Bates et al. [202] and improved further by various authors [82, 203, 204]. So-called Local Chemistry (LC) species already equilibrated to Quasi-Steady State (QSS) in local chemistry at the transport time-scale and it uses this fact to determine a reduced set of species and effective reaction rates.

Reduction methods are utilised not only in the area of plasma science but also in other fields with overlapping peculiarity [193, 190, 196]. Though developed independently, some of these techniques are remarkably similar. For example, in mathematical biology, some [190] use QSS assumptions, while certain combustion models [205] similarly assume partial equilibrium and steady state. Another reduction method that is extensively employed in combustion engine flame models is Intrinsic Low Dimensional Manifold (ILDM) technique. It was initiated by Maas et al. [193] and studied further by numerous authors [194, 206]. It makes use of characteristic principal frequencies of local interactions to determine an asymptotic state of the mass fractions that leads the chemical reduction.

CRMs are strong tools with low computational load for the investigation of the plasma species and their interactions, however, they suffer from a couple of inadequacies. The first one is the LC condition, which discriminates the species quickly reaching QSS. It is based on the ratio of the transport to local destruction frequencies. Since it excludes the role of the time dependent local production, it is insufficient in the assignments. The second inadequacy is the deviations from the QSS assumption that perturbs the derived quantities in the CRM. These deviations and the resulting perturbations are ignored in the conventional CRM formalism. In this study these inadequacies are addressed with the aid of the ILDM technique.

Inspired by the ILDM technique, we estimate a local source at the transport time-scale and assign it as an error on the QSS assumption of CRMs. This error quantifies a deviation from the assumption and its influence on the derived quantities of CRM is formulated. Furthermore, we propose a novel LC condition based on the error with a consistent measure that incorporates the local production. We apply this new approach to Ar or Hg containing fluorescent lamps separately. The comparison of the conventional and new LC conditions is presented together with the error. In section 8.2 governing equations are analysed for the plasma under investigation and the main points characterising the LC particles are discussed.
8.2. Particle balances

Section 8.3 introduces CRM and section 8.4 shows the analysis in a diagonal basis, which is similar to the first step of the ILDM technique. In section 8.5 we define the error and introduce the novel LC condition. Section 8.6 describes the Ar and Hg plasma parameters, and section 8.7 presents the results. In section 8.8 summary and conclusion are given.

8.2 Particle balances

The densities of the species are governed by particle balance equations. For species $i$, it is given by

$$\frac{\partial n_i}{\partial t} + \nabla \cdot \vec{\Gamma}_i = S_i, \quad (8.1)$$

where $n_i$ is particle density of species, $\vec{\Gamma}_i$ its particle flux and $S_i$ its net production rate. The first term expresses the time evolution of densities while second one represents convective, diffusive transport. The right hand side corresponds to the chemical reactions. This term explicitly couples several species to each other. Additionally, the transport term may couple them in the case of multicomponent diffusion [183], which is not considered here.

We introduce the notation used in [82] in order to compare the various chemical processes. Since losses are proportional to $n_i$, the source can be written in terms of the destruction and the production

$$S_i = P_i - D_i n_i, \quad (8.2)$$

where $D_i$ represents the destruction frequency and $P_i$ is the production rate. In general these are functions of all other densities and various system parameters. In equilibrium, the source satisfies

$$S_i = 0 \quad (8.3)$$

and leads the equilibrium density

$$n_i^{\text{Eqb}} = \frac{P_i}{D_i}. \quad (8.4)$$

Furthermore, the transport frequency of species $i$ is defined as

$$\nu_{tr,i} = \frac{\nabla \cdot \vec{\Gamma}_i}{n_i}. \quad (8.5)$$

As a result, the particle balances can be written as

$$\frac{\partial n_i}{\partial t} + \nu_{tr,i} n_i = P_i - D_i n_i. \quad (8.6)$$

Ratio of transport to destruction frequency determines dominant process among them. Keeping this in mind, we introduce the Damköhler number $D_{a,i} = \frac{D_i}{\nu_{tr,i}}$, then equation (8.6) further takes the form

$$\frac{1}{D_i} \frac{\partial n_i}{\partial t} + \frac{n_i}{D_{a,i}} = n_i^{\text{Eqb}} - n_i. \quad (8.7)$$
Chapter 8. Quasi-steady state error of collisional radiative models

<table>
<thead>
<tr>
<th>Label</th>
<th>Reaction</th>
<th>Rate</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>$A(i) + e \rightarrow A(j) + e$, $(i &lt; j)$</td>
<td>$n_i n_e k_{ij}$</td>
<td>Electron impact excitation</td>
</tr>
<tr>
<td>R2</td>
<td>$A(i) + e \rightarrow A(j) + e$, $(i &gt; j)$</td>
<td>$n_i n_e k_{ij}$</td>
<td>Electron impact de-excitation</td>
</tr>
<tr>
<td>R3</td>
<td>$A(i) + e \rightarrow A^+ + 2e$</td>
<td>$n_i n_e k_{i+e}^\prime$</td>
<td>Electron impact ionisation</td>
</tr>
<tr>
<td>R4</td>
<td>$A^+ + 2e \rightarrow A(j) + e$</td>
<td>$n_{i+e} n_e^2 K_{i+e}^{(3)}$</td>
<td>Three particle recombination</td>
</tr>
<tr>
<td>R5</td>
<td>$A(i) \rightarrow A(j) + \nu$</td>
<td>$n_i A_{ij}^\prime$</td>
<td>Spontaneous emission</td>
</tr>
<tr>
<td>R6</td>
<td>$A(i) + \nu \rightarrow A(j) + 2\nu$</td>
<td>$n_i \beta_{ij}(\nu)$</td>
<td>Stimulated emission</td>
</tr>
<tr>
<td>R7</td>
<td>$A(j) + \nu \rightarrow A^+ + e$</td>
<td>$n_j \alpha_j$</td>
<td>Photoionisation</td>
</tr>
<tr>
<td>R8</td>
<td>$A^+ + e \rightarrow A(j) + \nu$</td>
<td>$n_{i+e} \alpha_{ij}$</td>
<td>Radiative recombination</td>
</tr>
</tbody>
</table>

Table 8.1: Chemical reactions in atomic pure EEK plasmas. $A$ and $e$ represents atom and electrons, while $i$ specify the neutral species and $+$ ions. These neutral species are composed of ground and excited levels of the atom. In this work, we neglect the photoionisation and stimulated emission.

For large Damköhler number, $D_{a,i} \gg 1$ the transport term can be ignored in equation (8.6):

$$\frac{1}{D_i} \frac{\partial n_i}{\partial t} = \frac{P_i}{D_i} - n_i. \quad (8.8)$$

If $P_i$ is constant of time, then $n_i^{\text{Eqb}}$ is reached exponentially in characteristic time $1/D_i$, which is long before the transport time-scale $\tau_{tr} = 1/\nu_{tr,i}$. Bates et al. [202] realised that these species, called Local Chemistry (LC) species in CRM, are initially dominated by the local source. In this case, the destruction diminishes the net production rate and they reach Quasi-Steady State (QSS)

$$S_i = 0. \quad (8.9)$$

In order to manipulate the coupled particle balance equations more conveniently, vector notation is introduced. Let $\mathbf{n} = \{n_i\}$ be the column vector of species densities $n_i$. Similarly, the transport and source terms are $\mathbf{\nabla} \cdot \mathbf{\Gamma} = \{\mathbf{\nabla} \cdot \mathbf{\Gamma}_i\}$, $\mathbf{S} = \{S_i\}$. With this notation, the particle balance equations can be written as

$$\frac{\partial \mathbf{n}}{\partial t} + \mathbf{\nabla} \cdot \mathbf{\Gamma} = \mathbf{S}. \quad (8.10)$$

This work focuses on atomic Electron Excitation Kinetics (EEK) plasmas that is defined by van der Mullen [82]. The chemical reactions in these plasmas are dominated by radiative and electron induced transitions between atomic levels. Besides the ground state, the ion and the electron; the excited levels play a role in such reactions. Explicit forms of these reactions are listed in table (8.1). One common assumption in EEK plasmas is that the electrons act as “external agents” with density $n_e$ and temperature $T_e$ [82]. They are not included in density vector $\mathbf{n}$.

Since the source term of the other species are linear in their densities, these can be written as

$$\mathbf{S} = \mathbf{M}(n_e, T_e) \mathbf{n}. \quad (8.11)$$
The source matrix $M$ is composed of the reaction frequencies, combining equation (8.11) with table 8.1 yields

$$ M_{ij} = \begin{cases} - \left[ \sum_{p \neq j} n_e k_{jp} + n_e k_{j'p} + \sum_{p \leq j} A^*_p \right] & i = j \quad \text{R1, R2, R3, R5} \\ n_e k_{ji} & i < j \quad \text{R1, R5} \\ n_e k_{jj} & i = j' +' \quad \text{R2} \\ n_e^2 K^{(3)}_{ji} + n_e \alpha_i & j = '+' \quad \text{R3} \end{cases} $$

where photoionisation and stimulated emission are not included. For $i \neq j$, $M_{ij}$ is the production frequency of state $i$ from $j$ and $M_{ii}$ is the destruction frequency of state $i$. With this notation, the production term in equation (8.2) is $P_i = \sum_{j \neq i} M_{ij} n_j$ while the destruction frequency is $D_i = M_{ii}$.

### 8.3 Collisional radiative models

Solving too many coupled particle balance equations causes heavy computational load and stiffness. In order to prevent this, CRMs reduce the number of species, for which these equations are solved without neglecting the species or their role in the reactions. The model relies upon a classification of species into two types: Local Chemistry (LC) and Transport Sensitive (TS). LC species satisfies $D_{a,i} \gg 1$ and reaches QSS (equation (8.9)) before the transport time-scale. They feature vanishing local sources while the others do not.

The relations between LC and TS species is re-formulated by van Dijk et al. [204] in the following analysis. Reordering the vector indices such that the TS species are at top of the vector, $S$ and $n$ can be decomposed as [204]:

$$ S = \begin{bmatrix} S_l^t \\ S_l^l \end{bmatrix}, \quad n = \begin{bmatrix} n_l^t \\ n_l^l \end{bmatrix}, $$

where "$l$" labels the LC and "$t$" labels the TS species. Imposing QSS assumption on the LC species $S_l = 0$ and similarly decomposing the source matrix $M$, equation (8.11) becomes

$$\begin{bmatrix} S_l \\ 0 \end{bmatrix} = \begin{bmatrix} M_{lt} & M_{ll} \\ M_{lt} & M_{ll} \end{bmatrix} \begin{bmatrix} n_l^t \\ n_l^l \end{bmatrix}. $$

This yields two sets of equations:

$$ S_l = M_{lt} n_l^t + M_{ll} n_l^l, $$

$$ 0 = M_{lt} n_l^t + M_{ll} n_l^l. $$

Inverting equation (8.16), the LC densities are linearly coupled to those of TS:

$$ n_l^t = - \left( M_{lt}^{-1} M_{ll} \right) n_l^l. $$
Hence, once the TS densities are known, the complete state of the plasma is available with this linear relation. Moreover, putting this relation in equation (8.15) we introduce an effective TS source term

$$S_t = (M_{tt} - M_{tl}M_{lt}^{-1}M_{lt}) n_t.$$  (8.18)

The first term on the right hand side represents the direct processes between the TS states, while the second term describes ladder-like transitions, that is via the LC states. Equations (8.17) and (8.18) allow to take into account of the LC states without solving their balance equations.

In spite of their wide usage CRMs contain two weak points. Firstly, the classification condition of LC species ($D_{a,l} \gg 1$) is not always sufficient: Since the local production, $P_l$, is a function of all other densities (see equations (8.8, 8.9)), it is not constant in time. As a consequence, the exponential decay to the equilibrium density with characteristic time-scale $1/D_l$ is not valid. Secondly, the deviations from the assumption $S_l = 0$ are not quantified. These deviations may be significant and lead perturbations in the LC densities through equation (8.17) that propagate into the TS sources via equation (8.18). In following sections we estimate these deviations and assign them as error of the QSS assumption. We also quantify the resultant perturbations on equations (8.17, 8.18) and propose a novel condition to classify the LC species. Rudimentary aspects of the estimation and the assignment are developed in section 8.4 while the error and the novel LC condition are defined in section 8.5.

8.4 Diagonal basis

Similar to the plasma sciences, the combustion engineering studies physical systems containing large number of species that interact with complex chemical kinetics. Aforementioned numerical difficulties also arise in the models and Maas et al. [193] introduces ILDM technique to reduce the number of species. Adapting the notions of the ILDM technique, we introduce a diagonal basis to analyse the particle balances. Settling in this basis, decoupled set of equations are acquired with a characteristic time-scale assigned to each. This fact allows a classification of those equilibrated at a time-scale and forms the backbone of the error definition.

The technique starts with analysis of source matrix. In order to investigate the chemical nature of the particle balances, the transport term is omitted in equation (8.10) for the time being [193]:

$$\frac{\partial n}{\partial t} = Mn.$$  (8.19)

Assuming that it is diagonalisable, we have

$$M(n_e, T_e) = V\Lambda V^{-1}$$  (8.20)

where $V$ is a regular matrix, whose columns are the eigenvectors, and $\Lambda = \text{diag} [\lambda_i]$ is a diagonal matrix that contains the corresponding eigenvalues. These matrices are functions of $n_e$ and $T_e$ like $M$, although we leave out the parameters for readability.
Substitution of equation (8.20) into equation (8.19) and left multiplication with $V^{-1}$ yields

$$V^{-1} \frac{\partial n}{\partial t} = \Lambda V^{-1} n.$$  
(8.21)

Furthermore, let $\tau_M$ be the $M$ matrix time-scale, which represents how quick it changes, and scales with how fast electron density and temperature alters. For time-scales $t \ll \tau_M$, the variations of the source matrix are negligible. As a result, its eigenvalues and eigenvectors do not vary significantly in time. This leads to the form

$$\frac{\partial (V^{-1} n)}{\partial t} = \Lambda (V^{-1} n).$$  
(8.22)

This suggests the introduction of alternative density variables $\bar{n}$ according to

$$\bar{n} = V^{-1} n,$$  
(8.23)

which we call pseudo densities. Substitution into equation (8.22) yields

$$\frac{\partial \bar{n}}{\partial t} = \Lambda \bar{n}.$$  
(8.24)

Since $\Lambda$ is diagonal, the equations for $\bar{n}$ are decoupled and their treatment is relatively easy compared to those in original basis. For times $t \ll \tau_M$, the eigenvalues are constant and integration of equation (8.24) yields

$$\bar{n}(t) = e^{\Lambda t} \bar{n}(0).$$  
(8.25)

In other words, each pseudo species labelled by $i$ satisfy

$$\bar{n}_i(t) = e^{\lambda_i t} \bar{n}_i(0),$$  
(8.26)

where we used the component notation for the sake of simplicity.

### 8.4.1 Classification of pseudo densities

The peculiar behaviour of each pseudo density $\bar{n}_i$ is determined by the corresponding eigenvalue $\lambda_i$, inverse of which represents characteristic time-scale of the equation. Obviously, zero eigenvalue yields time invariant behaviour $\bar{n}_i(t) = \bar{n}_i(0)$, while negative real part of the eigenvalue imposes exponential decay and estimates a decay frequency, $Re(\lambda_i)$ (see Figure 8.1). Comparing the corresponding decay time-scale to previously determined time parameter $\tau$, the pseudo densities with smaller time-scales have already equilibrated to their asymptotic value: 0.

Following these observations, we classify three type of pseudo densities for a given time parameter $\tau$, for instance, the transport time-scale. (1) Fast pseudo densities posses eigenvalues with $Re(\lambda_i) \ll -1/\tau$ and they vanish at the time parameter: $\bar{n}_i(\tau) \approx 0$. The approximation asymptotically turns into equality. (2) Invariant pseudo densities have zero eigenvalue, and
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Figure 8.1: The behaviour of pseudo density \( \bar{n} \) for distinct real eigenvalues. The positive eigenvalues cause exponential growth, while the negative ones induce exponential decay. Comparison with the external time-scale \( \tau \) reveals pace of the decay.

they are constants of time. (3) Otherwise, they are discriminated as slow pseudo densities and these are still dynamically active.

<table>
<thead>
<tr>
<th>Eigenvalue Type</th>
<th>Behaviour</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Re(\lambda) \ll -1/\tau )</td>
<td>Fast</td>
</tr>
<tr>
<td>( \lambda_i = 0 )</td>
<td>Invariant</td>
</tr>
<tr>
<td>Else</td>
<td>Slow</td>
</tr>
</tbody>
</table>

Though they are not actual densities, the pseudo densities correspond to a physical quantity. The time invariant pseudo densities follow certain characteristics of the source matrix such as conservation of the total number of the particles in (sub-) set of reactions. This characteristic in closed systems shows itself as a vanishing row sum in the source matrix. Decaying pseudo densities represents the equilibrium of chemical processes. The imaginary part of the eigenvalue means oscillatory pseudo density, while the positive real part induces exponential growth. The oscillatory and growing pseudo densities are not observed for the analysed systems, hence they are not treated. Since most of the systems eventually equilibrate, lack of these eigenvalues is expected. However, they may appear during iteration or stable solutions and their treatment is addressed to [194] and future studies.
8.4. Diagonal basis

8.4.2 Reconfiguration in the density space

In this section, we reconfigure the density space based on the classification of the pseudo densities at the time-scale $\tau$. Firstly, we introduce a diagonal reduction matrix $R(\tau)$

$$R_{ii} = \begin{cases} 
1 & \text{if } i \in \{ \text{"Fast"} \} \\
0 & \text{else.}
\end{cases} \quad (8.28)$$

This matrix defines fast $n_f(\tau)$ and slow $n_s(\tau)$ components of the pseudo density $\tilde{n}(\tau)$:

$$\tilde{n}_f(\tau) = R(\tau)e^{A\tau}\tilde{n}(0), \quad \tilde{n}_s(\tau) = (I - R(\tau))e^{A\tau}\tilde{n}(0), \quad (8.29)$$

where $I$ is the identity matrix and $\tilde{n}$ satisfies

$$\tilde{n}(\tau) = \tilde{n}_s(\tau) + \tilde{n}_f(\tau). \quad (8.31)$$

The fast component $\tilde{n}_f(\tau)$ contains all fast pseudo densities and zero otherwise, while $\tilde{n}_s(\tau)$ includes the rest. Furthermore, they associate with the original density by the relations

$$\tilde{n}_f(\tau) = R(\tau)V^{-1}n(\tau), \quad \tilde{n}_s(\tau) = (I - R(\tau))V^{-1}n(\tau). \quad (8.32)$$

This form partitions any density-dependent quantity into the fast and the slow components. Accordingly, using the relation (8.11), the source at $\tau$ is given by

$$S(\tau) = MV\tilde{n}_s(\tau) + MV\tilde{n}_f(\tau). \quad (8.34)$$

This configuration is based on the two different regions of the density space, and each one is described by one type of the pseudo density. (1) The fast region is emptied before $\tau$ and, for any density dependent quantity, its corresponding component is depleted. (2) The slow one, however, is dominantly occupied around the time-scale $\tau$.

The fast pseudo densities are classified by their vanishing value at $\tau$ (see Figure 8.2) and imposing this, the pseudo density $\tilde{n}(\tau)$ is approximately described by the slow component

$$\tilde{n}(\tau) \approx \tilde{n}_s(\tau). \quad (8.35)$$

Similarly, implementing this in the source components leads to the approximation (depicted in Figure 8.3)

$$S(\tau) \approx MV\tilde{n}_s(\tau). \quad (8.36)$$

Furthermore, we express the source in terms of the original density, by defining a slow matrix, $M^s(\tau) = MV(I - R)V^{-1}$,

$$S(\tau) \approx M^s n(\tau). \quad (8.37)$$
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Figure 8.2: The upper limit for the infinite norm of fast pseudo density, $||\bar{n}_f||_\infty / n \leq ||Re^{A_\tau}||_\infty$, through time. For the external time-scale satisfying $|1/\lambda| = 0.01\tau$, $n_f(\tau)$ is negligible.

8.4.3 Role of the transport

In the previous analysis we omitted the transport in the particle balances and focused on the local source. In this section, we introduce an effective transport term and analyse its effect on the pseudo densities. Firstly, we assign a hypothetical transport frequency to all species

$$\vec{\nabla} \cdot \vec{\Gamma} = \nu_{tr} \mathbf{n},$$

and the particle balances take the form

$$\frac{\partial \mathbf{n}}{\partial \tau} = \mathbf{Mn} - \nu_{tr} \mathbf{n}.$$ (8.39)

By diagonalisation of $\mathbf{M}$ we acquire equation (8.26) in a new form

$$\bar{n}_i(\tau) = e^{(\tau\lambda_i - \tau\nu_{tr})} \bar{n}_i(0),$$ (8.40)

which defines the role of the effective transport on the pseudo densities.

Since the fast pseudo species are defined by the relation $\tau |Re(\lambda_i)| \gg 1$, the transport frequency that satisfies $\tau \nu_{tr} \leq 1$ does not affect their behaviour. If it fulfils $\tau \nu_{tr} \gg 1$, the transport is relatively quick and the fast pseudo density vanished long before time $\tau$. Otherwise, the transport does not play a role. Furthermore, such a transport imposes that the invariant pseudo density is no longer constant in time but exponentially decreases. In the case that $\tau \nu_{tr} \gg 1$, it is classified as a fast pseudo density and otherwise it is a slow pseudo
8.5 QSS Error of LC levels

CRMs assume that the LC levels have already reached QSS at $\tau_{tr}$, due to their large Damköhler number:

$$S_1|_{\tau_{tr}} = 0,$$

(8.42)
which is based on a production term that is constant in time (see equations (8.8, 8.9)). Furthermore, the analysis in the diagonal basis assigns an approximate, density dependent nonzero value to the source

\[ S_l|_{\tau_{tr}} \approx (M^s n)_l(\tau_{tr}). \]  

(8.43)

Regarding this, we use the latter to quantify the deviation from the assumption and define its absolute as the error that is made by the QSS assumption of the LC levels. Consistent QSS error at the transport time-scale is given by the relation

\[ (e_Q)_l(\tau_{tr}) = |(M^s n)_l|, \]  

(8.44)

where \(|.|\) represents the absolute value.

Furthermore, replacing it with zero sources in equation (8.15), the error also propagates through the following CRM relations. Mapping between TS and LC (equation (8.17)) perturbs with

\[ \delta n_l(\tau_{tr}) = M_{ll}^{-1}(e_Q)_l \]  

(8.45)

while the effective TS source - equation (8.18) - deviates

\[ \delta S_l(\tau_{tr}) = M_{ll}M_{ll}^{-1}(e_Q)_l. \]  

(8.46)

### 8.5.1 Density independent QSS error and novel LC condition

Let \( M_i^n \) be the \( i^{th} \) row of \( M^n \). The QSS error, \( (e_Q)_i \), is the inner product of \( M_i^n \) and \( n \) and it satisfies the Hölder’s inequality

\[ (e_Q)_i(\tau_{tr}) \leq \|M_i^n\|_1 \|n\|_1, \]  

(8.47)

where \( \|.|\|_1 \) represents the 1-norm of a vector. Since the 1-norm of the density vector is the total density, \( n \), this reduces to the form

\[ (e_Q)_i(\tau_{tr}) \leq (e_Q^1)_i(\tau_{tr}) n, \]  

(8.48)

where we define density independent consistent QSS error of LC species \( i \)

\[ (e_Q^1)_i(\tau_{tr}) = \|M_i^n(\tau_{tr})\|_1. \]  

(8.49)

Together with \( n \), it determines the upper bound for the density dependent error and in case the density values are not available, it can be used instead.

Furthermore, we define a novel LC condition based on the density independent consistent QSS error. In order to overcome the arbitrary scale of the error, which is intrinsically determined by each system, a dimensionless QSS error is defined by the relation

\[ \widehat{(e_Q)}_i(\tau_{tr}) = \frac{(e_Q)_i(\tau_{tr})}{n\zeta}, \]  

(8.50)
8.6 Model setup

### Parameters

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Ar</th>
<th>Hg</th>
</tr>
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<tr>
<td>$\sigma$</td>
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<td>$10^{-19}$ m$^2$</td>
</tr>
<tr>
<td>$n$</td>
<td>$10^{22}$ m$^{-3}$</td>
<td>$10^{22}$ m$^{-3}$</td>
</tr>
<tr>
<td>$R$</td>
<td>$2.0 \times 10^{-2}$ m</td>
<td>$2.0 \times 10^{-2}$ m</td>
</tr>
<tr>
<td>$L$</td>
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<td>1.80 m</td>
</tr>
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<td>1 eV</td>
</tr>
<tr>
<td>$T_h$</td>
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<td>300 K</td>
</tr>
<tr>
<td>$\tau_{tr}$</td>
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<td>$1.17 \times 10^{-03}$ s</td>
</tr>
<tr>
<td>$n_e$</td>
<td>$1.0 \times 10^{18}$ m$^{-3}$</td>
<td>$1.0 \times 10^{18}$ m$^{-3}$</td>
</tr>
</tbody>
</table>

Table 8.2: Main EEK atomic plasma parameters.

where $\zeta$ is a nondimensionalisation constant with unit $1/s$. The inequality suggests that

$$\left(\epsilon \Omega\right)_i(\tau_{tr}) \leq \epsilon_i(\tau_{tr}), \quad (8.51)$$

where we define a dimensionless error number

$$\epsilon_i(\tau_{tr}) = \frac{\left(\epsilon \Omega\right)_i(\tau_{tr})}{\zeta}. \quad (8.52)$$

If this number is sufficiently small compared to unity, it ensures a negligible dimensionless QSS error relative to $\zeta$. In this respect, we classify LC level as a species that satisfy

If $\epsilon_i \ll 1$ then $i$ is an LC level.

For the $\zeta$ we use the density independent error of the ground state, $(\epsilon \Omega)_0$, with the assumption that the ground state is a TS level with the highest density independent error. Since the ions do have complex transport phenomena, such as ambipolar diffusion, we do not classify them but assume that they are TS.

8.6 Model setup

The QSS errors and the error numbers are investigated in the cylindrical column of a fluorescent lamp. The plasma is contained in the radius $R = 2.0 \times 10^{-2}$ m within the length $L = 1.80$ m. We analyse either argon or mercury based atomic discharges, neglecting spatial inhomogeneities and the sheath phenomena. Additionally, we assume the two-temperature plasma condition of the Maxwellian distribution functions, together with the electron temperature $T_e = 1$ eV, the gas temperature $T = 300$ K and the electron density $n_e = 1.0 \times 10^{18}$ m$^{-3}$.

The atomic excited states above certain threshold energy are neglected in the model. In this way an infinite number of species is reduced to a reasonable finite set. For the discussion and the methods for these neglected levels we refer to a study by van Dijk et al. [189]. The Ar system contains totally 39 species including the ground, the excited states and the ion. The excited levels are chosen from smallest energy Ar($4s$) group up to the energy level Ar($8j$).
Transition rates between these species are taken from [174]. Together with the ground state and the ion, Hg plasma contains 20 species. The excited levels range from Hg(6p1) group with lowest energy to the level Hg(10p). The corresponding transition rates are adapted from [188].

8.6.1 Transport frequency

The transport frequency is determined from the flux term in the particle balances. A fluorescent lamp has negligible convective flux and the diffusive transport satisfies [78]

\[
\left| \nabla \cdot D \nabla n_i \right| = \frac{D}{\Lambda^2} n_i,
\]

(8.53)

where \( \Lambda \) is the diffusion length and \( D \) is the diffusion coefficient. The coefficient \( D \) relates with the mean free path of elastic collisions \( \lambda \) and thermal velocity \( v_{th} \):

\[ D = \frac{1}{3} \lambda v_{th}. \]

The mean free path is \( \lambda = \frac{1}{n\sigma} \), where \( n \) is the dominant gas density and \( \sigma \) is the momentum transfer cross-section. The thermal velocity satisfies \( v_{th} = \sqrt{8k_B T_h/\pi m} \) where \( T_h \) is the gas temperature, \( m \) is the particle mass and \( k_B \) is the Boltzmann constant. We assume that the fundamental diffusion mode dominates [78]:

\[
\frac{1}{\Lambda^2} = \frac{1}{\Lambda_0^2} = \left( \frac{\pi}{L} \right)^2 + \left( \frac{2.405}{R} \right)^2
\]

(8.54)

because the mean free path is smaller regarding the container dimensions. As a result, the transport frequency of neutrals is given by the relation

\[
\nu_{tr} = \frac{\sqrt{8k_B T_h/\pi m}}{3n\sigma \Lambda_0^2}.
\]

(8.55)

8.7 Results

We analyse the positive column of fluorescent lamp for Ar and Hg respectively. In the analysis, we define that a parameter \( r \ll 1 \) if \( r \leq \gamma \), where we set \( \gamma = 1.0 \times 10^{-2} \). Within this definition, the density independent QSS errors and error numbers together with inverse of the Damköhler numbers are presented at the calculated transport frequencies. The inverse values are shown for the sake of simplicity. The classification of the species in CRM formalism is also provided, while the conventional and the novel conditions are compared. The maximum scale of the consistent QSS errors are also presented for the LC levels. Additionally, the consistent QSS errors are also shown for equilibrium density values.

The time independent consistent QSS errors \( (e_Q)_{i} \), error numbers \( e_i \) and inverse of Damköhler numbers \( (D_{a,i})^{-1} \) for Ar gas are presented in Figure S.4. The transport time-scale is calculated as \( \tau_{tr} = 5.20 \times 10^{-04} \) s, using equation (8.53). In the system, the Ar(4s) group satisfies the QSS requirements according to the conventional condition. However, they posses larger error
8.7. Results

<table>
<thead>
<tr>
<th>Ar excited states</th>
<th>(D_{a,i})^{-1}</th>
<th>(e_Q)^1_i</th>
</tr>
</thead>
<tbody>
<tr>
<td>ground</td>
<td>10^-00</td>
<td>10^-00</td>
</tr>
<tr>
<td>4s1-4</td>
<td>10^-02</td>
<td>10^-02</td>
</tr>
<tr>
<td>3d</td>
<td>10^-04</td>
<td>10^-04</td>
</tr>
<tr>
<td>5s</td>
<td>10^-06</td>
<td>10^-06</td>
</tr>
<tr>
<td>7p</td>
<td>10^-08</td>
<td>10^-08</td>
</tr>
<tr>
<td>6s</td>
<td>10^-10</td>
<td>10^-10</td>
</tr>
<tr>
<td>6p</td>
<td>10^-12</td>
<td>10^-12</td>
</tr>
<tr>
<td>7s</td>
<td>10^-14</td>
<td>10^-14</td>
</tr>
<tr>
<td>7i</td>
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<tr>
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<td>8f</td>
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</tr>
<tr>
<td>8h</td>
<td>10^-24</td>
<td>10^-24</td>
</tr>
<tr>
<td>8j</td>
<td>10^-26</td>
<td>10^-26</td>
</tr>
</tbody>
</table>

Figure 8.4: Argon average consistent QSS error \((e_Q)^1_i\), inverse of Damköhler number \((D_{a,i})^{-1}\) and error number \(e_i\) for numbered species \((i)\). Note the double y axes with different scales. The transport time-scale is \(\tau_{tr} = 5.20 \times 10^{-04}\) s calculated from equation (8.53).

The transport time-scale is \(\tau_{tr} = 5.20 \times 10^{-04}\) s calculated from equation (8.53).

numbers \(e_i > 1.0 \times 10^{-2}\), hence, the novel condition suggests that they are TS instead. The rest of the species are classified LC, in agreement with the conventional method. Though \(\text{Ar}(7i)\) is defined as an LC level, it does not satisfy necessary conditions in both methods. We suspect that it is caused by poor formulation of the regarding transitions. Within LC species, \((e_Q)^1_i\) determines maximum value of QSS error \(1.0 \times 10^{18}\) m\(^{-3}\)s\(^{-1}\) for \(\text{Ar}(8g), \text{Ar}(8j)\) and between \(1.0 \times 10^{20}\) m\(^{-3}\)s\(^{-1}\) and \(1.0 \times 10^{24}\) m\(^{-3}\)s\(^{-1}\) for the others.

Same quantities for Hg states are plotted at transport time-scale \(\tau_{tr} = 1.0 \times 10^{-03}\) s in Figure 8.5. In this case both conditions are in agreement. All excited levels qualifies to be LC, while \(\text{Hg}(6p1), \text{Hg}(6p3)\) are TS levels. Upper bound of the density dependent error ranges between \(1.0 \times 10^{20}\) m\(^{-3}\)s\(^{-1}\) and \(1.0 \times 10^{23}\) m\(^{-3}\)s\(^{-1}\), where high values belong to by excited levels neighbouring ground state.

In both systems, errors and error numbers decreases with energy of the level in average while its slope lessens with energy. \(D_{a,i}\) also follows a similar trend, while it shows colossal jumps at various levels compared to those of errors. We think that this behaviour is effect of local production comparable to destruction at the specified times-scale. Both ground states have the highest error and numbers. The ions, on the other hand, are not classified by the number but assumed to be TS due to its complex transport properties.

We also present the consistent QSS errors \((e_Q)^{Eqb}_i\) at the equilibrium density distributions.
Figure 8.5: Mercury average consistent QSS error \((e_Q)^i\), inverse of Damkohler number \((D_{a,i})^{-1}\) and error number \(e_i\) for numbered species \((i)\). Note the double scales. Transport time-scale is \(\tau_{tr} = 1.17 \times 10^{-03}\) s, which is determined via equation (8.53).

The density distribution decreases the error compared to maximum values given by \((e_Q)^i\). The decrement is with a factor of \(1.0 \times 10^{-6}\) for argon, while it is about \(1.0 \times 10^{-10}\) for mercury. On the other hand, their values relative to each other did not change.

### 8.8 Summary and conclusion

We analyse atomic EEK plasmas and focus on the LC levels of the CRMs. These levels are assumed to be in QSS at a transport time-scale due to their large Damkohler number \(D_{a,i} \gg 1\). This assumption is only valid in case of a time independent local production. However the production implicitly depends on time via the densities. Furthermore, in CRMs, any kind of deviation from exact QSS behaviour and its role on the rest of the system is not quantified. In order to tackle this problem and describe the deviation, we analyse the plasma particle balance equations of all species in the diagonal basis of their source Jacobian. This analysis provides an approximate density dependent source at the transport time-scale and we set its absolute value as the error of QSS assumption on the LC levels. In case the densities are not foreknown, we further define an independent error, which forms an upper bound of the previous one. Additionally, a dimensionless number is provided and sufficiently
8.8. Summary and conclusion

Figure 8.6: The consistent QSS error \((e_Q)^{Eqb}i\) for equilibrium density \(n_{Eqb}^i\) of the argon plasma. The transport time-scale is \(\tau_{tr} = 5.20 \times 10^{-04}\) s.

A small number minimises the error and identifies a novel LC condition.

The technique is applied to positive column of fluorescent lamps with Ar and Hg separately. For the defined transport time-scale, Ar\((4s)\) group is identified to be a TS level, in contrast with conventional condition. The rest possess low error number \(e_i < 0.01\), which classify them as LC levels. Ar\((7i)\) substantially deviates from this. Though solid evidence lacks, it is reasonable that poor transition rate causes this deviation. The density dependent error maxima ranges between \(7.0 \times 10^{18}\) m\(^{-3}\)s\(^{-1}\) and \(1.0 \times 10^{24}\) m\(^{-3}\)s\(^{-1}\). For Hg system, all excited states are LC species, except Hg\((6p1)\), Hg\((6p3)\) levels. The error maxima, in this case, ranges from \(1.0 \times 10^{20}\) m\(^{-3}\)s\(^{-1}\) to \(1.0 \times 10^{23}\) m\(^{-3}\)s\(^{-1}\).

In both systems, the density independent error and the number decline with the energy of the excited level. This is in agreement with the fact that the energetic levels quickly settle in QSS compared to those with less energy. Additionally, the conventional QSS condition works for most of the levels but it can be inefficient for the low energy levels. For more accurate classification, the novel condition should be preferred.

The consistent QSS errors \((e_Q)^{Eqb}i\) are also shown for equilibrium density distribution \(n_{Eqb}^i\). Compared to the upper bound \((e_Q)^{1}i\), their scale is significantly smaller. In this respect, the density dependent errors should be used whenever the densities are available. On the other hand, the equilibrium density distribution assumes that \(n_i(\tau_{tr}) = n_{Eqb}^i\) and it should be used with care.
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Figure 8.7: The consistent QSS error \((e_Q)^{Eqb}_i\) for equilibrium densities \(n_i^{Eqb}\) of the mercury plasma. The transport time-scale is \(\tau_{tr} = 1.17 \times 10^{-03}\) s.

We defined a \(\gamma\) parameter to describe a number that is negligibly small compared to unity. In this work we set it to \(\gamma = 1.0 \times 10^{-2}\), yet its value is arbitrary. If smaller \(\gamma\) is chosen, then the description of a negligibly small value is further ensured. Additionally, it can set all species TS with a cost of higher computational burden in the CRM. Higher \(\gamma\) values can classify more excited species into LC levels, but they may still have large density independent errors. In this case, the novel condition can exactly proceed parallel to the conventional technique. If it is too high (above 0.1) even the fast pseudo species may not be negligible. At this point, the choice is left to the user. Depending on their needs, \(\gamma\) can be kept higher, while the resultant effect is defined by the QSS error. We suggest that this value should not exceed 0.1 since the source approximation is compromised by larger fast pseudo densities.

The error is not determined continuously but rather discretely with the transport time-scale. The distribution of the eigenvalues determines these discrete points that should be also taken into account to compute the errors. In the analysed systems, the classification of the pseudo densities and the errors are valid between \(1.0 \times 10^{-5} s < \tau_{tr} < 5.0 \times 10^{-3}\) s for Ar and \(1.0 \times 10^{-3} s < \tau_{tr} < 5.0 \times 10^{-2}\) s for Hg. As a caveat, around these discrete points the classification may change due to the arbitrary \(\gamma\) parameter. Furthermore, in this study the role of the initial density configuration is not taken into account in the classification. Excessively low initial pseudo densities may qualify to be fast even before the criteria is met. Hence, the error and the error number can be misleading around the discrete points of the eigenvalue distribution.
In the density independent definitions we chose the smallest 1-norm among the p-norms. This ensures that the maxima are kept closer to the density dependent values compared to higher norms. Furthermore, the nondimensionalisation constant $\zeta$, which defines the error number $e_i$ and the novel LC condition, imposes a QSS definition that is relative to $\zeta$. In this study, $\zeta$ is chosen to be the maximum dimensionless QSS error. We observe that a different $\zeta$ parameter, the transport frequency of the plasma, increases the error number and changes the classification of the low energy states Ar(4p) and Hg(6p2).

The system is studied for reactions, where two distinct types of species interact. Otherwise, a source term that is nonlinear function of the density vector appears. In the presence of these reactions, the method can be treated with source term linearisation within iterative schemes 28, 194.
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Chapter 9

Conclusion
Many modern plasmas include complex chemical kinetics with numerous species and entangled
networks of reactions. This induces challenges in the numerical implementations mostly due
to the implied computational load. The global (volume-averaged) models are strong tools
in the investigation of these plasmas, since they are characterised by light numerical load in
the simulations. Furthermore, they can be used to reduce the number of species to lower the
load in spatially resolved models. However, this approach is not always practical and more
advanced techniques are necessary for the simplification of the chemical kinetics.

In chapter 4 we investigate a cylindrical radio-frequency chlorine plasma with a global model.
The results show quite good agreement with the experimental data both for continuous and
modulated power inputs. When the power is switched off, an ion-ion plasma appears with
a life-time over ms range. In order to deal with this situation we provided a novel quasi-
neutrality implementation that shows excellent agreement with the conventional technique.
The plasma response is analysed with respect to the variation of the Cl wall recombination
probability and gas temperature. It is observed that these parameters dramatically alter the
discharge properties due to their influence on the chemical kinetics and the wall transport.
The excited Cl levels do not contribute to the ionisation via ladder like channels. This
suggests that in the pressure and power range they are negligible. Moreover an updated Cl
vibrational excitation cross-section significantly enlarges the Cl$_2$($v = 1$) levels, though they
do not contribute to ionisation either.

In chapter 5 we studied a microwave induced oxygen plasma with a global model for both
continuous and modulated power inputs. The wall transport rates are estimated from a two-
dimensional model of the setup discussed in chapter 6. The comparison of these models shows
good agreement for the volume-averaged quantities. We observe that the chemical kinetics is
insensitive to the particles O$_3$, O$_5^-$ and O$_2^-$ in the parameter range and they can be excluded
to reduce the computational load. The simulations with the modulation period of 50 ms show
that the plasma quantities at the pulse on mode is comparable to those at the steady power
input. As a consequence, a smaller period is necessary to achieve better plasma efficiency.
When the power is switched off, unlike the chlorine plasma, all charged particles recombine
in a $\mu$s time-scale. Additionally, we analyse the O$_2$/SiCl$_4$ mixture plasma with the global
model for the same wall ion loss rates. The plasma strongly varies with the SiCl$_4$ percentage
as the SiO$_2$ density increases with it. The electron density is insensitive to the wall transport
rate and the gas temperature, whereas that of ions strongly changes with it.

A stationary two-dimensional O$_2$ plasma model of the microwave reactor self-consistently
coupled to a calculation of the electromagnetic fields is presented in chapter 6. The simulations
show that the plasma is perfectly confined for an optimum choke depth. The optimum choke
dept is similar to the argon plasma and this similarity suggests that identical coupling is
present between the wave and the plasma for both gases. On the contrary, the argon plasma
features larger electron density and temperature mostly due to the less energy spent on the
chemical kinetics and gas heating. The model is based on an approximate diffusion description
of the charged particles and for a better analysis of the spatial profiles a detailed diffusion
formulation is necessary. The electromagnetic description is not appropriate for resonant
fields, hence the dominant ion densities at the wall are properly fixed rather than using a flux
boundary condition.
In chapter 7 we introduce the *Intrinsic Low Dimensional Manifolds* technique to simplify the chemical kinetics and discuss its applicability on plasmas. This technique is inspirational and promising for plasma models, however, the influence of the transport on the low dimensional manifolds is not taken into account. In this respect, we conclude that it can only be employed in phenomenological plasma studies, where the role of the transport is negligible. Otherwise, its effect on the manifolds must be properly analysed. Additionally, any implementation of the technique has to respect the diffusive transport due to complex charged particle interactions in a plasma.

The best known reduction technique in plasma science is the *Collisional Radiative Model* method. In chapter 8 we show that the conventional method to identify the quasi-steady states is poorly stated due to the time dependent local production term. Inspired by *Intrinsic Low Dimensional Manifolds*, we develop a novel approach to identify the quasi-steady state levels. Furthermore, the approach provides the deviation from the quasi-steady state as an error of the assumption and we formulated the resulting influence on the model results. In order to compare with the conventional technique, the novel method is applied to argon and mercury fluorescent lamps separately. We observe an agreement of the conventional and novel approaches for most of the excited levels but they often disagree for the low energy levels. We also discover that, for these low energy levels, the quasi-steady state errors are relatively large.
Bibliography


Acknowledgements

I would like to express my gratitude to various people who played a role in shaping this work and those in my life during this study.

First of all, my supervisors, Gerrit Kroesen and Jan van Dijk: Jan, your broad knowledge of plasma theory, expertise and pushing me in the right direction helped me to cope with not only the scientific research but also with the necessary time management to finish on time. Our discussions were precious for me; they helped to understand the underlying theory. Gerrit, we did not meet as much as Jan, but you are always there when we need any kind of assistance either from your deep knowledge in the field or your extraordinary management skills. You always answered any e-mail within at most one day in your busy schedule as a dean of the faculty, a group leader and a scientist.

I want to express my gratitude to the committee members: Jean-Paul Booth, Annemie Bogaerts, Anton Darhuber, Thomas Mussenbrock and Mathé van Stralen for all their efforts. I would like to sincerely thank Jean-Paul Booth for advising me in the chlorine study, with his deep wisdom in the field, and for his hospitality during the time I spent in École Polytechnique. I also would like to thank Jean-Luc Raimbault and Pascal Chabert for the helpful discussions on the global models, their interest and time. I am also grateful to our colleagues from the industry Mathé van Stralen and Eugen Aldea for the discussions regarding the microwave plasma deposition reactor.

I humbly express my gratitude to my friends and colleagues Manuel Jimenez-Diaz, Emile Carbone and Wouter Graef for the collaboration during the study and the joyful time we spent together. I also would like to thank Sander Nijdam, Sara Rahimi, Diana Mihailova, Ana Sobota, Roxana Tipa, Leroy Schepers, Jesper Janssen and Murat Mesta for their help in the writing process.

I would like to thank various colleagues for short but very fruitful discussions: Evgenia Benova and Antonio Gamero on the microwave plasmas, Peter Awakowicz on the plasma surface interactions and Margarita Baeva on the power modulation.

I had very nice moments within a cozy environment thanks to my roommates Li Chao, Anna Dubinova, Lei Liu, Ronny Brandenburg, Jeroen Nederlof, Tafizur Rehman, our beloved secretaries Anita, Rina and the rest of the group: Joost, Kim, Simon, Jose, Katia, Job, Eddy,
Evert, Chris, Sven, Tiny, Ruud, Luuk and Ferdi.

I spent joyful time thanks to my friends from Eindhoven: Murat, İlker, Nurcan, İrem, Orhan and those from Enschede: İmran, Akın, Burcu, Mustafa, Hao, Alfons, Giulia, Pietro, Balaji and my biggest gratitude is to NS (for all the trains delivering me to my wife).

I want to end with some Turkish words dedicated to my family. Sevgili çekirdek ve geniş aileme her zaman yanında oldukları için ve her ne kadar başka bir tür doktor olmamı çok isterlerken beni Fizik doktoru olarak kabul ettikleri için. Birtaneci eşime herşey için teşekkür ederim. Her akşam eve gelince onun güler yüzüyle karşılaşmak ve de tez sürecindeki anlayışı bana en büyük destekdi. Ayrılık yaşadığımız zamanlarda her haftasonu yorıcı ve uzun bir yolculuktan sonra beni karşılaması en büyük neşe ve güç kaynağındı. Seni seviyorum gözbebeğim.
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