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Experimental and numerical study of radio frequency atmospheric pressure glow discharges
A Doctoral Thesis

Submitted in partial fulfilment of the requirements for the award of Doctor of Philosophy at Loughborough University

Dawei Liu
9/25/2009
Radio frequency (rf) atmospheric pressure glow discharges (APGDs) have received growing attention for their exciting scope of new science and their immense potential for widespread applications. While geometrically similar to conventional low-pressure discharges used in the semiconductor industry for decades, rf APGDs present new physics that require investigation.

This thesis presents an experimental and computational study of helium rf-APGDs aimed at making a contribution to the current understanding of these discharges and enabling their optimization for different applications. The timely interest and significance of this work is highlighted by the publication of different parts of this thesis in 10 peer-reviewed international journals.

Starting with the electron trapping in rf APGDs, the thesis looks into the electron heating mechanism responsible for sustaining the discharges, the influence of the rf excitation frequency on the discharge characteristics, the role of impurities in the discharge chemistry as well as the evolution of the discharge as the size is reduced down to microplasma dimensions. The findings of this research are based on the synergistic use of electrical measurements, optical diagnostics and self-developed computational models.

With the knowledge gained from this thesis, rf-APGDs can be readily used for a wide-range of applications including biological decontaminations, nanostructure fabrication and portable gas analyzers.

**Key Words:** radio frequency, atmospheric pressure, glow discharges, electron trapping, electron heating, plasma chemistry, rf microplasmas
First of all, I would like to express my special gratitude to my supervisors, Professor Michael G Kong and Dr Felipe Iza, for their guidance through this intriguing research field of radio frequency atmospheric pressure glow discharges. Throughout my PhD study at Loughborough University they have shown me a religious attitude and pioneering spirit for high quality scientific research. Their unremitting encouragement has led me to take every challenge with aspiration and excitement. Furthermore, I would like to thank them for their care for my daily living during four years. It is really fortunate for me to have them as my supervisors.

My sincere thanks go also to Dr. Jianjun Shi for his kind help and useful discussions on the development of the theoretical model and on experiments reported in this thesis. I am pleased for the opportunity to work with Dr. Yuantao Zhang, Dr. James Walsh, Mr. Zhi Cao and Ms. Jingjing Liu in the Plasma & Pulse Power Group (P³G) and other colleagues in the University who offered me help and support. I am also thankful to all my friends outside the University for their help and encouragements during my study abroad all these years.

Finally, but certainly not the least, I would like to express my love to my parents for their support and love in various manners throughout my study in the UK.
Publications

Journal Papers - Academic Journals


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Chapter 1 *Introduction*

1.1 *Plasma, the 4\textsuperscript{th} state of matter*

Plasma, the fourth state of matter, accounts for more than 99\% of the matter in the universe.\(^1\) When a gas is heated sufficiently, electrons are detached from neutral atoms and the resulting mixture of electrons, ions, and neutral particles constitute a plasma (see Figure 1.1). Plasmas can therefore be defined as ionized gases and they display properties that are different from those of the original neutral gases.\(^2\) Flames and lightening are examples of naturally occurring plasmas. On the earth, however, most materials are encountered in solid, liquid or gas phase and plasmas are not as common as they are in space. Different plasmas are shown in Figure 1.2 as a function of their temperature and electron density.\(^2\)

![Figure 1.1 Schematic of an electrically driven plasma](image-url)
Chapter 1

Introduction

Systematic studies of plasmas can be dated back to the early 19th century. Following the development of sufficiently powerful electric batteries, V. V. Petrov reported the discovery of the arc discharge in 1803. Subsequent works include those of the English physicists Michael Faraday on direct current (dc) glow discharges in evacuated tubes (~1 Torr) in the 1830s and Sir William Crookes on what today are called Crookes tubes in the 1880s. John Sealy Edward Townsend also studied plasmas in dc electric fields contributing to the advancement of the field in the early 20th century. The term plasma, however, was not introduced until 1928 and it was coined by Irvine Langmuir. In this work, we will use the terms “plasma” and “discharge” interchangeably.

The use of plasma for technological purposes exploded in the 1970s with the growing demand for low temperature anisotropic processing of silicon for the semiconductor industry. Actually, half of the steps required to create a modern integrated circuit require plasma and the research on technological plasmas operating in vacuum has been strongly driven by this multibillion dollar industry. More recently, plasmas sustained at atmospheric pressure have attracted attention for their potential technological and economical advantages, and research is being
carried out to characterize these plasmas and explore their potential in material processing and biomedical applications.

1.2 Characteristics of the DC glow discharge

DC glow discharges have been widely used for various applications. The characteristics of a DC glow discharge are first introduced here to unveil the discharge features and gain some fundamental understanding of plasmas. DC glow discharges normally manifest a stratification into alternating dark and luminous layers as shown schematically in Figure 1.3. From cathode to anode, these layers are referred to as Aston dark space, cathode glow, cathode dark space, negative glow, Faraday dark space, positive column, anode dark space and anode glow.

![Figure 1.3 Structure of a DC glow discharge](image)

Figure 1.4 presents the voltage-current diagram of a DC low-pressure electrical discharge. The regime between A and E before gas breakdown on the voltage-current diagram is termed “dark discharge” because the discharge is insufficiently strong to be visible to the eye. Section C-E denotes the Townsend discharge regime, in which the discharge is self-sustained. The high applied voltage causes free electrons within the gap to ionize the gas molecules by electron impact as electron drift to the anode, inducing a multiplication of electrons and ions within the gas gap. Electrons are replenished via secondary
electron emissions when energetic particles and photons reach the cathode. As shown by the section D-E in Figure 1.4, the rate of electron multiplication increases quite fast when the applied voltage is increased, which means small changes in voltage can cause a large rise in the current.

Once the electrical breakdown happens at E, the discharge transits into the glow discharge regime, in which the current in the discharge is high enough for the plasma to be visible and the effect of space charges becomes significant. As ion mobility is considerably lower than that of electrons, a large concentration of ions forms in front of the cathode. This is known as cathode fall or sheath region. The voltage drop across the cathode fall is comparable to that across the gap. As the cathode fall region is small, the electric field in this region is much higher than the equally distributed mean electric field (applied voltage over the gap size).

As shown in the Figure 1.4, after a discontinuous transition from the breakdown (E) to point F, the discharge evolves into the normal glow mode.
(F→G), in which the voltage is independent of the discharge current over several orders of magnitude. At the end of the normal glow mode at point of G, the plasma covers the entire cathode surface. If the current is decreased, then the discharge will travel back from G to F and from F to F' rather than to E. This hysteresis indicates that the normal glow mode of the discharge is related to the initial condition of the discharge. From G to H, the discharge current increases with the voltage, corresponding to the abnormal glow mode. When the discharge current grows to H, this large discharge current will heat the cathode and trigger the discharge to transit into a high temperature arc discharge.(H→I)

1.3 Atmospheric pressure glow discharge (APGD)

Recently, because of their vast application potential and their unique advantage of dispensing the expensive vacuum system essential to low and medium pressures glow discharges, atmospheric pressure glow discharges (APGDs) have attracted much attention. APGD has been successfully generated under DC conditions⁶, at 60Hz⁷ and at high frequencies ranging from kilohertz (kHz) to MHz⁸ and microwave.

Knowing physical parameters on electrons, ions, metastables and neutral particles is essential for understanding their role in sustaining the glow discharge. Electrostatic Langmuir probes provide a means for measuring the electron temperature, plasma density, plasma and floating potentials, and electron energy distribution function in plasmas. This diagnostic technique is widely used in low-pressure plasmas but unfortunately it is not appropriate for the study of plasmas produced at atmospheric pressure because of the collisional nature of the sheaths and often the reduced dimension of the discharge itself.⁹,¹⁰,¹¹ As a result of these limitations, spectroscopic diagnostics including emission spectroscopy,
absorption spectroscopy, laser induced fluorescence, and nano-second CCD imaging have been used alternatively in many studies of high pressure plasmas.$^{12}$

### 1.3.1 APGD Generation

The gas breakdown voltage required to ignite plasma at atmospheric pressure is larger than that required at low pressure due to the higher number of collisions the electrons experience as they are accelerated by the applied field. To overcome this problem higher voltages and/or smaller gaps are required to generate glow discharges at atmospheric pressure. Also as a result of the higher collisionality, the heating rate of the neutral gas increases and atmospheric discharges tend to have a higher gas temperature. This is typically undesirable because it may limit the application of plasma, it represents an energy loss in the system, and it can lead to discharge instabilities. However, not all the gases are equally susceptible to developing instabilities. For example, argon discharges tend to become unstable and constrict more readily than helium discharges. The reason for this is often attributed to the better thermal conductivity of helium. Due to its better stability helium is typically used as the buffer gas for many applications.$^8$

Plasma can be generated capacitively between two parallel electrodes or inductively with a coil. The latter, however, needs high frequency and high power in order to strike a plasma at atmospheric pressure, resulting in very hot discharges not suitable for the treatment of temperature-sensitive materials. Existing inductively coupled APGD’s often require additional non-inductive means such as hot filaments and lasers for generating seed electrons in order to keep the discharge going.$^{13,14}$ Capacitively coupled APGDs generated between two parallel electrodes can have either uniform glow-like or radially constricted appearances (Figure 1.5).$^{15,16}$ They represent two different modes of APGDs. These two modes of operation have been investigated experimentally and computationally. Controlling the voltage applied across the gas gap by
incorporating a dielectric barrier onto the electrodes,\textsuperscript{17,18} using resistive electrodes,\textsuperscript{7} and increasing the frequency of excitation\textsuperscript{17} have been found to be effective in preventing the discharge constriction.

![Figure 1.5](image)

**Figure 1.5** Atmospheric helium-nitrogen glow discharge operating in (a) diffuse glow $\alpha$ mode and (b) radially constricted $\gamma$ mode.\textsuperscript{16}

### 1.3.2 APGD chemistry

Driven by the interest in biomedical applications where reactive oxygen and nitrogen species are really important, and the fact that any plasma open to the atmosphere contains oxygen and nitrogen, it is important to consider these species in the plasma. O$_2$ can be introduced into the discharge to create a reactive environment capable of affecting biomolecules. Atomic oxygen (O) generated in the plasma by dissociation of the molecular oxygen (O$_2$) is known to be a powerful oxidant for etching organic films and bacterial membranes.\textsuperscript{19,20,21} Oxygen containing plasmas are also known to alter the stability of polymeric surfaces and to oxidize cell membranes and embedded proteins.\textsuperscript{22,23} The concentration of O atoms, metastable oxygen molecules, $a^1\Delta_g$ and $b^1\Delta_g^+$, and ozone in the downstream region of an atmospheric-pressure He+O$_2$ discharge can
be determined by a combination of optical spectroscopy and numerical modelling of the chemical reaction kinetics.\textsuperscript{24} The most probable channel for the formation of oxygen atoms is through Penning ionization of $\text{O}_2$ molecules (ionization energy $\approx 12$ eV) by $\text{He}^+$ followed by the electron impact dissociation of $\text{O}_2^+$.\textsuperscript{25}

$$\text{He}^+ + \text{O}_2 \rightarrow \text{He} + \text{O}_2^+ + e$$
$$\text{O}_2^+ + e \rightarrow 2\text{O}$$

The concentration of $\text{O}_2$ in the feed gas plays a quite important role in an attempt to maximize atomic oxygen production in the plasma.\textsuperscript{26} The ground state oxygen atoms produced by a radio-frequency atmospheric pressure plasma operating with argon and oxygen was measured by NO titration.\textsuperscript{27} For helium discharge, the optical emission spectra shown in Figure 1.6 suggests the addition of $\text{O}_2$ to the plasma forming gas leads to a significant decrease of the plasma.\textsuperscript{28} This is due to the molecular nature of oxygen and its electronegativity. As a result, a small oxygen content (typically $<1\%$) is found to be optimum in terms of oxygen production and plasma treatment efficacy.

Nitrogen is also of interest in biomedical applications. For example, it is recognized that amino groups created by plasma functionalization of polymer surfaces provide an excellent basis for subsequent surface modification as they allow biomolecules to bond with high selectivity.\textsuperscript{29} The presence of nitrogen is also often exploited to characterize the discharge. The rotational temperature obtained from the emission of the second positive system of molecular nitrogen $N_2\left(C^3\Pi_u \rightarrow B^3\Pi_x\right)$ or from the emission of molecular nitrogen ions $N_2^+\left(B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+\right)$ is often used to infer the gas temperature of the discharge.\textsuperscript{30} Finally, nitrogen is also significant in biomedical applications because nitrogen based radicals, in particular NO, emit ultraviolet photons (Figure 1.7) that directly
interact with bonds in the DNA molecule causing genetic damage to living organisms.29

Figure 1.6 Emission spectra of the plasma jet ~1 mm downstream of the nozzle exit plane for $P = 1$ W. (a) 1 slm (standard litre per minute) He, (b) 1 slm He with 10 sccm (standard cube centimetre per minute) O$_2$ in the capillary electrode and (c) 1 slm He+ 1 v/v% O$_2$.28

Figure 1.7 Integrated UV emission (165–310 nm) power density as a function of driving frequency for three different concentrations of N$_2$: 1%, 10%, and 20% in a N$_2$ /He admixture.31
1.3.3 Applications of APGDs

The potential economic and technological advantages of creating a plasma without the need for a vacuum system have boosted the research of APGDs. The rapid growth in research activity experienced over the last years has broadened the application spectrum of APGDs, which have been suggested for bio-medical applications, displays, radiation sources, micro-chemical analysis systems, gas analyzers, photodetectors, microlasers, and microwave devices, microreactors, propulsion systems, aerodynamic flow control, material processing, and environmental applications.

1.4 Organization of the thesis

In this thesis, an experimental and numerical study on radio frequency atmospheric pressure glow discharges is presented. There are 8 chapters that discuss various aspects related to discharge dynamics, plasma physics and chemistry in radio frequency (rf) APGDs.

A brief introduction to plasma, and in particular to glow discharges is given in Chapter 1. Previous works on different kinds of APGDs are reviewed in this chapter, setting up the context for this thesis. This chapter also emphasizes the significance of APGD research which stems from their immense application potential. In Chapter 2, the experiment setup for the rf-APGD system used in this thesis is detailed. Experimental diagnostics techniques, required equipment, and interpretation methodology are also discussed in that chapter. In Chapter 3, the numerical model developed to understand the physics governing rf-APGDs is discussed.

The discharge breakdown mechanism, the frequency dependence of the breakdown voltage, and electron trapping are discussed in Chapter 4. The different discharge evolution at low and high currents is also investigated.
Chapter 5 discusses the electron heating mechanisms in rf-APGDs and different operation modes. Schemes to control mode transitions such as the use of dielectric barrier are also presented in that chapter. Chapter 6 focuses on the influence of the rf excitation frequency on APGDs. Fundamental understanding of the underpinning physics as well as practical implications are discussed. The plasma chemistry is studied both experimentally and numerically in Chapter 7. Finally, the evolution of the rf-APGD as the gap size is reduced to create microdischarges is discussed in Chapter 8.

1.5 Contribution of this thesis

The research carried out during this thesis has produced 10 journal papers and 11 contributions to international conferences including 4 invited talks. The key contributions reported in this thesis can be summarised as follows:

1. Electron trapping in rf-APGD

The work detailed in Chapter 4, shows experimental evidence of electron trapping in radio frequency atmospheric pressure glow discharges. Because of the fast oscillating rf voltage, the electron transition time across the gap is longer than the half rf period and consequently, the electrons become trapped in the gas gap. Electron trapping remained a theoretical prediction and its validity had not been supported with experimental evidence until the results presented in this chapter were published in ‘Electron trapping in radio-frequency atmospheric-pressure glow discharges’ D. W. Liu, J. J. Shi, M. G. Kong. *Applied Physics Letters*. Vol.90 Iss.4 No.041502, 2007.

2. Electron heating in rf-APGD
Chapter 1

Introduction

The work detailed in Chapter 5 is the first reported study on electron heating in radio frequency atmospheric-pressure glow discharges. Different from conventional low pressure plasmas, electron heating in atmospheric pressure glow discharges had not been studied thoroughly. Experimental and computational results aimed at elucidating the electron heating mechanism in atmospheric-pressure rf discharges were reported in 'Electron heating in radio-frequency capacitively coupled atmospheric-pressure plasmas' D. W. Liu, F. Iza and M. G. Kong. *Applied Physics Letters*. Vol.93 Iss.26 No.26 I S03, 2008.

3. Influence of rf excitation frequency on APGD

Chapter 6 details the frequency effect on atmospheric pressure glow discharges. Besides the experimental confirmation of existing theoretical predictions, the results in Chapter 6 explore the underpinning physics governing the frequency dependence of power coupling into electrons and ions in rf-APGDs. This has been published in 'Evolution of Atmospheric-Pressure rf Plasmas as the Excitation Frequency Increases' D. W. Liu, F. Iza, M. G. Kong. *Plasma Process and Polymers* Vol.6 Iss.6-7 No. 446, 2009.

4. rf APGD Chemistry

Chapter 7 investigates the gas discharge chemistry. Because of the impurity of the background gas and the addition of N2 and O2 for biomedical applications, comparisons between He+N2, He and He+O2 discharges are performed experimentally and numerically in chapter 7. The optimum atomic oxygen production base on the injection amount of O2 into He is also given. Results in chapter 7 have been published in 'Evolution of the Light Emission Profile in

5. Microplasmas

Unlike conventional APGD that operate in diffuse $\alpha$ or constricted $\gamma$ mode, experimental results shown in Chapter 8 are the first report on the existence of a diffused $\gamma$ mode in APGDs of reduced size. These results are summarized in ‘Electron avalanches and diffused $\gamma$-mode in radio-frequency capacitively coupled atmospheric-pressure microplasmas’ D. W. Liu, F. Iza, and M. G. Kong. *Applied Physics Letters* Vol. 95 Iss. 3 No 031501, (2009).
Chapter 2  Experiment setup and plasma diagnostics

2.1 Experiment setup

The radio frequency-APGD system used in this thesis consists of two water cooled stainless steel electrodes, each being 2cm in diameter. The discharge gap between the two electrodes can be varied between 0 and 10mm. As shown in Figure 2.1, the electrodes are enclosed in a Perspex box to minimize the environmental effect and to maximize the control over the background gas. Although not air tight, the box has only two openings, one is for gas inlet and the other one is for gas outlet. The working gas is helium (99.95% purity), fed through the gas inlet at a flow rate of 5 slm (standard litre per minute) controlled by a mass flow controller (MFC1179A and MKS PR4000B). Although, before the rf power is switched on, the gas flow is left to persist for at least 10 minutes to ensure the air originally contained in the rig is flushed out and replaced with helium, there are still traces of N₂, O₂, and H₂O in the discharge. From an academic/scientific point of view, an airtight enclosure would have been preferable. Nevertheless, atmospheric pressure plasmas are intended to be used in open air and incorporate admixtures of O₂ and/or N₂ to enhance the chemical properties of the discharge. In addition, impurities in concentrations of parts per million are known to affect helium discharges. Since the impurity concentration in the feed gas is already at this level, no attempt has been made to seal the Perspex box. As shown in later chapters, the spectra of all the discharges indicate the presence of oxygen, nitrogen and water derived species. Water cooling (Colora Messtechnik GMBH) is used to prevent the electrodes from turning too
hot when the input power is high. Typical cooling water temperature is around 40 degree Celsius.

A rf power amplifier (Amplifier Research 150A100B) and a function generator (Tektronix AFG3102) are used to deliver an rf voltage at 1 – 30 MHz to the electrode unit via a home-made matching network. Different matching networks were used to enable operation at different rf frequencies. Voltage and current are measured by a wideband voltage probe (Tektronix P6015A), a wideband current probe (Tektronix P6021) and a digital oscilloscope (Tektronix TDS 3000B). An iCCD camera (Andor i-Star DH720), a pulse generator (BNC Digital Delay Generator 7075) which works as an external trigger for the iCCD camera, and optical filters (Thorlabs FWHM 10nm) are used to take discharge images. A schematic of the whole system is shown in Figure 2.2.

![Experimental Rig](image_url)
2.2 Plasma diagnostics

In this thesis, electrical and optical diagnostics are used to characterise rf-APGDs. These diagnostics are discussed below, and a schematic of the overall setup is shown in Figure 2.2.

2.2.1 Voltage and current measurement

As shown in Figure 2.2, the voltage is measured across the discharge gap and the current probe is placed on a coaxial cable connected to the ground electrode. Since the voltage probe is placed outside the Perspex box, a loop of ~10cm in diameter is formed between the point at which the voltage is measured and the reference ground point. This represents a parasitic inductance of ~100nH, which would introduce a small error (typically <1%) in the voltage measurement and a shift in the observed phase angle.

Figure 2.2 Schematic of an rf-APGD

Due to the different length of the coaxial cables that connect the voltage and current probes to the oscilloscope and other parasitic effects, there is a delay
between the voltage and current measurements. This delay is about 10 nanoseconds, which can be neglected when the excitation frequency is in the kilohertz range, but it becomes important in rf-APGDs operating in the MHz range. For example, 3ns delay between the two probes is π/13 phase difference between the voltage and current signal at 13.56MHz. This phase difference is large enough to compromise the power measurement in the discharge.

In order to calibrate the probes and enable power measurements, a load of known impedance is used. Figure 2.3 (a) illustrates a circuit used to calibrate the probe delay. The current and voltage across a standard resistor of 50Ω is measured. The current and voltage signals should be in phase if there were no delay between the two probes. The measured phase difference is therefore attributed to the cable lengths and it is subtracted from subsequent measurements.

![RF Signal Circuit](image)

**Figure 2.3 (a) Voltage and current measurement on a standard resistor 50Ω (b) on the parallel plate without discharge**

This delay correction can also be checked by measuring the voltage and current before the plasma is ignited since in the absence of plasma, the gap impedance is purely capacitive, i.e., the phase difference between the voltage and current signal must be 90 degrees. A Matlab program (see Appendix A) was written to calibrate the probes and perform power analysis on measured signals.
In order to track the electrical evolution of the plasma from pre-breakdown to the constricted $\gamma$ mode, a LabVIEW program was used. This automatizes the data acquisition of the voltage and current signals.

LabVIEW programs are referred to as virtual instruments (VIs). Each VI has three components: a block diagram, a front panel, and a connector panel. The last is used to represent the VI in the block diagrams of other, calling VIs. Controls and indicators on the front panel allow an operator to input data into or extract data from a running virtual instrument. However, the front panel can also serve as a programmatic interface. Thus a virtual instrument can either be run as a program, with the front panel serving as a user interface, or, when dropped as a node onto the block diagram, the front panel defines the inputs and outputs for the given node through the connector pane. This implies each VI can be easily tested before being embedded as a subroutine into a larger program.

![Figure 2.4 User interface of the LabVIEW program developed to measure the voltage and current across the APGD.](image-url)
The graphical approach also allows building programs simply by dragging and dropping virtual representations of lab equipment. The LabVIEW programming environment makes it simple to create small applications.

![LabVIEW program block diagram](image)

**Figure 2.5 LabVIEW program block diagram**

We can use LabVIEW to communicate with hardware such as data acquisition, vision, and motion control devices, as well as other GPIB, PXI, VXI,
Chapter 2  Experiment setup and plasma diagnostics

RS232, and RS485 instruments. In the case that concerns us the LabVIEW program communicates with the oscilloscope via a GPIB card. Besides displaying the waveform, the program shown in Figure 2.4 also records the peak to peak and the root mean square values of each channel, the phase difference between the channels, and exports the data as a "*.dat" file that can be further processed with Origin or Matlab. Figure 2.5 shows the LabVIEW program block diagram.

2.2.2 Optical emission measurement

Optical emission spectroscopy (OES) is a convenient and non-intrusive way to study atmospheric pressure glow discharges. The Andor Shamrock SR-303i shown in Figure 2.6a is used in this thesis. Its mechanical scan range is from 0 nm to 1450 nm and its wavelength resolution <0.2nm. The Shamrock 303i uses the triple grating turret shown in Figure 2.6b, designed to offer flexibility and control interchange of gratings. The three gratings are 300, 1200 and 2400 lines/mm, and their spectral regions are 250-1800nm, 200-1200nm and 250-600nm, respectively.

Figure 2.7 shows the software interface of the Andor Shamrock SR-303i system, through which the spectral functions such as wavelength selector, slit control, filter selection, shutter control and exit port selector can be chosen.

Figure 2.6 a) Andor Shamrock SR-303i, b) triple grating turret

Figure 2.8 illustrates the optical emission spectrum of an APGD and how different emission lines and bands can be used to identify atoms and molecules
present in the discharge. It should be noted, however, that ground state atoms/molecules can not be observed by this diagnostic technique since they do not emit light. Different species and excited states in the discharge can be detected by the OES measurement. Gas temperature is an important factor that can dictate the suitability of APGD for a given application. If the plasma is too hot, it can become unstable and damage temperature sensitive materials.

Figure 2.7 Software interface of the Andor Shamrock SR-303i system.

The optical emission of OH (A2∑+, v=0) at 309nm can be used as an indicator of the gas temperature, if it is assumed that the high collisionality of atmospheric pressure glow discharges thermalises rotational and translational temperatures. The shape of the emission band depends on the molecule rotational temperature. This is measured with the grating of 2400 lines/mm, and the gas temperature is determined by fitting a theoretical spectrum calculated with LIFBASE.47 Similarly, N2 (357nm) and N2+ (391nm) can also be used to estimate the gas temperature.
Chapter 2  Experiment setup and plasma diagnostics

Figure 2.8 Optical emission spectrum of a 10MHz rf-APGD.

Figure 2.9 Gas temperature calculated by fitting the experimental spectrum to a synthetic one created with LIFBASE.

rf-APGDs are dynamic systems and the time averaged spectrum recorded by the OES system does not capture the temporal evolution of the discharge. To gain insights into the discharge temporal evolution, fast images with nanosecond resolution are needed. These are obtained with an Andor iStar 720 Gen III intensified CCD camera (Figure 2.10). This system is designed for low-light spectroscopy applications requiring fast gating and provides 1024x256 pixel
images. The filmed Gen III image intensifier provides excellent quantum efficiency in the visible region (see Figure 2.11). With the trigger signal from the external trigger device (BNC Digital Delay Generator 7075), 5ns exposure time pictures can be taken with this iCCD camera. An example of a 5ns exposure time image of a rf-APGD is shown in Figure 2.12a. In order to visualise the temporal evolution of the plasma emission, multiple images at different phase of the rf cycle are taken. An example of 9 such images are shown in Figure 2.12b. Here each image has been cropped to visualise only the plasma region. This is done automatically with a Matlab program (Appendix B).

![Figure 2.10 ANDOR iStar 720 Gen III intensified CCD camera](image)

![Figure 2.11 Peak quantum efficiency of the iCCD camera at room temperature. The intensifier used in the experiment is 18F-53 (VIS+/HR/P43).](image)
Figure 2.12  a) Plasma image taken with the iCCD camera using raw data. b) single shot 5ns exposure time images over one rf cycle, all displayed with the same data scale.

Figure 2.13 Spatio-temporal evolution of the light emission of an RF APGD. Different colours indicate different light intensity, with red and blue being high and low intensity respectively. The emission profile at a given time is obtained by integrating in the radial direction the emission pattern recorded in a 5ns exposure time shot (e.g. Figure 2.12 b). The graph on the right indicates the correspondence between time and the applied rf voltage.
In addition, we can integrate the images in the radial direction and collate the resulting curves to produce a 2D plot that portraits the spatio-temporal evolution of the discharge emission (Figure 2.13).

Bandpass optical filters (Thorlabs FWHM 10nm) can be used to collect a well-defined wavelength band of the light emitted by the plasma, while rejecting other unwanted radiation. A combination of iCCD and optical filters allow the study of space-, time-, and wavelength-resolved optical emission from the plasmas.

### 2.3 Summary

In this chapter, the experiment setup of the rf parallel plate discharge used in this thesis is presented along with the electrical and optical techniques used to characterize the plasma.
Chapter 3  Computational modelling of rf-APGDs

Over the course of the past 20 years, great efforts have been made to develop suitable numerical models in the field of low-temperature plasmas. Numerical models provide a unique way of studying plasma that complements theoretical analyses and experimental measurements. Although computer simulations incorporate various assumptions, computer models can account for higher complexity than analytical analyses and provide valuable diagnostics not available experimentally. Thanks to the fast development of the IT industry, the higher computational capabilities of current computers provide an opportunity for not only qualitative but also quantitative agreement between simulation and experiment results.

Glow discharges are complex systems involving physical, chemical and electromagnetic processes. The mathematical representation of these processes results in a set of coupled non-linear differential equations. Furthermore, different space and time scales need to be solved simultaneously and self-consistently. As a result, a computational model that incorporates a detailed description of all physical processes involved in a plasma would be computationally unfeasible even with today's supercomputers.

Fortunately, it is possible to simplify the plasma model by neglecting less important details while still capturing the main physics. Usually, transport equations coupled with Poisson's equation are used to study plasma dynamics.
Physical and chemical interactions between electrons, positive ions, negative ions (electronegative gas), metastables, and background neutral particles also need to be considered to predict plasma characteristics accurately. Kinetic, fluid and hybrid schemes have been developed over the last decades to model plasmas numerically.

In this work, a one-dimensional fluid model based on the solution of Poisson’s, continuity, and electron energy balance equations is used to study rf-APGDs. Fluid models have been used successfully in the past to study low pressure discharges. Only recently this simulation approach has been applied to the study of capacitively coupled atmospheric pressure glow discharges. This simulation approach is often suitable for studying APGDs, and it represents a good compromise between accuracy and computation efficiency. Sheath dynamics through spatial and temporal profiles of charged densities, electric field, electron mean energy, sheath thickness, sheath voltage, and other fundamental characteristics can be optimised through computer simulations to tailor the operation of rf-APGDs to their intended applications.

3.1 Introduction to fluid models

3.1.1 The Boltzmann equation

In a plasma, particles interact with each other and with the confinement vessel while responding to the applied electric field. Unfortunately, it is impossible to track each particle individually because there are too many particles. In rf APGD, electron density is typically $10^8$-$10^{12}$ cm$^{-3}$. Therefore, a statistical method is employed instead to model the plasma. A probability function $f_s(\vec{r}, \vec{v}, t)$ is used to describe each species, where $f_s(\vec{r}, \vec{v}, t)d\vec{r}d\vec{v}$ represents the number of particles in
a differential element $d\vec{r}d\vec{v}$ of the 6 dimensional space $(\vec{r},\vec{v})$ of position $\vec{r}$ and velocity $\vec{v}$ at time $t$.

The time evolution of the density function for each species is governed by the Boltzmann equation\textsuperscript{63,64}
\begin{equation}
\frac{\partial f_s}{\partial t} + \vec{v} \cdot \nabla_s f_s + \frac{\vec{F}}{m} \cdot \nabla_s f_s = \frac{\partial f_s}{\partial t} \bigg|_e \tag{3.1}
\end{equation}
where $\nabla_s$ is the space gradient, $\nabla_v$ is the velocity gradient, $\vec{F}$ the applied electromagnetic forces, $m$ the particle mass and $\frac{\partial f_s}{\partial t} \bigg|_e$ the change in the distribution function due to collisions and radiative processes. The Boltzmann equation contains all the information regarding the plasma, however, the direct solution of the time dependent Boltzmann equation is very complex, especially when the collision/radiative term cannot be neglected. Analytical solutions are impossible except for very few simple cases and even computational solutions generally require some approximations.\textsuperscript{64,65} Therefore, although the Boltzmann equation describes the plasma accurately and accounts for nonlinear and kinetic effects, a direct solution of the Boltzmann equation is rarely attempted. Instead, a set of moments of the Boltzmann equation are typically solved. This approach gives rise to the fluid models.\textsuperscript{17}

### 3.1.2 The fluid model

Typically, only the first three moments of the Boltzmann equation are used to model the plasma.\textsuperscript{63} These three moments give rise to the mass, momentum and energy conservation equations, each with a characteristic time-scale that is related to ionization, momentum relaxation and energy relaxation, respectively:

Mass balance: \begin{equation}
\frac{\partial n}{\partial t} + V \cdot n \vec{v} = R_e - R_i \tag{3.2}
\end{equation}
Momentum balance: \[ \frac{\partial (nmv)}{\partial t} + \nabla \cdot (nmv^2) - nF = R_m \] (3.3)

Energy balance: \[ \frac{\partial (e)}{\partial t} + \nabla \cdot (ne) - nF \cdot v = R_{en} \] (3.4)

where \( n \) is the particle density, \( F \) the force acting on the particles, \( v \) the mean velocity, \( R_c \) the creation rate, \( R_l \) the loss rate, \( e \) the mean energy, \( R_m \) the rate of momentum loss and \( R_{en} \) the energy gain (or loss) rate.

The high collisionality in atmospheric pressure discharge makes particle inertia negligible and the so called drift-diffusion approximation can be used to simplify the above equations.\(^6\) The set of balance equations further simplified for 1-dimensional analysis then becomes:

**Mass balance:** \[ \frac{\partial n_{i,*}}{\partial t} = - \frac{\partial n_{i,*}}{\partial x} + \sum K_{i,j}(e)n_i n_j \] (3.5)

**Drift diffusion:** \[ \Gamma_{e,*} = -D_{e,*} \frac{\partial n_{e,*}}{\partial x} + \mu e n_e E \] (3.6)

**Energy balance:** \[ \frac{\partial (ne)}{\partial t} = - \frac{\partial \Gamma_e}{\partial x} + e \Gamma_e E - K_{i,j}(e)n_i n_j - 3 \frac{m_e}{m_{new}} NK_{en} n_e k(T_e - T_{new}) \] (3.7)

**Energy flux:** \[ \Gamma_e = \frac{5}{3} \Gamma_e e - n_e D_e(e) \frac{\partial e}{\partial x} \] (3.8)

where \( K_{i,j} \) is the rate constant for collisions between the \( i \) and \( j \) species, and \( \Gamma \) is the flux. Subscript \( e \) stands for electrons, + for positive ions and * for metastables. \( D \) is the diffusion coefficient, \( \mu \) is the mobility and \( Z \) is 1 for single charged positive ions, 0 for metastables and -1 for electrons. \( \Gamma_e \) is the energy flux. The terms on the right-hand side of the electron energy balance eq. (3.7) represent, respectively, the electron thermal energy flux, the electron joule heating, the
energy gain or loss due to inelastic collisions and the energy loss due to electron-neutral momentum transfer collisions. The last term of eq.(3.7) is typically negligible for low-pressure discharges, but it becomes significant at atmospheric pressure because the electron and neutral gas densities are much higher. For the atomic and molecular helium metastables in the discharge, their mass conservation equations are the same as the balance equations of electrons and positive ions, except that their fluxes are only attributed to diffusion, i.e. no drift because they are neutral particles (Z=0 ⇒ μ=0).

The ionization and recombination rate constant \(K_i(\varepsilon)\), energy loss rate constant \(K_L(\varepsilon)\) and momentum transfer rate constant \(K_m(\varepsilon)\), are functions of the electron mean energy.\(^{53,66,67}\) The momentum transfer frequency is estimated from the momentum transfer collision cross section of the particle interacting with the background gas and their mean speed.

The electric field is calculated by solving Poisson's equation:

\[
\varepsilon_0 \frac{\partial E}{\partial x} = e \left( \sum_p Z n_p - n_e \right) \tag{3.9}
\]

where subscript + represents different ions and e represents electrons in the discharge.

### 3.1.3 The global model

In a global model all spatial and time derivatives are neglected to enhance computation efficiency.\(^{68}\) Therefore, the plasma is simply described by its volume \((V)\), surface area \((A)\), averaged absorbed power \((P)\) and gas composition. The governing equations are derived from mass and energy conservation arguments and may be expressed as a set of nonlinear ordinary differential equations. A general particle (mass) balance equation may be expressed as follows:
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\[
\frac{dn_k}{dt} = \sum_{i=1}^{N_k} q_i K_i \prod_{j=1}^{N_k} n_{i,j} - \Gamma \frac{A}{V} (\Gamma_+ = \frac{1}{4} n_e v_{th}, \Gamma_- = n_e u_B) \tag{3.10}
\]

where \(n_k\) is the particle density of the \(k^{th}\) plasma species, \(K_i\) is the rate constant associated with the \(i^{th}\) chemical process, \(N_k\) is the number of reactants involved in the \(i^{th}\) chemical process and \(n_{i,j}\) is the number density of the \(j^{th}\) reactant involved in the \(i^{th}\) chemical process, \(\Gamma\) is the flux to the walls, \(v_{th}\) is the thermal velocity and \(u_B\) is the Bohm velocity.\(^6\) The terms on the right-hand side of eq.(3.10) account for particle production and loss within the chamber due to volume and surface chemical processes. To solve the above equation the electron temperature is needed as the rate constants depend on \(T_e\). The electron temperature is typically determined by solving the power balance equation. Alternatively, the algorithm shown in Figure 3.1 can be used to find a self-consistent solution without having to solve the energy equation explicitly:

```
Set desired n_e
n_e_set

Initialize density (set n_e 0 = n_e_set)

Display results

Determine T_e
that satisfies dn_e / dt = 0

Advance time and update the rest of densities

Steady state?
No
```

Figure 3.1 Global model flow chart

The above algorithm can employ large time steps leading to quick steady state solutions. The results from the global model can be used to estimate the initial densities in more complex simulations, reducing the computation time.
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Furthermore, the global model can be used to identify main species and reactions for a given plasma chemistry. This will be discussed later in section 3.3.4.

3.2 Numerical algorithm: Fluid model

All governing equations described in the previous section need to be discretised in order to be solved numerically. In general, the discretisation leads to "explicit" and "implicit" models. The explicit models calculate quantities at a time step using the values of physical quantities at the previous time step. In these schemes, the calculation can lead to numerical fluctuations or even instabilities. To overcome this, restrictions must be imposed to the choice of the time step, increasing the computational time. On the other hand, implicit methods are computationally more efficient. They calculate the state of a system at a later time by solving an equation involving both the current state of the system and the later one. These schemes are numerically more stable and allow larger time step to be used for the time integration. It should be noted that an entirely implicit scheme is difficult to be successfully accomplished in any numerical model.

Various approaches can be found in the literature to solve the set of the governing eq.(3.5)-eq.(3.8). One way is to use the centred finite difference representation of the spatial derivatives and a fourth-order Runge-Kutta integration in time from an assumed set of initial conditions, which is a simple explicit method of easy implementation. As mentioned above, however, explicit methods need to meet severe time constraints in order to avoid non-physical fluctuation and stability problems. Alternatively, some other numerical algorithms have been proposed to solve eq.(3.5)-eq.(3.8) more efficiently. A technique of centred differences for the diffusive contribution and an unwinding method for the convective terms in space were used by E. Gololides et al. They solved the discretised equations each time step using the Newton-Raphson
method. Considering the need for a computationally stable and efficient scheme, a semi-implicit self-consistent scheme is implemented in this thesis. The model is described below in detail.

![Diagram of uniform grid with electrodes and grid nodes and cell centers.](image)

**Figure 3.2 Uniform grid. Circles represent nodes and diamonds cell centres.**

To solve eq.(3.5) - eq.(3.8) numerically, they are first discretised. A uniform grid is used to discretize the computational space in our model and grid nodes are located at:

\[ x_i = L \times \left( \frac{i-1}{(N_p-1)} \right) \quad i = 1, N_p \quad (3.11) \]

where \( L \) is the interelectrode gap distance and \( N_p \) is the number of nodes. Typically 501 points are used in the simulations reported in this thesis. Particle density and electron energy are defined on the grid points, whereas the electric field and particles fluxes are defined on the cell centres, allowing a second order centred finite difference formulation of spatial derivatives. These are illustrated in Figure 3.2.

A non-uniform grid was also tested during the program development. In this case the grid nodes were located at:

\[ x_i = \frac{L}{2} \left( \frac{i-1}{(N_p-1)/2} \right)^2 \quad x_{N_p-i+1} = L - x \quad i = 1, (N_p - 1)/2 + 1 \quad (3.12) \]

The non-uniform grid gathers grid nodes on the edges of the simulation domain where the plasma sheaths form. Although this approach seems to suggest...
that fewer total number of grid points are needed to resolve the sheaths, the model develop instabilities in the sheath region that are not observed when the uniform grid is used. The instabilities are attributed to the lower order of the finite difference formulation in non-uniform grids. 71

In most numerical methods the standard centred difference scheme is used for the discretization of the spatial derivative of the drift and diffusive fluxes. However, when the voltage between two adjacent mesh nodes is of the order of or larger than the characteristic energy \( D/\mu \), this scheme becomes numerically unstable. To alleviate this problem, the exponential scheme of Sharfetter and Gummel 72, 73 is used. This is especially effective for handling large density gradients or/and large voltage changes as those present in plasma simulations. The particle flux, diffusion coefficient and drift velocity are all assumed to be constants between adjacent grid nodes.

For the uniform grid, the governing equations discretised by the exponential scheme become:

\[
\frac{n_{i}^{k+1} - n_{i}^{k}}{\Delta t} = \frac{\Gamma_{i+1/2}^{k+1} - \Gamma_{i-1/2}^{k+1}}{\Delta x} + S_{i}^{k} \tag{3.13}
\]

Drift diffusion:

\[
\Gamma_{i+1/2} = \frac{\left[ n_{i} D e^{(z_{i+1/2})} - n_{i} D_{i+1/2} \right] z_{i+1/2}}{\Delta x \left[ e^{(z_{i+1/2})} - 1 \right]} \tag{3.14}
\]

where \( z_{i+1/2} = \frac{Z_{\mu_{i+1/2}}}{D_{i+1/2}} (V_{i+1} - V_{i}) \)

where \( S_{i}^{k} \) is the source term at the mesh point \( i \) and time step \( k \) and \( Z \) the charge of the particle, i.e. +1 for positive ions and -1 for electrons and 0 for neutrals. The advantage of this exponential scheme is that it provides numerically stable estimates of the particle flux both at large (\( |z_{i+1/2}| > 1 \)) and small (\( |z_{i+1/2}| << 1 \)) voltage differences. This allows larger space and time steps to be used in the simulation, and as such reduces computation time substantially.
The above balance equations are coupled to Poisson equation, which is resolved in a semi-implicit manner:\textsuperscript{72,74}

\[
\frac{d(eE^{k+1})}{dx} = \sum_{p} q_p \left( n_p^k + \Delta t \frac{d \Gamma_p}{dx} \right)
\]

(3.15)

where \( p \) represents different charged species and the space charged densities at time \((k+1)\) are predicted based on the value at time \( k \) \((n_p^k)\) and a correction factor \( \Delta t \cdot \nabla \Gamma_p \).

The flow chart in Figure 3.3 summarises the procedure used to solve eq. (3.13) - eq.(3.15).

First, the electric field is estimated using eq.(3.15). Then the density of every species \( (p) \) at time \( k+1 \) \((n_p^{k+1})\) is evaluated using eq.(3.13). After the spatial profiles of all plasma species are obtained, the electric field is re-evaluated.
solving Poisson's equation (eq.(3.9)). Finally, the electron mean energy \( n_e^{k+1} = n_e^{k} e^{k+1} \) is calculated from eq.(3.7).

In the above procedure, it is worth mentioning that all source terms are evaluated explicitly because a fully implicit treatment is not feasible. The percentage difference in the maximum electron density between two consecutive rf cycles is used to check if the dynamic steady state has been reached. In particular, the program stops when \( (n_{e,\text{max}}^f - n_{e,\text{max}}^{f-1}) / n_{e,\text{max}}^f \leq 10^{-3} \). The time evolution of the maximum density of each species during a typical simulation is shown in Figure 3.4.

![Figure 3.4](image)

Figure 3.4 Time evolution of a) electron density percentage difference between continuous rf cycles, b) the maximum electron density, c) the maximum He\(^{+}\) density, d) the maximum He\(^{+}\) difference, e) the maximum He\(_2\)\(^{+}\) density, f) the maximum He\(_2\)\(^{+}\) density.

### 3.2.1 Boundary conditions

The continuity equation of each species (eq.(3.13)) requires boundary conditions at each electrode.

For electrons, this is given by:
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LHS Electrode:
\[ \Gamma_i = -\frac{1}{4} v_{th}^e n_{e,1} - a \gamma_e \Gamma_{i+1} + (a - 1) \mu_e E_2 n_{e,1} \]  \hspace{1cm} (3.16)

RHS Electrode:
\[ \Gamma_{i+1} = -\frac{1}{4} v_{th}^e n_{e,1} - b \gamma_e \Gamma_{i+1} + (b - 1) \mu_e E_{i+1} n_{e,1} \]

where \( v_{th}^e = \left( \frac{8kT_e}{\pi m_e} \right)^{1/2} \) is the electron thermal velocity, and \( \gamma_e \) is the effective secondary electron emission coefficient due to ion bombardment. The induced electron density, electric field and electron flux are shown in Figure 3.5.

![Figure 3.5 Schematic showing the indices used in the computer model.](image)

A general expression is given by introducing parameters \( a \) and \( b \), which are set equal to unity if the electric field is directed towards the electrode, and zero otherwise (Figure 3.6).

![Figure 3.6 Electric field near the electrode and its effect on parameters \( a \) and \( b \).](image)

The corresponding boundary condition for positive ions is given by
\[ \Gamma_i^+ = -\frac{1}{4} v_{th}^i n_{i}^+ + a \mu_i E_2 n_{i}^+ \]
\[ \Gamma_{i+1}^+ = -\frac{1}{4} v_{th}^i n_{i+1}^+ + b \mu_i E_{i+1} n_{i+1}^+ \]  \hspace{1cm} (3.17)
Where the subscript $1$ is the point on the left electrode, the subscript $s_{h+1}$ is the point on the right electrode (see Figure 3.5), $\Gamma^{+}$ is the ion flux and $v_{th}^{+} = \left(\frac{8kT_g}{\pi M}\right)^{1/2}$ is the ion thermal velocity.

In eq.(3.16) and eq.(3.17), if the electric field is directed towards the electrode ($a=1$, or $b=1$), the electron flux to the electrodes equals the thermal flux minus the secondary electron emission flux, while the ion flux equals to the ion thermal flux plus the ion drift flux. Because of the low mobility of ions at atmospheric pressure, the ion flux can be of the same order of magnitude of as the ion drift flux when the electric field strength at the electrode is below $10 \text{kVcm}^{-1}$. On the other hand, if the electric field is directed away from the electrode ($a=0$, or $b=0$), the electron flux to the electrode equals the electron thermal flux plus the electron drift flux, while the ion flux equals to the ion thermal flux.

The boundary conditions for the neutral species are given by

$$
\Gamma_{i}^{m} = -\frac{1}{4} n_{i}^{m} v_{th}^{m}
$$

$$
\Gamma_{s_{h+1}}^{m} = \frac{1}{4} n_{s_{h}}^{m} v_{m}^{m}
$$

where $\Gamma^{m}$ is the metastable flux to the electrode and $v_{th}^{m} = \left(\frac{8kT_g}{\pi M}\right)^{1/2}$ is the metastables thermal velocity. For simplicity, it is assumed that the temperature of the metastables equals to the gas temperature. Because the metastables are not affected by the electric field, only thermal flux is considered in eq.(3.18). 75

### 3.3 Pure helium model: species and chemical reactions

In this section we discuss the main species and reactions involved in atmospheric pressure helium rf APGD. Although the discharge is affected by impurity traces (such as nitrogen, oxygen and water vapour), these are not considered here and will be discussed in the Chapter 7 instead.
3.3.1 **Species and transport coefficients**

The diffusion and the mobility coefficients of the main species in a pure helium plasma are listed in Table 3.1. They are obtained for a fixed gas temperature of 393 K.\(^{17}\) The electron temperature \(T_e\) in Table 3.1 is in Kelvin. The mobility for metastables and helium atoms is zero because neutral particle motion is not affected by the electric field. The coefficients of diffusivity and mobility for electrons, positive ions and metastables are considered as constants except the diffusivity of electrons, which depends on the electron temperature. This assumption can be made because these coefficients vary slightly for the range of electron temperature in our simulations.\(^{17, 59}\)

<table>
<thead>
<tr>
<th>Species</th>
<th>(D) ((\text{cm}^2/\text{s}))</th>
<th>(\mu) ((\text{cm}^2/\text{Vs}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electron</td>
<td>(1.737 \times 10^3 \left( \frac{T_e}{17406} \right))</td>
<td>(-1.132 \times 10^3)</td>
</tr>
<tr>
<td>He(^+)</td>
<td>0.5026</td>
<td>14.82</td>
</tr>
<tr>
<td>He(_2^+)</td>
<td>0.8148</td>
<td>24.03</td>
</tr>
<tr>
<td>He(^+)</td>
<td>4.116</td>
<td>0</td>
</tr>
<tr>
<td>He(_2^+)</td>
<td>2.029</td>
<td>0</td>
</tr>
<tr>
<td>He</td>
<td>4.116</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 3.1 Diffusion and mobility coefficients for species in atmospheric pressure.\(^{17}\)

3.3.2 **Reactions in a pure helium rf-APGD: Non-radiative model.**
<table>
<thead>
<tr>
<th>Reaction</th>
<th>Reaction Rate ( K )</th>
<th>( \Delta \epsilon ) (eV)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>Ground state excitation ( e + He \rightarrow He^* + e )</td>
<td>( 4.2 \times 10^{-9} T_e^{-0.31} \exp \left( -\frac{19.8}{T_e} \right) )</td>
<td>19.8</td>
</tr>
<tr>
<td>R2</td>
<td>Superelastic collision ( e + He^* \rightarrow He + e )</td>
<td>( 1.999 \times 10^{-10} T_e^{-0.31} )</td>
<td>-19.8</td>
</tr>
<tr>
<td>R3</td>
<td>Ground state ionization ( e + He \rightarrow He^+ + 2e )</td>
<td>( 1.5 \times 10^{-9} T_e^{-0.68} \exp \left( -\frac{24.6}{T_e} \right) )</td>
<td>24.6</td>
</tr>
<tr>
<td>R4</td>
<td>Step-wise ionization ( e + He^* \rightarrow He^+ + 2e )</td>
<td>( 1.28 \times 10^{-7} T_e^{-0.6} \exp \left( -\frac{4.78}{T_e} \right) )</td>
<td>4.87</td>
</tr>
<tr>
<td>R5</td>
<td>Superelastic ionization ( e + He_2^* \rightarrow He_2^* + 2e )</td>
<td>( 9.75 \times 10^{-10} T_e^{-0.71} \exp \left( -\frac{3.4}{T_e} \right) )</td>
<td>3.4</td>
</tr>
<tr>
<td>R6</td>
<td>Dissociative recombination ( e + He_2^+ \rightarrow He^* + He )</td>
<td>( 5.386 \times 10^{-9} T_e^{-0.5} )</td>
<td>5.386 \times 10^{-9} T_e^{-0.5}</td>
</tr>
<tr>
<td>R7</td>
<td>Metastable pooling ( He^* + He \rightarrow He^+ + He + e )</td>
<td>( 2.7 \times 10^{-10} )</td>
<td>-15.0</td>
</tr>
<tr>
<td>R8</td>
<td>Three-body quenching ( He^* + 2He \rightarrow He_2^* + He )</td>
<td>( 1.3 \times 10^{-33} )</td>
<td>76</td>
</tr>
<tr>
<td>R9</td>
<td>Ion conversion ( He^* + 2He \rightarrow He_2^+ + He )</td>
<td>( 1.0 \times 10^{-31} )</td>
<td>76</td>
</tr>
<tr>
<td>R10</td>
<td>Dimer metastable pooling ( He_2^* + He \rightarrow He_2^+ + 2He + e )</td>
<td>( 1.5 \times 10^{-9} )</td>
<td>78</td>
</tr>
<tr>
<td>R11</td>
<td>Dissociative recombination ( e + He_2^* \rightarrow 2He )</td>
<td>( 1.0 \times 10^{-9} )</td>
<td>-10.7</td>
</tr>
<tr>
<td>R12</td>
<td>Dissociative recombination ( e + He_2^* + He \rightarrow 3He )</td>
<td>( 2.0 \times 10^{-27} )</td>
<td>79</td>
</tr>
</tbody>
</table>

Table 3.2 Elementary reactions in an atmospheric pure helium glow discharge. Units of reaction rate are \( \text{cm}^3/\text{s} \) for two-body reactions and \( \text{cm}^6/\text{s} \) for three-body reactions, respectively.

The main chemical reactions in an atmospheric pressure helium discharge are listed in Table 3.2 together with their collision rate \((K)\) and the associated electron
energy change ($\Delta \varepsilon$). The electron temperature ($T_e$) needed to determine the collision rate of the reactions in which electrons are involved is in eV.

In the early stage of the program development, only 9 reactions (R1 to R9) were used. This reduced set of equations is typically used in models of atmospheric pressure helium discharges.\(^{62}\) We found, however, that the time evolution of the density of He\(_2^+\) did not reach steady state because processes that destroy He\(_2^+\) had been neglected. More realistic results are obtained when reactions R10-12 are considered.

### 3.4 Diagnostics available from simulation data

Simulation results can be analyzed to unveil underlying principles governing species can be identified. As an example, Figure 3.7 shows the space and time averaged contribution of each reaction in Table 3.2 in the particle balance of each specie in an rf-APGD. For electrons, ground state ionization (R3) and helium
dimmer metastables pooling (R10) are the main generation channels, whereas wall loss (R13) is the dominant loss mechanism. Similarly, most helium dimmer ions are produced by the ion conservation (R9) and metastable pooling (R10) reactions and losses to the walls (R13) are also the dominant loss channel. On the other hand, the main loss mechanism of He⁺, He₂⁺ and He⁺ are volume reactions rather than wall losses. Three body quenching (R8), ion conversion (R9) and dimer metastable pooling (R10) quench He⁺, He⁺ and He₂⁺, respectively.

![Figure 3.8 Visualization of the chemical reactions taking place in an rf-APGD.](image)

Figure 3.8 Visualization of the chemical reactions taking place in an rf-APGD. Nodes represent the four main helium species (He⁺, He⁺, He₂⁺, He₂⁺) and the arrows the reaction rates leading to the generation/loss of each species. The arrow thickness is related to the reaction rate and are colour coded: Red x100, Green x10, Blue x1.

The relation between the four helium species (He⁺, He₂⁺, He₂⁺, He⁺) is captured in Figure 3.8 where each species is a node and each reaction is indicated by an arrow. Arrows arriving to a node indicate generation of that species, arrow leaving from a node indicate loss of the species, and the thickness of the arrow is related to the reaction rate. Figure 3.8 indicates that most He species originate from the electron excitation of neutral He atoms into He⁺, which is rapidly converted by a three body reaction into He₂⁺, and in turn He₂⁺ leads to the
formation of He$_3^+$. This contrast with low pressure helium discharges where three body reactions are unlikely and therefore He* and He$^+$ ions dominate.

Simulation results also provide electrical properties of the discharge. Voltage and current forms can be obtained in the simulation without the difficulties experienced experimentally (parasitic impedances, delays, etc as discussed in Section 2.2.1). As an example, Figure 3.9 shows the typical current and voltage traces obtained from a simulation. The signals are mostly sinusoidal with the discharge current waveform leading the voltage waveform across the gap. This is expected due to the capacitive nature of the plasma source. The phase difference between the two signals is 65 degrees, which highlights the power delivery to the discharge and the resistive nature of the rf-APGD.

![Figure 3.9 Typical current density and voltage waveforms of an rf-APGD (Simulation).](image)

As discussed earlier, density measurements in atmospheric pressure discharges are quite challenging. Simulation results, on the other hand, can easily provide this information in space and time resolved manner. As an example, Figure 3.10 shows the time-averaged density profiles of 5 species in a pure helium rf-APGD. The peak electron density is $\sim2.8\times10^{11}\text{cm}^{-3}$ at the sheath edge and is close to the experimental estimate of $3\times10^{11}\text{cm}^{-3}$. The main ionic species
is He$_2^+$, which is present in a concentration that is two orders of magnitude higher than He$^+$. The bulk plasma remains quasineutral with charges due to electrons and dimer ions cancelling each other, and two sheath regions of positive space charge form near each electrode. This is a typical feature of plasmas and is caused by the faster mobility of the electrons. The double humped profile of the charged species is a distinct feature of atmospheric discharges and results from the localized generation of excited species near the electrodes and volume recombination processes in the centre of the plasma. In contrast, low pressure discharges tend to have bell-shape profiles with peak densities at the centre. Regarding excited species, dimer metastables are more abundant than helium metastables, and their densities are larger than the ionic densities.

![Figure 3.10 Time-averaged density profiles.](image)

While time averaged profiles can provide valuable information, simulation results can also provide time resolved data. Space and time resolved density information for electrons, ions and metastables are shown in Figure 3.11. He$^+$ has been omitted due to its small role in the discharge. Figure 3.11 reveals the oscillating nature of the electron density profile as a result of the applied rf field.
The more heavy dimer ions, however, are too massive to respond to the rapidly varying electric field and their profile is virtually constant in time. The same is true for the metastables profiles because metastables do not respond to electric fields.

Figure 3.11 Density of He*, He2*, HCl*, electron between two electrodes over two rf cycles. Besides quantities related to the particle balance, simulation results provide insights into energy considerations. For example, the shielding of the applied electric field by charge species in the plasma, the resulting sheaths and the localized heating of the electron are clearly identifiable in the simulation results.

Figure 3.12 shows the spatio-temporal evolution of the electric field and the electron mean energy. The electron mean energy reaches its maximum in the sheaths where the electric field is also maximum.
Figure 3.12 (a) Electric field (V/cm) between the two electrodes and (b) electron mean energy (eV) as a function of time and position

It should be noted, however, that although density profiles and electron energy provide information related to the generation of particles in the plasma, on their own none of them provides a complete picture. It is the product of the reaction rate, which depends on the electron energy, and the electron and background helium densities that determine the generation/loss of particles. This information can also be obtained from the simulation results. As an example, Figure 3.13 shows the spatio-temporal evolution of the net electron generation/loss and as just explained, the profile differs from those of the electron temperature and densities shown earlier. According to Figure 3.13, most electrons are generated at the sheath edge during the expansion and retreat of the sheaths, with more generation taking place during the expansion phase. This feature is further analysed in Chapter 5.
Finally, the time-averaged contributions of volumetric source/sink terms that contribute to the electron energy balance are shown in Figure 3.14. These include joule heating, inelastic heating and elastic heating. At atmospheric pressure ohmic (Joule) heating is the dominant heating mechanism and the energy transferred to the electrons is predominantly lost in elastic collisions (gas heating) with only a small fraction being invested in inelastic collisions. \(^8\)

Figure 3.13 Electron generation rate between two electrodes over two rf cycles

Figure 3.14 Time averaged contribution of Joule heating, and elastic and inelastic collisions to the electron energy balance in the discharge.
3.5 He+N$_2$ APGD model

Optical emission spectroscopy of pure He atmospheric pressure rf-APGD reveals the presence of various species (impurities) that are not deliberately introduced in the plasma. The purity of helium used in the experiment is 99.95%, which implies that 0.05% of impurities are present in the discharge. The partial pressure of these impurities is 380mTorr, a pressure with in the range of conventional low-pressure plasma processing. Since most of the spectrum is dominated by nitrogen species, a realistic simulation model of the discharge needs to incorporate N$_2$. Furthermore, in order to study the spatio-temporal evolution of the optical emission, radiative states not accounted in the simplified non-radiative model of section 3.3 should also be taken into consideration.

In Table 3.3, 26 additional reactions involving nitrogen, helium and electrons are listed along with their collision rates ($K$) and their associated mean electron energy change ($\Delta\varepsilon$). These reactions complement the previous reaction set for pure He discharges given in Table 3.2.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Reaction Rate (k)</th>
<th>$\Delta\varepsilon$ (eV)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>R13 $He^+ (2^3S) + N_2 \Rightarrow (r6)N_2^+ (B^2 \Sigma_g^+) + (1- r6)N_2^+ (X^2 \Sigma_g^+) + He + e$</td>
<td>$7.6 \times 10^{-11}$</td>
<td>81</td>
<td></td>
</tr>
<tr>
<td>R14 $He^+ (2^3S) + N_2 + He \Rightarrow (r7)N_2^+ (B^2 \Sigma_g^+) + (1- r7)N_2^+ (X^2 \Sigma_g^+) + 2He + e$</td>
<td>$3.3 \times 10^{-30}$</td>
<td>81</td>
<td></td>
</tr>
<tr>
<td>R15 $He^+ + N_2 \Rightarrow (r8)N_2^+ (B^2 \Sigma_g^+) + (1- r8)N_2^+ (X^2 \Sigma_g^+) + 2He + e$</td>
<td>$7.0 \times 10^{-11}$</td>
<td>17</td>
<td></td>
</tr>
<tr>
<td>R16 $He^+ + N_2 \Rightarrow (1- r_1)N_2^+ (X^2 \Sigma_g^+) + (r_1)N + (r_1)N^+ + He$</td>
<td>$1.2 \times 10^{-9}$</td>
<td>81</td>
<td></td>
</tr>
<tr>
<td>R17 $He^+ + N_2 + He \Rightarrow (1- r_2)N_2^+ (X^2 \Sigma_g^+) + (r_2)N + (r_2)N^+ + 2He$</td>
<td>$2.2 \times 10^{-29}$</td>
<td>81</td>
<td></td>
</tr>
<tr>
<td>Reaction</td>
<td>Equation</td>
<td>Rate Coefficient</td>
<td>References</td>
</tr>
<tr>
<td>----------</td>
<td>----------</td>
<td>------------------</td>
<td>------------</td>
</tr>
<tr>
<td>R18</td>
<td>$He^+_2 + N_2 \Rightarrow (r4)N_2^+(B^2 \Sigma_u^+)+(1-r4)N_2^+(X^2 \Sigma_g^+)+2He$</td>
<td>$1.1 \times 10^{-9}$</td>
<td>81</td>
</tr>
<tr>
<td>R19</td>
<td>$He^+_2 + N_2 + He \Rightarrow (r5)N_2^+(B^2 \Sigma_u^+)+(1-r5)N_2^+(X^2 \Sigma_g^+)+3He$</td>
<td>$1.36 \times 10^{-29}$</td>
<td>81</td>
</tr>
<tr>
<td>R20</td>
<td>$N_2^+(B^2 \Sigma_u^+) \Rightarrow N_2^+(X^2 \Sigma_g^+) + hv$</td>
<td>$1.5 \times 10^9 / s$</td>
<td>- 82</td>
</tr>
<tr>
<td>R21</td>
<td>$N_2^+(B^2 \Sigma_u^+) + e \Rightarrow 2N$</td>
<td>$1.0 \times 10^{-7}$</td>
<td>- 81</td>
</tr>
<tr>
<td>R22</td>
<td>$N_2^+(X^2 \Sigma_g^+) + e \Rightarrow 2N$</td>
<td>$1.0 \times 10^{-7}$</td>
<td>- 81</td>
</tr>
<tr>
<td>R23</td>
<td>$N^+ + e \Rightarrow N$</td>
<td>$5.0 \times 10^{-9}$</td>
<td>81</td>
</tr>
<tr>
<td>R24</td>
<td>$e + N_2 \Rightarrow 2N + e$</td>
<td>$2.7976 \times 10^{-9}(T_e)^{-0.7} \exp\left(-\frac{9.757}{T_e}\right)$</td>
<td>9.75 83</td>
</tr>
<tr>
<td>R25</td>
<td>$e + N \Rightarrow N^+ + 2e$</td>
<td>$8.401 \times 10^{-5} \exp\left(-\frac{14.5}{T_e}\right)$</td>
<td>14.5 83</td>
</tr>
<tr>
<td>R26</td>
<td>$e + N_2 \Rightarrow N_2^+(X^2 \Sigma_g^+) + 2e$</td>
<td>$2.705 \times 10^{-8}(T_e)^{-0.3} \exp\left(-\frac{15.6}{T_e}\right)$</td>
<td>15.6 83</td>
</tr>
<tr>
<td>R27</td>
<td>$e + N_2^+(X^2 \Sigma_g^+) \Rightarrow N_2^+(B^2 \Sigma_u^+) + e$</td>
<td>$1.3 \times 10^{-7}(T_e)^{-0.65} \exp\left(-\frac{3.17}{T_e}\right)$</td>
<td>3.17 84</td>
</tr>
<tr>
<td>R28</td>
<td>$e + N_2 \Rightarrow N_2^+(B^2 \Sigma_u^+) + 2e$</td>
<td>$6.5 \times 10^{-8}(T_e)^{-0.37} \exp\left(-\frac{19}{T_e}\right)$</td>
<td>19 85, 86</td>
</tr>
<tr>
<td>R29</td>
<td>$e + He \Rightarrow He^*(3^3 S) + e$</td>
<td>$9.7 \times 10^{-10}T_e^{0.31} \exp\left(-\frac{22.7}{T_e}\right)$</td>
<td>22.7 87</td>
</tr>
<tr>
<td>R30</td>
<td>$e + He \Rightarrow He^*(2^3 P) + e$</td>
<td>$7.7 \times 10^{-10}T_e^{0.31} \exp\left(-\frac{20.9}{T_e}\right)$</td>
<td>20.9 87</td>
</tr>
<tr>
<td>R31</td>
<td>$He^<em>(2^3 P) + 2He \Rightarrow He^</em> + He$</td>
<td>$1.6 \times 10^{-32}$</td>
<td>87</td>
</tr>
</tbody>
</table>
Chapter 3 Computational modelling of rf-APGDs

| R32 | \( \text{He}^* (3^3 S) \Rightarrow \text{He}^* (2^3 P) + hv \) 706nm | 2.78 \times 10^7 | 88 |
| R33 | \( \text{He}^* (2^3 P) \Rightarrow \text{He}^* (2^3 S) + hv \) 1083nm | 1.022 \times 10^7 | 88 |
| R34 | \( \text{He}^* (3^3 S) + \text{He} \Rightarrow \text{He}^2 + e \) | 0.21 \times 10^{-11} | 89 |
| R35 | \( \text{He}^* (3^3 S) + e \Rightarrow \text{He}^* + e \) | 6 \times 10^{-10} T_e^{0.31} | -22.7 | 17 |
| R36 | \( \text{He}^* (2^3 P) + e \Rightarrow \text{He}^* + e \) | 4 \times 10^{-10} T_e^{0.31} | -20.9 | 17 |
| R37 | \( \text{He}^* (3^3 S) + \text{He}^* (3^3 S) \Rightarrow \text{He}^* + \text{He} + e \) | 1.0 \times 10^{-9} | -20.8 | 90 |
| R38 | \( \text{He}^* (2^3 P) + \text{He}^* (2^3 P) \Rightarrow \text{He}^* + \text{He} + e \) | 1.0 \times 10^{-9} | -17.2 | 90 |

Table 3.3 Elementary reactions in an atmospheric pure helium+N\(_2\) glow discharge. * Units of reaction rate are cm\(^3\)/s for two-body reactions and cm\(^3\)/s for three-body reactions, respectively.

In the extended model, \( \text{N}_2^+ (B^2 \Sigma_u^+) \) is explicitly considered and as a result it is possible to study the emission at 391nm \( (\text{N}_2^+ (B^2 \Sigma_u^+) \Rightarrow \text{N}_2^+ (X^2 \Sigma_g^+) + hv) \). The emission pattern predicted in the simulation by dividing the density of the radiative state \( (\text{N}_2^+ (B^2 \Sigma_u^+)) \) by their radiative lifetime. Alternatively the density can be multiplied by the radiative reaction rate (R20) given in Table 3.3. Furthermore, three electronic excited states of helium are included: \( \text{He}(2^3 S) \) (19.8eV), \( \text{He}(2^3 P) \) (20.9eV) and \( \text{He}(3^3 S) \) (22.7eV). The latter is responsible for the radiation at 706nm \( (\text{He}^* (3^3 S) \Rightarrow \text{He}^* (2^3 P) + hv) \), a strong emission line observed in He discharges. The addition of more species and reactions to the model affects the simulation time, and the extended code requires typically twice as long as the pure helium model to reach steady state.

In Table 3.3, the reaction rates are given as a function of the electron temperature and it is therefore assumed that the electron energy distribution function is Maxwellian. Unfortunately this assumption is not sufficiently accurate
as the simulation results do not reproduce experimental observations. This is shown in Figure 3.15 where the spatio-temporal evolution of the 706nm emission in a typical rf-APGD discharge is presented. Experimental data show that the emission takes place mostly within the sheaths, which are indicted by a dotted white line on the figure. On the other hand, simulation results predict the emission to be maximum on the sheath edges. This is not only a quantitative disagreement but also a qualitative one.

![Figure 3.15 Time and space resolved 706nm emission profile. a) Experimental data. b) Simulation results assuming a Maxwellian electron distribution function.](image)

In order to improve the agreement between the simulation results and the experimental data, the assumption of a Maxwellian electron energy distribution function needs to be relaxed. It is possible to do so by determining the reaction rates as a function of the mean electron energy (rather than the electron temperature). Reaction rates are then obtained from the solution of the homogeneous Boltzmann equation. Bolsig+, a freely available Boltzmann solver, is used in this thesis for this purpose. Figure 3.16 shows the electron energy distribution function for various mean electron energies when a Maxwellian distribution and the local field approximation (Bolsig+) are used. While for large mean electron energies (>10eV) the distribution in both cases are quite similar(Figure 3.16 a) and b)), it is clear that for electron mean energies of less than 7eV the assumption of a Maxwellian distribution overestimates the presence
of energetic electrons (Figure 3.16 c and d)). This overestimation is responsible for the large 706 nm emission predicted by the model in regions outside the sheath which does not agree with experimental observations.

![Figure 3.16 EEDF for various mean electron energies. (a) (c) Maxwellian distributions (b) (d) Distributions obtained from the solution of the homogeneous Boltzmann equation using Bolsig+](image)

In this thesis, a user friendly Boltzmann solver, Bolsig+, is used to calculate transport coefficients and reaction rates. The reaction rate for a collision process \( k \) is given by:

\[
k_k = \gamma \int_0^\infty \varepsilon \delta_k \, F_0 \, d\varepsilon
\]

where \( \gamma = (2e/m)^{1/2} \) is a constant, \( \varepsilon \) is the electron energy in electron volts, \( \delta_k \) is the (energy-dependent) effective cross section and \( F_0 \) is the electron energy distribution function. The cross section for electronic excitation of ground state He atoms (He 1^1S) to different levels is shown in the Figure 3.17. This data is introduced in Bolsig+, which determines the self-consistent electron energy distribution function, mean kinetic energy of the electrons and reaction rates. In the calculation we used the nitrogen cross section data provided in Bolsig+. The
resulting electron energy distribution function depends on the collisional processes and therefore on the gas composition. Therefore, although the cross section data are independent of the gas mixture, new reaction rates need to be obtained each time the nitrogen concentration is changed in the simulation.

![Excitation from 1S](image)

**Figure 3.17** Electron-impact excitation cross section for transitions between atomic terms of He I with \( n_s, n_f \leq 4 \).

### 3.6 Summary

Global (zero dimensional) models and one dimensional fluid models have been developed to study atmospheric glow discharge in pure helium and admixtures of He+N₂. These models provide valuable insights into the chemistry and dynamics of the plasma that are hard to obtain experimentally.
Chapter 4 *Electron trapping in APGDs*

Electron trapping has been proposed theoretically as a primary mechanism for generating rf APGDs and was used as an explanation of the enhanced stability of high frequency APGDs\(^{62,91}\). Compared to the half period of the applied voltage, the electron transit time across the electrode gap is considered to be large in an rf discharge and hence most electrons can be trapped in the electrode gap. This contrasts with the situation encountered in a conventional dc glow discharge in which electrons are continuously drifted towards the anode by the applied field and a source of secondary electrons is needed for sustaining the discharge. The trapping of electrons would allow the balance between electron creation and loss to be achieved at a comparatively low rf voltage, thus mitigating the glow-to-arc transition and sustaining the generated atmospheric plasma as a glow discharge. While electron trapping is plausible as a possible mechanism for generating rf APGD, it remains a theoretical prediction and its validity has not so far been supported with experimental evidence. Here we present an experimental study of electron trapping phenomena in rf APGD by means of electrical measurements, nanosecond plasma imaging, and optical emission spectroscopy. To enhance generic applicability of the findings, the study covers from pre-breakdown, through discharge sustained in a glow mode, to arcing over a frequency range of 1 – 10 MHz. On the other hand, due to better plasma stability in the very high frequency (VHF) band, one dimensional fluid model introduced in Chapter 3 is employed to investigate the characteristics of VHF APGD.
Chapter 4  

Electron trapping in rf-APGDs

The experiment setup is the same as what described in Section 2.1. The gas gap is fixed at 2.4 mm, and the working gas is helium (99.99% purity) with a flow rate of 5 slm.

4.1 rf-APGD

![Figure 4.1 Current-voltage characteristics from pre-breakdown (dotted lines), through a glow mode (markers), to arcing (immediately after the last point of each curve).](image)

In the experiments, the discharge current is predominately sinusoidal with one positive peak and one negative peak in each rf cycle of the applied voltage although the harmonic content varies with frequency. Figure 4.1 shows the current-voltage characteristics at five different frequencies from pre-breakdown (indicated with dotted lines), through a glow discharge (indicated with markers), to the point immediately before arcing (as the last point on each curve). Once the gap voltage is applied, it is increased until the gas breakdown occurs. This period before breakdown occurs is referred to as the pre-breakdown period. The pre-breakdown sections of all curves go through the origin of the diagram in Figure 4.1 in straight lines. At 10 MHz, the transition from the pre-breakdown regime to the discharge regime is marked with a step change in the slope of the voltage-
current curve, signifying a significant change in the differential conductivity of the discharge plasma. This is similar to reported observations of most rf-APGD generated typically at 13.56 MHz. For future reference, we refer this transition point to as the breakdown point. In the cases of 5 MHz and 7 MHz, a similar but smaller step change in the differential conductivity is evident at the breakdown point. As the excitation frequency reduces below 4 MHz, the step change in the differential conductivity becomes negligible as shown in Figure 4.1. This invariance from the pre-breakdown to the discharge regimes has not been reported before and is likely to be characteristic in APGD at low radio frequencies (<4 MHz). Therefore, the current-voltage characteristics in rf-APGD manifest themselves differently at different frequencies. The breakdown voltage $V_{br}$ undergoes a reduction with increasing frequency. It is due to a decreasing contribution of drifted electrons wall loss and may be explained by considering electron oscillation in the radio frequency field of $E_0 \cos \omega t$ with an oscillation amplitude given by

$$x_m = \frac{eE_0 / m_e}{\sqrt{(\omega^2 - (\omega_p^2 / 2x_m / d)^2) + \omega^2 \nu_c^2}} \tag{4.1}$$

where $m_e$ is the electron mass, $d$ is the electrode gap distance, $\omega_p = \sqrt{e^2 n_e / \varepsilon_0 m_e}$ is the plasma frequency with $e$ and $n_e$ being electron charge and electron density, and $\nu_c$ is the electron-neutral collision frequency respectively. When $x_m / d \geq 1/2$, most electrons can reach the electrodes in half rf cycle. Electron density is estimated to $10^{10}$ cm$^{-3}$ according to typical value of helium rf-APGD. With increasing frequency, the electron oscillation amplitude eventually becomes smaller than $d/2$ suggesting that the drift loss of electrons to the electrodes decreases and more electrons are trapped inside the electrode gap. Thus, the breakdown voltage decreases with increasing frequency.
4.1.1 rf-APGD circuit model

In the prebreakdown regime, the electrical character of the gas gap can be modelled as a capacitor, \( C_g = \varepsilon_0 A/d \) where \( d \) is the gap distance between two parallel electrode and \( A \) is the area of one electrode. After breakdown, the plasma can be modelled as two capacitors, each representing one of the electron-depleted plasma sheaths near the electrodes, in series with a resistor, which represents the bulk plasma. The current through the bulk plasma is dominated by electron conduction current whereas in the sheaths it is mainly carried by displacement current. The structure is shown in Figure 4.2:

![Figure 4.2 A simple circuit model for rf-APGD, each capacitor represents the electrode sheath, and the resistor represents the bulk plasma.](image)

Although the sheaths oscillate and the sheath thickness varies with time, the total sheath thickness of the two sheaths at a given rms voltage and current remains approximately constant.\(^{17}\) Therefore the overall reactance of the plasma is given by \( X = X_1 + X_2 = d / \omega \varepsilon_0 A \), where \( d \) is the sum of the width of the two sheaths \( (d_{s1}+d_{s2}) \), and the plasma impedance \( Z = R - j \omega \varepsilon_0 A \).\(^{66}\)

4.1.2 Electron trapping

To interpret the results presented in Figure 4.1, we model the rf-APGD using the equivalent circuit shown in Figure 4.2, i.e. a capacitor and a series resistor. If most electrons generated in the discharge regime can easily reach the electrodes during one half rf period \( \tau_{rf} \), their presence in the gas gap is short-lived and they
are unlikely to increase significantly the average electrical conductivity of the gas gap. As a result, \( Z \approx -j/\omega C_g \) and the electrical character of the gas gap remains similar to that in the pre-breakdown regime. Assuming an electric field of \( E=500 \) V/0.24 cm at the breakdown point for the case of 2 MHz and an electron mobility of \( 1,132 \text{ cm}^2\text{V}^{-1}\text{s}^{-1} \), the electron transition time across the electrode gap of 0.24 cm is found to be \( \tau_e = 102 \) ns. This is significantly smaller than \( \tau_{rf} = 250 \) ns at 2 MHz, suggesting that most generated electrons can easily reach the electrodes during one half of the rf cycle.

Electron trapping is therefore temporary and the gas impedance is approximately \( Z \approx -j/\omega C_g \). This may be responsible for the invariance in the differential conductivity in the 2 MHz case in Figure 4.1. As the excitation frequency increases to 3 MHz, our calculation shows that \( \tau_{rf} = 166 \) ns and \( \tau_e = 134 \) ns, much closer to each other than those at 2 MHz. As \( \tau_e < \tau_{rf} \), many generated electrons can still reach the electrodes and the gas gap can retain its electrical conductivity in the pre-breakdown regime. Again, this explains why the slope of the voltage-current curve changes little at 3 MHz. Raising the frequency to 5 MHz, we find that \( \tau_e = 195 \) ns is now larger than \( \tau_{rf} = 100 \) ns. This suggests that many electrons can no longer reach the electrodes during one half-period and will be trapped in the electrode gap. Further frequency increment leads to \( \tau_e \) becoming increasingly larger than \( \tau_{rf} \) and so a greater level of electron trapping. If sufficient electrons are trapped, they will increase the electrical conductivity of the gas gap and change the slope of the voltage-current curves as in the cases of 5, 7 and 10 MHz. In other words, a step change in the slope of the voltage-current curve is indicative of electron trapping. Figure 4.1 suggests a progressively increasing level of electron trapping with increasing frequency.
4.1.3 Nanosecond images of a 10MHz APGD

![Figure 4.3 Nanosecond images of a 10 MHz rf-APGD over one complete rf cycle and at an rms current of (a) 70.0 mA; and (b) 140.5 mA.](image)

To support the above argument of electron trapping, it is perhaps most logical to measure the electron density and its spatial profile across the electrode gap. For rf-APGD in helium, the electron density is below $10^{12}$ cm$^{-3}$ typically $^{56, 94}$ for which the Stark broadening technique is inadequate. Langmuir probes are also inappropriate because of the difficulty in interpreting their data for atmospheric plasmas. These highlight the current lack of suitable techniques for measuring the electron density of APGD. As an alternative, we studied possible optical signatures of electrons. In Figure 4.3(a), five plasma images with an exposure time of 10 ns are shown for the 10 MHz case at $I_{rms} = 70.0$ mA. They are periodic at the driving frequency with the brighter images at $7/4$ and $37/4$ taken at the discharge current peaks.
Figure 4.4 Spatial profile of the total optical emission across the electrode gap at an rms current of (a) 70.0 mA, and (b) 140.5 mA. The power electrode was located at x = 0.0 mm and the excitation frequency was 10 MHz.

Their spatial profile is bell-like, spreading over most of the electrode gap and indicating a volumetric discharge. This suggests that the excited plasma species are produced volumetrically and are most numerous in the gap centre. When the discharge current is doubled to $I_{\text{rms}} = 140.5$ mA, the discharge dynamics remain periodic at 10 MHz but the plasma structure changes to a double-humped profile as shown in Figure 4.3(b). The optical emission is no longer volumetric but localized near the electrodes. At $T/4$, a bright thin layer is evident near the top electrode and it reappears near the bottom electrode one half rf cycle later at $3T/4$. This bright thin layer is likely to be the negative glow, formed by a localised concentration of excited plasma species which in turn are generated by energetic electrons. These spatial profiles are more clearly shown in Figure 4.4 as a function of the inter-electrode position. As the current increases, the spatial profile of optical emission evolves from a bell-like shape to a double-humped
shape, both tailing off towards the electrodes. So excited plasma species are trapped in the electrode gap. Since the optical intensity increases with increasing frequency (data not shown), their trapping enhances with increasing current. As electrons are largely responsible for generating excited plasma species, Figure 4.4 suggests that energetic electrons are also trapped and their trapping enhances with increasing discharge current. It should be noted that optical emission remains visible in all images in Figure 4.3 and so electron trapping is permanent. While not relevant to this study, it is also worth noting the small hump near \( x = 0 \) mm. This is a dc bias and will be discussed in a future note.

The link of nanosecond plasma images to energetic electrons can be further supported by optical emission spectroscopy. For all experiments reported here, the most intense emission is from the helium line \( (3^3S_1 \rightarrow 2^3P_{0,1,2}) \) at 706.5 nm and the nitrogen line at 391 nm. The helium \( 3^3S_1 \) state can be populated by a number of processes including through electron collisions with helium ground state atoms, \( E_{\text{threshold}} = 22.72 \) eV, and the helium metastable state, \( E_{\text{threshold}} = 2.9 \) eV, and also via the following sequence of reactions,

\[
\begin{align*}
He^* (n \geq 3) + He & \rightarrow He^+_2 + e \quad (4.2) \\
He^* + 2He & \rightarrow He^+_2 + He \quad (4.3) \\
He^+_2 + e & \rightarrow He^* + He \rightarrow 2He + h\nu \quad (4.4)
\end{align*}
\]

which are associative ionization, \( He^+_2 \) production in a three-body collision and dissociative recombination,\(^99\) respectively. The reactions rates for eq.(4.2) and eq.(4.3) are known to be fast, with frequencies of about \( 5 \times 10^8 \) s\(^{-1}\) and \( 5 \times 10^7 \) s\(^{-1}\), respectively, in atmospheric pressure helium.\(^{100}\) Additionally, in Section 3.5 the He excitation and emission reactions are shown in details. While direct electron impact excitation might be considered a dominant \( He^* \) production process in low pressure discharges with relatively high electron temperatures, here the high atom–atom collisionality means that the multi-step process cannot be ignored.
priori and has been recognized as an important process for He 706.5 nm light emission by others.\textsuperscript{101} The helium line at 706 nm indicates in general the presence of either energetic electrons or He\textsuperscript{2+} ions and low energy electrons.\textsuperscript{99} In Chapters 7 and 8, however, we will show that in fact emission at 706 nm can be used to indicate mainly the presence of energetic electrons.

The $N_2^+(B^2\Sigma_u^+,v_B=0) \rightarrow N_2^+(X^2\Sigma_g^+,v_x=0)$ transition at 391.4 nm is a strong transition in He/air (He/N\textsubscript{2}) plasmas. The 391 nm emission line is known to result from $N_2^+(B^2\Sigma_u^+,v_B=0)$ transition to $N_2^+(X^2\Sigma_g^+,v_x=0)$, and contains signatures of helium metastables and He\textsuperscript{2+} ions.\textsuperscript{99} As the most numerous ionic species are He\textsuperscript{2+} ions in helium rf-APGD,\textsuperscript{60} the combination of the 706 nm line and the 391 nm line is an excellent indicator of the energetic electrons and the most significant ions. Therefore, the spatial profile of optical emission in Figure 4.4 is likely to mirror that of energetic electrons. Consequently, the bell-like profile at $I_{rms} = 70.0$ mA suggests volumetric electron trapping across the electrode gap whereas the double-humped profile at $I_{rms} = 140.5$ mA suggests localized electron trapping near the electrodes.

### 4.1.4 Simulation analysis

To relate to the original theoretical prediction,\textsuperscript{63} we performed one-dimensional simulation of the 10 MHz APGD using the fluid model described in Chapter 3.\textsuperscript{18} The gas gap is also fixed at 2.4 mm for this pure helium simulation. Figure 4.5 shows the spatial-temporal profile of the product of the electron density and the mean electron energy as a measure of energetic electrons. In a broad term and ignoring the dc bias, these profiles match well those in Figure 4.4. The density-energy product at the large current density is larger than that at the small current density, consistent with the experimental observation that the optical emission was more intense at 140.5 mA than at 70.0 mA.
Figure 4.5 Spatial temporal profiles of the product of the electron density and the mean electron energy at a current density of (a) 10 mA/cm²; and (b) 50 mA/cm².

**4.2 VHF APGD**

In summary, we have presented experimental and computational evidence of electron trapping in rf APGDs by using current-voltage characteristics, nanosecond plasma imaging, optical emission spectroscopy and fluid modelling. As the excitation frequency is increased to even higher frequencies such as 100MHz, the breakdown voltage $V_{br}$ is found to increase after the initial decrease shown in Figure 4.1.\textsuperscript{102} The monotonic decrease of $x_{pl}/d$ with increasing frequency would suggest a monotonic decrease of $V_{br}$ if the rf breakdown voltage is controlled mainly by electron wall loss. The increase, however, is attributed to the electron thermal inertia.\textsuperscript{102} Actually, as the excitation frequency is continuously increased, the half rf cycle $\tau_{rf}/2$ decreases, consequently, the time electrons are
accelerated is shorter than at low frequency. This compromises the electron heating and therefore the subsequent gas ionization.

![Graph](https://example.com/graph.png)

**Figure 4.6** Power dependence of (a) the maximum and (b) the minimum mean electron energy at various rf excitation frequencies. (simulation data)

Because the electron kinetics is not considered in the eq.(4.1), it is ineffective in accessing the effect of electron heating. To this end, the one dimensional fluid model simulation introduced in section 4.1.4 was used to analyse the effect of the excitation frequency on the electron kinetic energy. Figure 4.6 shows the power
dependence of the maximum and minimum electron energy at various frequencies. At a certain power level, with increasing frequency, the electrons are deprived of sufficient acceleration time, consequently, the maximum energy decreases.

Figure 4.7 The electron generation rate and the averaged electron kinetic energy at 13.56 MHz and 2.0W. (simulation data)

In the case of 13.56MHz, Figure 4.7 suggests that the electron energy is significantly rf-modulated, and its modulation is dynamically correlated with that of the electron generation rate. This correlation indicates that the maximum electron energy can represent the most efficient electron generation rate and hence gas breakdown. With the decrease of the maximum electron temperature as the rf frequency increases, the ionization efficiency reduces and this reduction is responsible for the breakdown voltage increase observed at VHF frequencies.  

4.3 Summary

By linking electron density to nanosecond plasma images and optical emission at 391 nm and 706 nm, electron trapping has been shown to persist at 1 – 10 MHz. It has also been demonstrated that electron trapping enhances with increasing discharge current or/and increasing excitation frequency. In terms of its
frequency dependence, the level of electron trapping has been found to manifest itself in the change of the differential conductivity at the breakdown point. Finally, the underpinning reason for electron trapping has been shown to be related to whether the electron transition time across the electrode gap is larger than the half rf period.
Chapter 5  *Electron heating in rf-APGDs*

Radio frequency capacitively coupled plasma (CCP) sources have been the workhorse of the semiconductor industry for several decades. Although for certain applications CCPs have been substituted by other plasma sources, CCPs continue to be an important technological tool in many etching processes. Despite their simple geometrical configuration, CCPs involve complex and interesting physics particularly with regard to the electron heating mechanisms and the resulting electron energy distribution function. Not only are the electrons far from thermodynamic equilibrium, but also their energy distribution function present abrupt transitions when external parameters are varied, e.g. transitions induced by changes in the operating pressure\(^{103}\) and input power\(^{104}\) have been reported and are now relatively well understood.

In low-pressure capacitively coupled plasmas, high energy electrons are collisionlessly heated by the high electric field in the sheath area, while low-energy electrons are confined in the bulk plasma by the ambipolar potential. Because of the nonlocal kinetics, high energy electrons can overcome the electrostatic potential well and interact with the oscillating sheaths. As a result, these electrons are strongly heated. However, low energy electrons are trapped inside the electrostatic potential well and gain energy mainly through collisional heating. Actually, these low energy electrons in the bulk bounce inside the electrostatic potential well. Those that oscillate with a frequency equal to the rf excitation frequency are efficiently heated by the coherent interaction with the rf field. It is shown in Figure 5.1 that for the 13.56MHz case, the kinetic energy of a
test particle satisfying the bounce resonance condition has large energy excursions from its initial value with energy gains of $\sim 0.5 \text{ eV}$ per bounce.$^{105}$

![Figure 5.1 Kinetic energy $E_x$ of a collisionless test particle as a function of time in a 2 cm capacitively coupled discharges driven at 40 V and 13.56 MHz. The test particles is initially placed in the centre of the discharge with an initial energy of 1 eV. $^{105}$](image)

Most studies in the literature, however, have focused on low-pressure discharges for conventional material processing. In recent years there has been a growing interest on low-temperature plasma sources operating at atmospheric pressure. These sources eliminate the need for costly vacuum systems$^{106,107,108}$ and have potential application in new scientific/industrial fields where vacuum operation is not practical, e.g. biomedicine.$^{109,110}$

Electron heating in atmospheric-pressure discharges has not been studied as thoroughly as in low-pressure plasmas. This is in part because of the more recent interest on low-temperature atmospheric-pressure discharges but also because of the experimental and theoretical challenges. In this chapter, we present experimental and computational results aimed at elucidating the electron heating mechanism in atmospheric-pressure rf discharges. Differences with low-pressure plasmas are highlighted both in the low current and high current modes, more commonly known as the $\alpha$ and the $\gamma$ modes respectively.
Atmosphere-pressure discharges tend to operate in the local regime and are dominated by collisional (ohmic) heating. This is because $vL/vth>>1$ and $\lambda_e<<L$ are typically satisfied. Here, $v$ is the electron collision frequency of $2 \times 10^{10}$ s$^{-1}$, $L$ is 0.2 cm, $vth$ is the electron thermal velocity and equals to $4.19 \times 10^7 T_e^{1/2}$ cm/s, $\lambda_e$ is the electron energy relaxation length and is only tens of micrometers. While this is true for most atmospheric-pressure rf discharges with gaps on the order of millimetres, for the rf microplasmas where $L$ is reduced to tens of microns, nonlocal kinetics can be important.

The experiment setup has been described in Chapter 2. The experimental results presented in this chapter are obtained with a helium flow rate of 5 standard litre per minute (slm). Nano-second images are employed to analyse the time evolution of the discharge in its dynamic steady state. To gain a better understanding of the physics of electron heating, the plasma is also simulated using the one-dimensional model introduced in Chapter 3.

### 5.1 $\alpha$ and $\gamma$ modes

$\alpha$ and $\gamma$ modes are known to exist in RF APGD. In the $\alpha$ mode, the gas ionization and excitation occurs volumetrically throughout the discharge and it is a result of the heating of electrons in the bulk plasma by the oscillating rf electric field. This heating is typically most efficient in regions close to the sheath edge and as a result APGD emission patterns often present two bright layers above the electrodes (see figure 5.2). On the contrary, in the $\gamma$ mode, secondary electrons emitted from the electrodes and accelerated across the sheaths are responsible for the ionization in the discharge. Atmospheric pressure discharges operating in the $\gamma$ mode are found to typically constrict in the radial direction (see figure 5.2), forming a filamentary discharge that can quickly convert into an arc. Since in the $\gamma$ mode, the ionization and excitation is localized inside the sheaths, the brightest
optical emission of the discharge is localized closer to electrodes than in the $\alpha$ mode.\textsuperscript{15}

The visual appearance of the discharge as the input power is increased is shown in Figure 5.2. After the discharge breakdown, only a tiny weak plasma forms and as the applied power increases the volumetric discharge gradually covers the whole electrode and the optical emission intensifies. Additionally, as the plasma density increases and the sheaths become thinner, two bright layers arise near the electrodes. This feature will be studied in detail in the following sections. When the discharge transits into the $\gamma$ mode a radial constriction often takes place and the optical emission gets closer to the electrodes. However, it should be noted that $\gamma$ mode can exist in non-constricted state. The diffused $\gamma$ mode is found in the DBD with high current density\textsuperscript{114} and microplasmas,\textsuperscript{115} which will be discussed in Chapter 8.

![Figure 5.2](image)

Figure 5.2 i-CCD image of an rf-APGD (1$\mu$s exposure time) at different input power

Figure 5.3 shows the current voltage characteristics of a typical 13.56MHz He atmospheric-pressure glow discharge from pre-breakdown to the $\gamma$ mode. The two modes of operation are clearly identifiable from the voltage-current curve. The
voltage and current increase with the applied power in the so-called \( \alpha \) mode and drop drastically when the discharge transits into the \( \gamma \) mode.

![Figure 5.3 Current-voltage characteristics of rf-APGD (13.56MHz, 2mm)](image)

### 5.2 Optical emission: Low-pressure CCP vs. APGDs

Figure 5.4 shows the time and space-resolved optical emission of an rf He discharge in the \( \alpha \) mode, in the \( \alpha-\gamma \) transition and in the \( \gamma \) mode. The data shown was obtained by the technique introduced in Chapter 2.2.2.

The emission profile is strongly time modulated due to the rapid energy relaxation of energetic electrons at atmospheric pressure (\( \tau_e = 1-10 \text{ ps} \ll \tau_{rf} = 10-100 \text{ ns} \)) and the collisional quenching of radiative states. Although the simplest fluid model introduced in section 3.3 does not calculate the radiation pattern explicitly, a good agreement is found between the experimentally observed optical emission profiles (Figure 5.4 a-c) and the He excitation profiles predicted by the simulations (Figure 5.4 d-f).
Chapter 5 Electron heating in rf-APGD

The optical emission of the discharge in the α and γ modes are markedly distinct, with difference in both their spatial and temporal evolution (Figure 5.10). As in low-pressure CCP (capacitively coupled plasma), the γ mode is characterised by ionisation/excitation being mostly sustained by electron avalanches that are created by the high electric fields within the sheaths. In atmospheric-pressure discharges, however, avalanches are not only initiated by secondary electrons but also by electrons generated in pooling reactions among helium metastable atoms and metastable dimers (\( \text{He}^+ + \text{He}^+ \rightarrow \text{He}^+ + \text{He} + e, \text{He}_2^2 + \text{He}_2^2 \rightarrow \text{He}_2^2 + 2\text{He} + e \)).\(^{116,117}\) Some of the electrons generated by these reactions are produced inside the sheaths seeding avalanches that are similar to those originated by secondary electrons. As a result, it is possible, at least computationally, to obtain a γ-like discharge at atmospheric pressure even in the absence of true secondary electron emissions.
Figure 5.4 - (a,b,c) Space- and time-resolved optical emission profile of an atmospheric-pressure rf He discharge in (a) the α mode, \( I = 31 \text{mA} \); (b) the α-γ transition, \( I = 93 \text{mA} \); and (c) the γ mode, \( I = 65 \text{mA} \). (d,e,f) Space- and time-resolved excitation profile obtained with a 1D fluid code. (g,h) Space- and time-resolved excitation profile obtained with a 1D fluid code with the secondary electron coefficient set to 0: (g) low current α mode, (h) high current γ-like mode. White dotted lines indicate the approximate location of the sheath edges.

Figure 5.5 shows numerically calculated \( J_c E \) plotted as a function of time and space. Here, \( J_c \) is the electron current and \( E \) is the electric field. In contrast to the γ
mode, the $\alpha$ mode is characterised by the power being absorbed mostly at the sheath edges instead of within the sheaths (Figure 5.5). As the input power increases and the discharge transitions from the $\alpha$ to the $\gamma$ mode, the amount of power coupled to the electrons decreases (Figure 5.5d) and the spatio-temporal evolution of the power density profile changes (Figure 5.5a-c). This is true in both low pressure\textsuperscript{53} and atmospheric pressure discharges.

![Figure 5.5](image)

**Figure 5.5** Power absorbed by the electrons calculated as $J,E$ (mW/cm$^3$) from the simulation data. (a) $\alpha$ mode; (b) $\alpha$-$\gamma$ transition, (c) $\gamma$ mode, (d) percentage of input power dissipated by the electrons calculated as $J,E/ J_{input}E$.

At atmospheric pressure, however, the simultaneous emission in the $\alpha$ mode from the two sheath edges\textsuperscript{118} (Figure 5.4a) that is also captured in the simulation results (Figure 5.4d) suggests that the electron heating takes place not only during the expansion of the sheath but also during its retreat. In fact Figure 5.5a indicates that at atmospheric pressure close to 50% of the input power delivered to the electrons is absorbed in the neighbourhood of the retreating sheath. This contrasts with the situation encountered in low-pressure He discharges, where the heating is
appreciable only during the expansion of the sheath. Simulation results in Figure 5.6 show that the heating in the neighbourhood of the retreating sheath decreases rapidly with decreasing pressure and as a result, while at atmospheric pressure He excitation takes place simultaneously at both edges (expanding and retreating), at 2 Torr the excitation is completely dominated by the expanding sheath.

Figure 5.6 Simulation results (a) (b) space- and time-resolved helium excitation profiles in a rf He discharge at (a) 2 Torr and (b) 760 Torr; (c) Electric field (V/cm); and (d) space charge density (/cm³); in an atmospheric-pressure rf He discharge. In (c), negative values are set to 0 to facilitate the visualization of the evolution of the field profile.

The additional heating of the electrons in atmospheric pressure discharges caused by the formation of a field enhanced region at the retreating sheath (Figure 5.6c). While at low pressure electrons can diffuse fast enough to follow the retreating sheath, at atmospheric pressure collisions prevent electrons from diffusing fast enough. As a result, electrons are not able to follow the retreating sheath merely by diffusion and a self-consistent electric field builds up to drive
electrons. The electric field develops when electrons not being able to diffuse fast enough towards the retreating sheath pile up at the edge, creating a region of negative space charge (Figure 5.6d). The resulting electric field accelerates the electrons towards the electrode, helping them to follow the retreating sheath and heating them in the process.

Although heating at the edge of the retreating sheath edge is negligible in low pressure discharges of the noble gases (in fact collisionless interaction of electrons with retreating sheaths leads to cooling of electrons\textsuperscript{63}), a similar heating mechanism has been observed in low pressure rf discharges when the electrons are subject to an increased collisionality in the presence of the molecular gases.\textsuperscript{118} It is noted, however, that while at low pressure heating at the retreating sheath edge is accompanied by a strong field reversal. The field is reversed in the sense that it is drawing electrons into the sheath region. This is attributed to the collisional drag force on the electrons advanced into the sheath.\textsuperscript{118} At atmospheric pressure no field reversal is observed (Figure 5.6c). Instead, a region of the enhanced electric field without change to the field polarity is formed at the retreating sheath.

The week emission observed experimentally in the centre of the discharge (Figure 5.4) which is underestimated by the simulation is attributed to impurities (mostly N\textsubscript{2}) present in the experiment but not in the simulation. As seen in Figure 5.5 a-c, where the electron power density in the $\alpha$ and $\gamma$ modes are compared, the simulation results indicate that energy is deposited in the centre of the discharge with the same pattern as that of the optical emission shown in Figure 5.4 a-c. It is argued that the deposited power leads to the optical emission observed in the experiments, although in the pure He environment of the simulations, electrons do not reach high enough energy as to excite He atoms (Figure 5.4 d-f). In addition,
it is possible that light collected experimentally from out of focus planes contributes to the light recorded in the centre of the discharge.

### 5.3 Extending the α mode by means of dielectric barriers

The α mode is the preferred mode of operation of an APGD because it creates a repeatable diffuse plasma well-suited for applications. However, densities of reactive species in the α mode are low due to low current densities. Therefore it is desirable to increase the current density within the α mode. The transition into a constricted γ mode as the input power is increased represents therefore an undesirable feature of APGDs and one would like to retard this transition as much as possible. One way of achieving this is to put dielectric barriers over the electrodes of an APGD.\(^{123}\) The current and voltage waveforms remain predominately sinusoidal, with the current leading the voltage by a phase shift less than 90 degrees. These results are consistent with the simulation results and similar to those found in bare electrode rf APGD.\(^{124}\) On the contrary these sinusoidal character is quite different from the pulse like waveform of the conventional kilohertz atmospheric-pressure dielectric barrier discharges (DBD).

To illustrate the benefits of dielectric barriers, Figure 5.7 shows the comparison of experimentally obtained current-voltage characteristics between an rf APGD and an rf DBD. For both the rf APGD and the rf DBD, the gas gap is fixed at 2.4 mm. In the case of rf DBD, each electrode is covered by a ceramic sheet with thickness of 0.5 mm and a relative dielectric constant of \(\varepsilon_r=5.9\). For both cases, the current has an initially linear relationship with the applied voltage. Both straight lines goes through the origin, and they represent the pre-breakdown discharge regime for two discharges. The slope of the rf DBD is greater than that
of the rf APGD. It is because of the higher total impedance of rf DBD in the absence of discharge.

In the case of the rf APGD, breakdown occurs at an applied voltage of $V_{a,\text{rms}}=276.2\,\text{V}$ and $I_{\text{rms}}=50.2\,\text{mA}$. As the applied voltage is increased further, the discharge current almost increased linearly until a transition point of $V_{a,\text{rms}}=470.3\,\text{V}$ and $I_{\text{rms}}=102.5\,\text{mA}$, where the glow discharge of 20mm in diameter shrinks into a narrow constricted column of about 1mm in diameter indicated as point b in Figure 5.7. The transition from the constricted point to point b is rapid and abrupt, and this constricted discharge is not stable and moves around between two electrodes. Gas breakdown occurred at an applied voltage of $V_{a,\text{rms}}=319.0\,\text{V}$ and $I_{\text{rms}}=50.2\,\text{mA}$ when one ceramic sheet was added to the plasma-facing side of electrode and the gas gap was still 2.4mm. The larger breakdown voltage was due to the addition of the ceramic sheet that divided into the applied voltage. Additionally, this voltage difference increases as the increasing discharge current.

![Figure 5.7](image_url)

Figure 5.7 Current-voltage characteristics of the atmospheric rf DBD and the rf APGD, marked with the gas breakdown point, the plasma constrict point, and the $\alpha$-$\gamma$ mode transition point. Points (a), (b), (c), and (d) indicate conditions where plasma images in Figs 5.8 and 5.9 were taken. The dashed line indicates conditions of plasma constriction.
This is due to the increment of total voltage across the dielectric barrier $V_{\text{m,rms}}=I_{\text{rms}}/\omega C_m$, with $C_m$ being total barrier capacitance. As the applied power increases further, a step change in the differential conductivity in the $V_{\text{a,rms}}-I_{\text{rms}}$ curve is apparent at 530.4V and 95.5mA. As will be shown later, the rf DBD retains its volume above $I_{\text{rms}}=95.5$mA. This suggests that the plasma constriction is avoided in the rf DBD and the cross-sectional area of the discharge remains the same over the entire current range.

![Plasma images of the rf-APGD](image)

**Figure 5.8** Plasma images of the rf-APGD at (a) $I_{\text{rms}}=75.7$ mA and point a in Figure 5.7 and (b) $I_{\text{rms}}=57.8$ mA and point b in Fig. 5.6. The images in (1) were taken with 1 ms exposure time. Images in (2), (3), (4), (5), and (6) were taken with 10 ns exposure time at $t=0$, $T/4$, $T/2$, $3T/4$, and $T$, respectively, with $T$ being the rf cycle period.

To support the discussion above, iCCD camera is used to take images of rf-APGD and rf DBD. Figure 5.8 (a) shows a millisecond exposure time image of the rf-APGD and its five nanosecond images at $I_{\text{rms}}=75.7$mA corresponding to point a in Figure 5.7. Images (3) and (5) of Figure 5.8 (a) were taken at the instants of $t=T/4$ and $3T/4$ when the discharge current reach its positive and negative maxima. It is clear that the rf-APGD is horizontally homogeneous. Its optical emission covers the majority of the gas gap with the peak optical signal
located in the gap centre. This suggests a volumetric discharge with a bell-like profile of optical emission centred at the middle of the gas gap. These features are characteristic of the \( \alpha \) mode, and provide experimental confirmation of the \( \alpha \) mode operation of the rf APGD in the 50.2-102.5 mA range. At point \( b \) in Figure 5.7 and \( I_{\text{rms}}=58.7 \text{mA} \), Figure 5.8 b shows that the rf-APGD is now a constricted plasma column of about 1mm in diameter. The constricted plasma is unstable, moving around, as shown in the nanosecond images of (2)-(6) in Figure 5.8b. This confirms that the rf APGD is susceptible to plasma constriction and its constriction is evolved from the \( \alpha \) mode directly.

![Plasma images](image)

**Figure 5.9** Plasma images of the rf DBD at (a) \( I_{\text{rms}}=69.0 \text{mA} \) and point \( c \) in Figure 5.7 and (b) \( I_{\text{rms}}=166.2 \text{mA} \) and point \( d \) in Figure 5.7. The images in (1) were taken with 1 ms exposure time. Images in (2), (3), (4), (5), and (6) were taken with 10 ns exposure time at \( t=0 \), \( T/4 \), \( 7T/8 \), and \( 3T/4 \), respectively.

However this constriction can be avoided by the introduction of the dielectric barrier. Figure 5.9a shows a millisecond images of rf DBD and its five nanosecond images corresponding to point \( c \) in Figure 5.7. Images (3) and (5) of were taken at the instants of \( t=T/4 \) and \( 3T/4 \) when the discharge current reach its positive and negative maxima. The discharge is horizontally homogeneous, covering the gas gap with a bell like profile, which is similar to Figure 5.8a and
characteristic of the \( \alpha \) mode. As the current is increased to \( I_{\text{rms}} = 166.2 \text{ mA} \) corresponding to point \( d \) in Figure 5.7, images in Figure 5.9b suggests that the plasma retains the same volume as that in Figure 5.9a and the plasma constriction is avoided. The discharge is again horizontally homogenous but now exhibits localized gas ionization and excitation. This indicates a spatial profile of double hump similar to that in Figure 4.4b, and characters of a \( \gamma \) mode. The images in (3) and (5) indicate a thin bright layer locates near to the instantaneous cathode. These are the negative glow and indicate localized gas ionization and excitation near the sheath bulk. Figure 5.9 supports further that dielectric barrier can mitigate plasma constriction.

![Figure 5.10 Optical emission spectrum of the rf DBD at \( I_{\text{rms}} = 104.4 \text{ mA} \), with the insert being the current dependence of the 706 nm line intensity.](image)

A typical optical emission spectrum of the rf DBD is shown in Figure 5.10 from 200 nm to 800nm at \( I_{\text{rms}} = 104.4 \text{ mA} \). Because our plasma rig is not air tight and there are impurity traces in the feed gas (see section 2.1), \( \text{N}_2 \), \( \text{OH} \) and \( \text{O} \) are identifiable in the optical emission spectrum of the discharge. Since the electron energy is yet to be measured reliably for rf APGD, Helium emission at 706nm (\( \text{He}^+ (3^3S) \rightarrow \text{He}^+ (2^3P) + \text{hv}(706\text{nm}) \) and \( e + \text{He} \Rightarrow \text{He}^+ (3^3S) + e \ 22.7\text{eV} \)) can
be used as an indirect measurement. The inserted picture in Figure 5.10 shows the 706nm emission intensity evolution as discharge current increases. The 706nm intensity changes little until \( I_{\text{rms}} = 91.2 \text{mA} \) after which it grows rapidly with the discharge current. The corner point of \( I_{\text{rms}} = 91.2 \text{mA} \) is similar to the point of current voltage line slope change at \( I_{\text{rms}} = 95.5 \text{mA} \) in Figure 5.7.

5.4 Summary

In conclusion, atmospheric-pressure glow discharges are sustained by ohmic heating of the electrons. In the \( \alpha \) mode, the electrons are heated both during the expansion and the retreat of the sheaths. This is observed both in time resolved experimental and computational measurements and results in a simultaneous emission from both sheath edges. In the \( \gamma \) mode, the heating takes place mostly in avalanches across the sheaths, giving rise to an emission pattern that alternates between the two electrodes. While secondary electrons seem the primary source of seed electrons for the avalanches in the \( \gamma \) mode, a contribution from metastable pooling reactions is also identified as a source of seed electrons in atmospheric-pressure discharges.

Since the \( \alpha \) mode is often the preferred mode of operation, dielectric barriers can be used as a means to extend this operation mode to higher input power. This allows increasing the discharge intensity and arguably the discharge efficacy for a desired application. It is noted, however, that introducing dielectric barriers can lead to the contamination of the discharge by possible sputtering of dielectric materials and an alternative means of extending the \( \alpha \) mode operation is discussed in the next chapter.
Chapter 6  Frequency effects in rf-APGD

As already discussed, low-temperature atmospheric pressure rf plasmas offer an interesting alternative to conventional low-pressure and are being explored for a wide range of applications.108,119,120 The plasma density that can be achieved in this discharges, however, is limited by the loss of plasma uniformity with increasing input power. Although at low power, uniform glow-like discharges suitable for practical applications can be generated, atmospheric-pressure discharges are very susceptible to constrict radially.61,121 One of the mechanisms leading to this constriction is the transition from the \( \alpha \) to \( \gamma \) mode. This transition is very fast because the negative differential impedance of the plasma, eventually turning the plasma into a high-temperature arc. An ability to control the operation of the plasma in this negative differential impedance region allows for the stabilisation of the discharge, extending the glow like operation regime. Such stabilisation can be achieved by using a current controlled power supply122 or by introducing dielectric barriers in the discharge.123,124,125 The latter has been discussed in Chapter 5.

An alternative approach would be the increase of the operating frequency, as proposed theoretically by J.J.Shi and M.G.Kong.62 In their study, the critical current density at the \( \alpha \) to \( \gamma \) mode transition point \( (J_{cr}) \) increases substantially by a factor of 10 (\( \approx 176.8/17.7 \)) over the four fold frequency increment from 6.78MHz to 27.12MHz as shown in Figure 6.1.62 In addition to the increase in \( J_{cr} \) with the increasing frequency, the applied voltage at \( J_{cr} \) decreases with increasing frequency. Although low-pressure rf discharges operating at frequencies above the conventional 13.56MHz have been widely studied in recent years, particularly
after the introduction of dual frequency capacitively coupled plasma sources, the evolution of atmospheric pressure discharges as a function of the rf frequency remains unexplored.

In this Chapter, we examine the characteristics of rf-APGD using experimental and computational tools, and we analyse the consequences of increasing the driving frequency on the discharge characteristics. The goal is two fold: firstly, to provide an experimental confirmation of the previous theoretical predictions made in the reference, namely the delay of the transition into the γ mode, a reduction of the transition voltage and sheath width and an increase in the plasma density and the peak electron temperature at the point before the transition into the γ mode as the frequency increases; and secondly, to explore the underpinning physics by investigating the frequency dependence of power coupling into electrons and ions.

The experiment setup is described in section 2.1. The gas gap is fixed at 2mm and the helium flow rate at 5 standard litre per minute. To gain a better
understanding of the experimental observations, the plasma is simulated the one dimensional model introduced in Chapter 3.

6.1 Current-voltage characteristics

Figure 6.2 presents the current-voltage characteristics of atmospheric pressure He rf discharges driven at 6.78MHz, 13.56MHz and 27.12MHz obtained experimentally. Each curve can be divided into 2 parts. The first part is the straight line that crosses the origin and corresponds to the pre-breakdown regime, i.e. the current measured is merely the displacement current that flows across the gap in the absence of plasma. The second part (symbols) contains the electrical signature of the plasma. The first point represents the condition soon after the gas breakdown when the plasma just cover a small area of the electrode. The last point (the maximum current) represents the condition just before plasma transition into the constricted γ mode discharge.

A good qualitative agreement is found between these experimental data and theoretical prediction made in the reference 62. The breakdown voltage decreases with the increasing frequency as shown in the Figure 6.2, a tendency is attributed to the enhanced confinement of electrons within the discharge gap.\textsuperscript{126, 127} Not only the breakdown voltage decreases with increasing frequency, but also the voltage required to sustain the discharge is also lower as the frequency increases. In contrast with the pre-breakdown section, the differential impedance (slope of the curves in Figure 6.2) decreases with increasing frequency at a rate larger than $1/\omega$. 
Figure 6.2 Experimentally obtained current-voltage characteristic of rf atmospheric-pressure He discharges driven at different frequencies

The difference between the maximum current before the transition into the γ mode and the minimum current required to sustain a discharge expands from ~15 mA at 6.78 MHz to ~150 mA at 27.12 MHz. That is a 10x increase for a 4x increase in frequency, which agrees with the theoretical prediction of ref 62.

6.2 Optical emission

Figure 6.3 shows the time averaged emission profile of the discharges driven at 3 different frequencies at the point before the transition into the γ mode (red stars in Figure 6.2. The same colour map is used in the three images for a fair comparison between the pictures taken at different frequency. It is clear that increasing the operation frequency allows for the generation of a more intense discharge (Figure 6.3), which is likely to translate in enhanced performance. This is consistent with the results of the theoretical study,⁶² which suggested that the electron density and the mean electron temperature at the maximum current before the transition into the γ mode increase with increasing frequency.
Figure 6.3 Experimentally obtained time integrated optical emission from a parallel plate rf He discharge operating at atmospheric pressure at the point before the α-γ transition (red stars in Figure 6.1): (a) 6.78MHz, (b) 13.56MHz, (c) 27.12MHz; (d) simulated helium excitation profiles.

For the three cases, the emission profiles are double-humped with light being emitted from the regions close to the electrodes.\(^{128}\) Space- and time-resolved experimental and simulation results\(^ {129}\) reveal that the emission originates from the expanding and retreating sheath edge, the location where electron heating is most efficient (see Chapter 5). As the frequency increases, it is also noticeable that the bright emitting layer becomes thinner and closer to the electrodes. This behaviour is also captured in the simulation results and is because of the reduction of the sheath width with increasing frequency. The reduction is caused by the lower driving voltage required at the higher frequency and the increase of the displacement current for a given electric field.\(^ {78}\)

### 6.3 Discharge efficiency

Although Figure 6.3 clearly indicates that more intense discharges can be obtained at the higher frequency, it is not clear whether the improvement is due to an enhanced electron heating for a given applied power or the capability of driving the plasma with higher input power without transitioning into the γ mode.
To address this question, three discharges driven at different frequencies but sustained with the same input power of (5W) are compared in Figure 6.4. The current-voltage conditions are shown by the symbol of black diamonds in Figure 6.2. Although the emission pattern indicates the same underlying physics governs the plasma formation, the discharge becomes less intense as the rf frequency increases. Actually, as the frequency increases the plasma become so weak that they even do not cover the whole electrode. Therefore the advantage of operating the rf discharge at higher frequencies originates from the possibility of driving plasma with higher input power instead of a more efficient utilisation of the input power.

This result may look a priory contradictory because increasing rf frequency is normally linked to enhanced electron heating. Since the operating voltage decreases with increasing frequency (Figure 6.2), the energy spent in accelerating ions inside sheaths decreases. As a result, if the input power is kept constant and the power coupled into the ions decreases, the power consumed by electrons must increase. Indeed, simulation results shown in Figure 6.5 suggests that the power coupled to electrons increases with increasing frequency at a given dissipated...
Chapter 6  
Frequency effect on rf-APGD

power. Consequently, the electron density and/or the electron temperature is expected to increase with increasing frequency. However, the experimental and computational results shown in Figure 6.4 indicate that the discharge becomes weaker at a given dissipated power.

![Graph showing the fraction of input power delivered to the electrons as a function of the input power at different driving frequencies.](image)

Figure 6.5 Fraction of input power delivered to the electrons as a function of the input power at different driving frequencies.

The apparent contradiction of decreasing optical emission intensity with increasing percentage power coupled into electrons as the frequency increases can be understood by examining the evolution of the electron temperature profiles shown in Figure 6.7. As the frequency increases, the electron temperature decreases because of the reduction of the applied voltage (Figure 6.2). This reduction results in less efficient excitation and ionization of the background gas, a tendency observed experimentally and computationally (Figure 6.4). Nonetheless the overall power absorbed by electrons increases because simultaneously the electron temperature in the bulk plasma increases. This increase in the bulk electron temperature is due to the increase of the rf field acceleration experienced by the electrons trapped in the ambipolar potential as shown in Figure 6.6. Assuming that the current in the sheaths is dominated by the
displacement current, that the bulk conductivity approaches the DC limit (a reasonable approximation since at atmospheric pressure the collision frequency is much larger the driving rf frequency), it can be shown\textsuperscript{109} that the ratio between the electric field in the bulk plasma to the electric field in the sheaths increases as $\sim \omega_{pe}^2 \nu / \omega_{pe}^2$. Here $\omega_{pe}$ is the electron plasma frequency, $\omega_{rf}$ the rf driving frequency and $\nu$ the electron-neutral collision frequency. As a consequence of the increase in the ratio of the bulk electric field to the sheath electric field, the spatial profile of the electron temperature across the electrode gap becomes flatter as the frequency increases, i.e. it lowers in the sheath region and increases in the bulk as shown in figure 6.7. Because the number of electrons in the bulk is larger than that at the sheath edges, the net power consumed by electrons increases with the frequency. Nevertheless, since the temperature at the sheath edges, where most excitation and ionization events take place, decreases, the discharge become fainter when the frequency is increased at the constant input power.

![](image)

**Figure 6.6 Maximum electric field at the gas gap centre at different driving frequency.**
Figure 6.7 Electron temperature profiles for discharges driven at different frequencies at constant input power (Simulation results).

Finally, it is anticipated that the increase in electron temperature in the bulk plasma will result in a gas temperature increase because the energy in the electron-neutral collisions is a strong heating mechanism in the atmospheric pressure rf discharges. Nonetheless, changes in the driving frequency could be used to tailor the plasma chemistry for a given application.

6.4 Summary

In this Chapter, we have performed an experimental and numerical study of rf atmospheric pressure helium discharges to investigate their characteristics as a function of the driving frequency. It can be seen that the maximum power can be coupled to the plasma before the transition into the constricted $\gamma$ mode increases with frequency. Consequently, rf discharges operating at frequencies above the conventional 13.56MHz are capable of generating more intense discharges.

When the frequency is increased at a constant input power, however, the discharge becomes less intense. This is particularly profound when more power is coupled into electrons. The apparent contradiction is resolved when the non-uniform spatial profile of the electron temperature is taken into account. As the frequency increases, the electron temperature in the sheath regions decreases.
because the reduction of the driving voltage. This results in the decrease in the excitation and ionization observed both experimentally and in simulations.

At the same time, the electric field in the bulk plasma increases, leading to an enhanced electron heating of bulk electrons. Despite the increase in the electron heating and power absorbed in the bulk plasma with increasing frequency, the electron temperature in the plasma bulk region is too low for the electron to contribute significantly to the excitation of the background gas. The net result of the reduction of the electron temperature in the sheaths and the increase in the bulk is an overall increase in the electron power consumption but a decrease on the excitation/ionization of the neutral gas. This strong dependence of the electron temperature on the excitation frequency could be exploited to tailor the plasma chemistry for a given application.

From a practical standpoint, increasing the frequency enables a wider operation window and more intense discharges. Nevertheless, the gas temperature of the discharge also increases due to the loss of ionization efficiency, and as a result increasing the frequency needs to be assessed against the thermal constrains of a particular application.
Chapter 7 RF-APGD chemistry in He mixture with N\textsubscript{2} and O\textsubscript{2}

Helium is normally used as the plasma forming gas in APGDs because its inertness and high thermal conductivity favour the discharge uniformity. However, chemical reactivity of a pure helium plasma is very limited and admixtures of other molecular gases are typically needed for practical applications. Since atmospheric pressure plasmas operate in open air, air mixture into the plasma is inevitable and so admixtures of nitrogen and oxygen are of particular interest. Furthermore, these species can provide reactive oxygen and nitrogen species that are relevance for many applications. For example, molecular oxygen can be dissociated in helium plasma to create powerful oxidants such as atomic oxygen and ozone for etching bacterial membranes and organic films.\textsuperscript{63}

A practical question that arises is the following: what is the optimum amount of oxygen that needs to be present in the discharge to maximize the production of reactive oxygen species? Some reactive species can be easily detected. For example, excited atomic oxygen production in He-O\textsubscript{2} atmospheric pressure glow discharges can be studied by optical emission spectroscopy.\textsuperscript{25} Such a study can also provide insights into the generation and transport mechanism of relevant species (He(2\textsuperscript{3}S), O, OH, O\textsubscript{2} (a\textsuperscript{1}Δ\textsubscript{g}), O\textsubscript{2} (b\textsuperscript{1}Σ\textsubscript{g}\textsuperscript{+}), O\textsubscript{3}, N, N\textsubscript{2}, NO...) in the afterglow. Emission spectroscopy, however, cannot detect non-radiative states such as ground state atoms and molecules. These can be detected by laser spectroscopic techniques (e.g. absorption and fluorescence).\textsuperscript{131,132}
In this chapter, we present experimental and computational results aimed at understanding the influence of \( \text{N}_2 \) and \( \text{O}_2 \) on the a He rf-APGD and its possible implications from a practical point of view.

### 7.1 He APGD with air impurities

The role of impurities in a helium discharge is very significant because helium metastables (\(-20\text{eV}\)) have sufficient energy to ionise most impurities (typical ionization potential \(\sim 10-15\text{eV}\)). Impurities in the discharge are originated from two sources. In the first place, the helium gas has a finite purity (99.95% in our case) which implies that impurities (typically \(\text{N}_2\), \(\text{H}_2\), \(\text{H}_2\text{O}\), ...) are present with a partial pressure of \(\sim 400\text{mTorr}\). In addition, atmospheric air can back-diffuse into the discharge region introducing \(\text{N}_2\), \(\text{O}_2\) and \(\text{H}_2\text{O}\).

A typical emission spectrum of an atmospheric helium discharge is shown in Figure 7.1. Despite the small concentration of the admixture gases, the optical emission reveals significant excitation of these additives. Analysis of Figure 7.1 indicates that the optical emission can be attributed \(\sim 55\%\) to \(\text{N}_2\), \(\sim 16\%\) to He, 15% to OH and 14% to \(\text{O}_2\).

![Figure 7.1 Typical optical emission spectrum of a He rf-APGD operated in the \(\alpha\) mode](image)
Figure 7.2 Space and time resolved emission for all wavelength, 391nm, 706nm and 777nm in the α mode, the α→γ and the γ mode.

Given the different mechanisms leading to their formation of each radiative state, one should expect spatio-temporal differences in the emission profiles of each line/band. To investigate these differences and gain insight into the underpinning physics of the discharge, 5ns exposure time filtered images are taken. These images record the space and time resolved emission, and in this thesis we have selected the following emission lines: 391nm (N₂⁺(B^2Σ_u) → N₂⁺(X^2Σ_g) + hν), 706nm (He⁺(3^3S) → He⁺(2^3P) + hν) and 777nm (O(3^3P) → O(3^3S) + hν). The radiative decay lifetime of N₂⁺, He, and O are 60, 64 and 27ns, respectively. These are shorter than the rf period (74ns).
fact, the actual lifetime of these excited states is much shorter than the rf period because the collisional quenching at atmospheric pressure further shortens their lifetime. Therefore, the spatio-temporal evolution of the emission can be used to infer when and where the excited states $N_2^+(B\Sigma_g^+)$, He($3^3S$) and O($3^3P$) are populated.

Figure 7.2a,d,g,j show the spatial and temporal evolution of the optical emission in the $\alpha$ mode. The majority of the 706nm (Figure 7.2d) emission is near to the electrode, and the maximum intensity arises at the time of the maximum applied voltage within the expanded sheath. Energetic electrons ($\varepsilon \approx 22.7\text{eV}$) accelerated by the high electric field inside the sheaths are the main mechanism populating He($3^3S$) through ground state excitation of He atoms. Consequently, the 706nm emission is closely related to the sheath evolution in the discharge.

The overall emission (all wavelengths integrated) follows mostly the pattern of the emission at 391nm (Figure 7.2a,g). These differ from the pattern of 706nm and in this case most of the emission is located outside the sheaths. This suggests that the nitrogen molecular and ionic bands dominate the optical emission of the discharge, as also supported by the OES measurement shown in Figure 7.1.

The spatial–temporal profile of atomic oxygen at 777nm is yet different from that of $N_2^+$ at 391nm and He at 706nm. The low temporal dependence of the oxygen emission indicates that the O($3^3P$) is mainly populated by collisions with long-lived particles.

In the $\alpha \rightarrow \gamma$ transition (Figure 7.2b,e,h,k), the spatio-temporal profile of each case is similar to the profiles in the $\alpha$ mode. Although nitrogen still dominates the overall emission in the $\alpha \rightarrow \gamma$ transition, the 706nm emission inside the sheaths starts to contribute significantly to the overall emission. As the current increases further and the plasma transits into the constricted $\gamma$ mode, the 706nm emission dominates the overall emission (Figure 7.2c,f,l,l). This is an indication of the
dominant role of excitation and ionization inside the sheath in the $\gamma$ mode. These observations are also supported by the optical emission spectrum shown in Figure 7.3, in which He related emission dominates the spectrum. It is interesting to note that He emission at 587nm and 667nm, which correspond to He ($3^3D$) (23.07eV), is larger than emission at 706nm from He($3^3S$) (22.7eV). This relative change of the emission lines suggest an increase in the electron temperature in the sheath region as the discharge transits from the $\alpha$ to the $\gamma$ mode.

![Optical emission of discharge in the $\gamma$ mode.](image)

Figure 7.3 Optical emission of discharge in the $\gamma$ mode.

Figure 7.4 shows the 391nm and 706nm emission profiles predicted by the simulation model introduced in Section 3.5. It agrees well with the experimental data shown in Figure 7.2 and supports the arguments used above. Since most of the electron generation is outside the sheath (Figure 7.4b), it can be concluded that the discharge operates in the $\alpha$ mode. It can be noted that the 706nm emission is confined inside the sheath (Figure 7.4a,d) but electron generation and 391nm emission are outside the sheath.
Figure 7.4 Simulated spatial-temporal evolution of the a) electric field b) electron generation c) 391nm emission d) 706nm emission in a 2mm 13.56MHz He+N<sub>2</sub>; 0.04% discharge.

The emission intensity ratio between 391nm(N<sub>2</sub><sup>+</sup>), 706nm(He) and 777nm(O) is investigated for different frequencies in Figure 7.5. Each line starts at the point when plasma just covers the whole electrode and ends at the last point before the transition into the constricted γ mode. As discussed in Chapter 6, the higher the rf frequency the larger the operation window.<sup>126</sup>

Although the emission intensity of each line increases as more power is coupled to the plasma, the increase for each specie is different due to the different excitation mechanisms. For the 13.56MHz case, the 391nm / 706nm ratio is found to decrease from 1.21 at 3.9W to 0.4 at 11.4W, and the 777nm / 706nm ratio is also found to decrease from 2.49 to 0.98. These tendencies are similar for the 6.78MHz and 27.12MHz cases. These observations indicate that emission at 706nm increases faster than that at 391nm and 777nm, and this is attributed to the
increasing sheath electric field as the power (and the applied voltage) increases and the discharge approaches the \( \gamma \) mode.

![Graph](image)

Figure 7.5 The OES intensity ratio of 391\text{nm}/706\text{nm} and 777\text{nm}/706\text{nm} for 3 frequencies

### 7.2 He + \( \text{O}_2 \) rf-APGD

In the previous section we have seen that nitrogen and oxygen impurities affect the plasma and that under some conditions most of the optical emission is dominated by the impurities (see Figure 7.1). It is of interest, however, to vary the impurity level as a mean to optimize the plasma characteristics for a given application. For sterilization, oxygen reactive species are known to be of great importance and therefore in this section we look at the characteristics of a He discharge with different admixtures of \( \text{O}_2 \).

Figure 7.6 shows the current voltage characteristics of atmospheric-pressure He and He +\( \text{O}_2 \) (0.5\%) rf discharges driven at 13.56MHz. Each curve can be divided into two parts. The first part is a straight line through the origin and corresponds to the pre-breakdown regime, i.e. the current is merely displacement current that flow through the discharge gap in the absence of plasma. The first point represents the point soon after the gas breakdown and the last point represents the condition just before the transition into a \( \gamma \) discharge. The breakdown voltage \( V_{br} \) is found to increase from 235V for pure helium to 340V.
for He+O\textsubscript{2} 0.5%. The voltage drop from pre--breakdown to breakdown is only 10V in pure helium but increases substantially to 45V from 385 to 340V when 0.5% O\textsubscript{2} is introduced in the helium flow. The ratio between the breakdown current \(J_{\text{breakdown}}\) and the last current before transition into the \(\gamma\) mode \(J_{\text{transition}}\), \(J_{\text{transition}} / J_{\text{breakdown}}\) is 3.4 in the pure helium case. At 0.5% O\textsubscript{2} injection case, \(J_{\text{transition}} / J_{\text{breakdown}}\) decrease to 2.3. This reduction suggests that the window of stable operation becomes smaller as the oxygen content increases. Consequently, it is difficult to maintain stable glow discharge with high oxygen content.

![Figure 7.6 Current and voltage curve for He and He+O\textsubscript{2} rf-APGD](image)

Figure 7.7 shows the relation between current and consumed power as a function of the gas composition. Each curve starts with the minimum power \(P_{\text{min}}\) obtained immediately after breakdown. The consumed power increases with the discharge current until the point before the transition to the constricted \(\gamma\) mode. For the 0.1% O\textsubscript{2} injection case, \(P_{\text{min}}\) is 2.76W at a discharge current of 63mA. As the oxygen content is increased to 0.5% and 0.9%, \(P_{\text{min}}\) increases to 6.0W to 10.6W, respectively. So \(P_{\text{min}}\) increases substantially by a factor 3.8 (10.6/2.76) over the 9 fold O\textsubscript{2} increment from 0.1% to 0.9%. The curves overlap but the
minimum power required to ignite the discharge increases when more oxygen is added. The shorter curves of the higher oxygen content also suggest the difficulty to maintain stable glow discharge at high oxygen concentration.

![Graph showing current dependence of power consumed by the plasma](image)

**Figure 7.7 Current dependence of the power consumed by the plasma**

The phase angle between the voltage and current waveforms is shown in Figure 7.8. As the current increases from 63mA to 92mA, for the 0.1% O₂ injection case, the phase difference is observed to decrease from 85 to 67 degrees, a net reduction of 21.2% in Figure 7.9a. Then it decreases to 64 degrees at 208mA by a much smaller amount of 4.5%. The pictures inserted in the figure suggest that before the plasma covers the whole electrodes, the phase difference decreases substantially, and then the phase difference decreases only slowly. This is easy understood from the resistive nature of the bulk plasma. We model the rf-APGD using an equivalent circuit consisting of a capacitor and a series resistor. The capacitor of capacitance $C_s$ models the electron-depleted sheath regions, $C_s = \varepsilon \frac{A}{d}$ (A is the capacitor area, d is the capacitor gap distance) whereas the resistor of resistance $R_p$ models the quasi-neutral region of the bulk plasma.
Before the plasma covers the whole electrode, $C_f$ models the part between the two electrodes that remains without plasma (Figure 7.9b). The absolute value of the phase difference during this initial period is $|\theta| = \arctg \left( \frac{C_f + C_x + \alpha C^2_f C_x R_p^2}{\alpha R_p C^2_x} \right)$.

![Figure 7.8 Current dependence of the phase angle between voltage and current. Inserts are images of the rf-APGD evolution from gas breakdown to the point before arcing.](image)

As the plasma expands, the initial capacitance is substituted by an impedance that contains a resistive component (the bulk plasma) and therefore $\theta$ decreases. When the plasma covers the whole electrode, (Figure 7.9b), the equivalent impedance of the gap is $Z_g = R_p - j/\alpha C_s$. The impedance $R_p = \rho \ell / A$ ( $\rho$ is the resistivity, $A$ is the area and $\ell$ is the length) and the phase angle is then given by $|\theta| = \arctg \left( \frac{1}{R_p \alpha C_s} \right) = \arctg \left( \frac{d}{\rho \ell \varepsilon} \right)$. As more power is coupled to the plasma, $\rho$ and $d$ decrease, whereas $\ell$ increases. The changing of these three factors leads to a relative stable phase angle. Similar evolution is observed for the 0.5% and 0.9% O$_2$ injection cases. The breakdown phase decreases to 82 and 80 degrees,
respectively, due to the higher power needed to ignite the discharge at higher O\textsubscript{2} concentration.

![Diagram](image)

**Figure 7.9 Gas discharge structure evolution.** (a) Soon after breakdown the plasma does not cover the whole electrodes. (b) At higher input power, the plasma covers the whole electrodes.

The time integrated light emission profile as the current and power increase is shown in figure 7.10. Each picture was captured with 500 ns exposure time (~7 rf cycles), and the corresponding points in the current-voltage characteristics are highlighted by the symbol of blue diamonds in Figure 7.6. Immediately after the breakdown, the plasma is weak and only covers the electrode partially. As the current increases, the plasma expands until it covers the whole electrode, and the emission profile evolves from a bell-like profile to a double humped profile with one bright layer above each of the electrode.

For the plasma with the dissipated power of 15W and an oxygen content of 0.5%, a tiny plasma arises immediately after the breakdown, but for the pure helium case, the plasma almost covers the whole electrode from the beginning and shows the double humped structure. For the last point before the transition into a constricted $\gamma$ mode, although the dissipated power of the 0.5% O\textsubscript{2} case is 42W, 31.3% larger than the 32W for the pure helium case, the optical emission of the plasma with 0.5% O\textsubscript{2} is much weaker than that of the pure helium discharge. This is attributed to the electron affinity and molecular nature of oxygen.
Figure 7.10 Time integrated optical emission in (a) pure Helium and (b) He+O\textsubscript{2} 0.5%.

The optical emission spectra for different He+O\textsubscript{2} mixtures are shown in Figure 7.11 for a constant input power of 30W. As discussed earlier, one can note the presence of nitrogen emission (300nm- 500nm range) even though nitrogen is not introduced deliberately into the discharge.\textsuperscript{62} The excited neutral He atomic line (706nm) decreases from 2.23 at 0.1% O\textsubscript{2} injection, through 1.55 at 0.5% O\textsubscript{2} injection, to 1.3 at 0.9% O\textsubscript{2} injection. The increment of O\textsubscript{2} also leads to a decrease of the emission of oxygen atomic line at 777nm. These decreases are attributed to the overall decrease of the plasma intensity as electrons are lost in attachment reactions and input power channelled to roto-vibrational states of oxygen molecules.
Figure 7.11 Optical emission spectrum comparison at 30W. (a) 0.1%, (b) 0.5% and (c) 0.9% O₂ content.

Figure 7.12 shows the current dependence of the rotational temperature for the O₂ injection of 0.1%, 0.5% and 0.9%. The gas temperature was estimated according to the optical emission of OH line around 309nm measured with the 2400 groves/mm grating. Comparison between the measured spectrum and a synthetic spectrum constructed with LIFBASE (Figure 7.12), the gas temperature is estimated to vary from 320K to 450K with a slight increase as the oxygen concentration increases.

For the 0.1% O₂ injection case, the 777nm emission intensity increases from 4 at 73mA to 149 at 199mA by 37 fold (≈149/4). Besides only 10 fold (≈76/7) and 7 fold (≈43/6) increment at 0.5% and 0.9% O₂ injection cases respectively, the peak 777nm emission intensity before the transition into the γ mode is also much smaller than that of the 0.1% O₂ injection. This tendency indicates that
introducing too much oxygen into the discharge may be detrimental from a practical point of view.

![Graph showing current dependence of the rotational temperature and the 777nm emission line for various He+O2 mixtures.](image)

7.3 *He, He+N2, He+O2 optical emission comparisons*

In this section we deliberately introduced nitrogen and oxygen into the discharge to study if qualitative changes are observed as a function of the impurity level. Figure 7.13 shows the current and voltage curves for He, He+N2, and He+O2 rf-APGD with a 2mm electrode gap. Each curve describes the evolution from pre-breakdown until the last point before the plasma constricts into the $\gamma$ mode. The more oxygen and nitrogen is introduced in the discharge, the higher the voltage required to sustain the discharge becomes. Another observation is that the discharge regime of the He+O2 discharges are wider than those of the He+N2 discharges.
Figure 7.13 Current and voltage curve for He, He+N₂ and He+O₂ rf-APGD

Figure 7.14 shows the spatial-temporal evolution of plasma as a function of N₂ and O₂ concentration. The discharge conditions are marked with red stars in Figure 7.13. Besides the emission at 391nm, 706nm, and 777nm emission introduced in Figure 7.2, the emission at 357nm (N₂(C₃Πₜ) → N₂(B₃Πₑ)+hν) and at 844nm (O(3³P) → O(3¹S)+hν) are also studied. The radiation lifetime of these radiative states are 40.5ns and 31ns, respectively. They are also shorter than the rf period (74ns). Consequently, these emission profiles can suggest when and where N₂(C₃Πₜ) and O(3³P) are populated. For the pure helium case, the optical emission pattern of the all wavelength, 391nm, 706nm and 777nm emission are the same as in Figure 7.2. Emission at 357nm has a similar pattern to the 391nm emission, suggesting that similar processes are responsible for the excitation of the corresponding radiative levels. Unlike the weak temporal dependence of oxygen emission at 777nm, 844nm oxygen emission present a significant temporal modulation suggesting that electron collisions contribute to the population of O(3³P).

For each wavelength series, the images are normalised to the maximum emission intensity. As a characteristic of the discharge operated in the α mode, the all wavelength emission pattern for the 5 cases has the same pattern as nitrogen
emissions. The discharge in He+N₂(0.03%) is the most intense of the five but no qualitative difference are observed as a function of the impurity concentration. This suggests that helium rf discharges containing between 0.05-0.3% nitrogen/oxygen impurities operate in similar fashion.

![Diagrams and charts](image)

**Figure 7.14** Spatial-temporal evolution of the optical emission of (a,f,k,p,u,z) He+N₂(0.3%), (b,g,l,q,v,aa) He+N₂(0.1%), (c,h,m,r,w,ab) He, (d,i,n,s,x,ac) He+O₂(0.1%) and (e,j,o,t,y,ad) He+O₂(0.1%) discharges. (a-e) Wavelength integrated, (f-j) N₂ 337nm, (k-o) N₂⁺ 391nm, (p-t) He 706nm, (u-y) O 777nm, (z-ad) O 844nm. For each wavelength, the image is normalised to the maximum emission intensity. White dash lines indicate the estimated sheath region based on the 706nm emission pattern.

### 7.4 Summary

In summary, due to the high energy of helium metastables, impurities play a very important role in helium APGDs. N₂ and O₂ are significant impurities as they are the main constituents of air but also because they have interesting practical
applications, e.g. reactive oxygen and nitrogen species for biomedical applications. This study suggests that the underpinning discharge physics remain qualitatively the same for impurity concentrations within the range of 0.05-0.3%, and that optimum performance is likely to be obtained within that range of admixtures. The different generation and excitation mechanisms of different species give rise to distinct spatio-temporal emission profiles and future studies could be directed towards optimising the discharge to favour the generation of particular species.
Chapter 8  *Microplasmas: Diffused $\gamma$ mode*

The term microplasmas is usually used to refer to discharges with dimensions that around a few micrometers. Therefore, microplasmas are at least an order of magnitude smaller than the conventional low-temperature low-pressure discharges used for material processing in the semiconductor industry. Microplasmas combine the potential of low-temperature plasma with the advantages of being on a micro scale. The discharges create a highly reactive environment that contains charged particles, excited species, radicals, and photons, and the reduced dimensions enable low-power sources with small footprints suited for integration in microsystems and portable devices. Indeed, microplasmas represent a new realm in plasma physics that is attracting growing attention for its potential economic and technological impact. Despite the interest they have attracted, the physics governing these discharges remains far from fully understood.

The experiment setup used for this chapter is described in Chapter 2. The gas gap is varied from 2mm down to approximately 300$\mu$m. The excitation frequency is fixed at 6.78MHz unless otherwise noted. Similar results are obtained at 13.56MHz. The interpretation of the experiment data is helped by the He+N$_2$ APGD optical emission model simulation described in Section 3.5.
8.1 Current-voltage characteristics

Figure 8.1 shows the current-voltage (IV) curves of atmospheric-pressure He rf discharges in different electrode gaps. As the discharge gap decreases, the required voltage to ignite and sustain the discharge also decreases. The reduction, however, is not proportional to the reduction in gap size and higher electric fields are required to ignite smaller gaps. This tendency is attributed to the increasing surface to volume ratio and thereby increasing electron loss to the electrodes as the gap is reduced. One can also note that the dynamic plasma impedance (slope of the IV curve) decreases as well. The last point of each curve, i.e. the point of the maximum current, corresponds to the discharge condition right before the transition to the constricted γ-mode. At 2mm, the transition from the pre-breakdown regime to the gas discharge regime is marked with an abrupt change in the slope of the current-voltage curve, signifying a step change in the gap impedance. In the cases of 1mm and 0.5mm, a similar but smaller step change is observe at the breakdown point. The step change eventually becomes negligible at 0.3mm.

![Figure 8.1 Current-voltage curves of diffused glow-like rf helium discharges in various gaps.](image)
The phase angle between the current and the voltage signals can be obtained by analysing the recorded current and voltage waveforms. The evolution of the phase angle as a function of the input power and the discharge gap size is shown in Figure 8.2. For a given input current, the impedance of the smaller discharge is more capacitive due to the larger capacitance of the electrode configuration and reduced bulk plasma.

![Figure 8.2 Current-voltage phase difference of rf helium discharges in various gaps.](image)

For the 2mm gap discharge, the phase angle right after breakdown (I=11mA) is 78 degrees, it decreases to 73 degrees at 17mA as the plasma expands to cover the whole electrode and remains mostly constant until the last point before the plasma transition into the constricted $\gamma$ mode. The evolution of the phase angle for the smaller gap sizes (1mm, 0.5mm and 0.3mm), however, is slightly different. For these discharges, the plasma covers the whole electrodes right after breakdown happens and the phase angle decreases continuously until the last point before the transition into the constricted $\gamma$ mode.

The transition into the constricted $\gamma$ mode is not fully understood and one possible mechanism triggering the constriction is a thermal instability. To probe this hypothesis, the gas temperature as a function of the applied power was
measured and the results are shown in Figure 8.3. The gas temperature is estimated from the rotational temperature of the N2 second positive system (emission at 391nm) using the fitting procedure introduced in Section 2.2.2. As expected the gas temperature increases as the applied power increases for each gap size. For a given input power, the plasma in the smaller gap has the higher power density and consequently, the gas temperature increases with decreasing gap size. Since active cooling was used (the water temperature remained at 303±3 K for all cases), and the plasma presents a large surface-to-volume ratio, the gas temperature difference is small despite the drastic changes in power density. If a thermal instability drives the constriction of the discharge, figure 8.3 suggests that this one takes place when the gas temperature is ~365K. Future studies, however, are required to examine further this hypothesis.

![Figure 8.3 Rotational temperature as the function of the applied power at the different gaps.](image)

8.2 Optical emission

Figure 8.4 shows the spatio-temporal evolution of the plasma optical emission as a function of the gap size. The discharge conditions are marked with red stars in Figure 8.1 and the emission pattern in a constricted \( \gamma \) mode is also shown for completeness. The patterns shown in Figure 8.1 are characteristic for each gap
size, i.e. no qualitative changes are observed if the current is changed within the current range shown in Figure 8.1. As an example, the emission patterns for the 500μm discharge at low and high currents (blue squares in Figure 8.1) are shown in Figure 8.5.

![Image](image_url)

**Figure 8.4** Spatio-temporal evolution of the optical emission of (d,i,n,s) 2mm, (c,h,m,r) 1mm, (b,g,l,q) 500μm and (a,f,k,p) 300μm rf diffused glow-like discharges: (a-e) wavelength-integrated, (f-j) N2+ 391nm, (k-o) He 706nm and (p-t) O 777nm. (e,j,o,t) Emission pattern in the constricted γ mode. White lines indicate the estimated sheath region based on the emission pattern of 706nm and are shown to guide the eye. Images are not normalized to highlight their pattern rather than their relative intensity.
Figure 8.5 Spatial-temporal evolution of the optical emission at 500μm (a,c,e,g) low current cases, (b,d,f,h) high current cases corresponding to blue square in Figure 8.1. White dash lines indicate the sheath region based on the emission of 706nm emission. The low current images are normalized to high current images at each wavelength.

For large gaps (1-2mm), the all-wavelength emission pattern is similar to that of nitrogen despite its low concentration in the neutral gas (<0.05%). This is not surprising as small concentrations of impurities in a helium discharge can significantly affect the plasma. Indeed the emission spectrum (Figure 7.1) is dominated by nitrogen molecular and ionic bands. It is interesting to note, however, that not only the emission of helium at 706nm is less intense than the nitrogen emission, but it also has a different pattern (compare Figure 8.4h,i with Figure 8.4m,n). The emission patterns indicate that nitrogen ion excitation takes place outside the sheaths whereas helium excitation occurs predominantly inside
the sheaths. Simulation results also capture this behaviour and provide insights into different excitation mechanisms of $N_2^+(B^2\Sigma_g^+)$ and He($^3\Sigma$). Whereas $N_2^+(B^2\Sigma_g^+)$ is excited by the combined action of He metastables (Penning ionization) and low energy electrons ($\varepsilon<3\text{eV}$), helium excitation requires high energy electrons ($\varepsilon>20\text{eV}$) because their main excitation mechanism is direct ground state electron excitation. It can also be observed that the spatio-temporal emission profile of the atomic oxygen at 777nm (Figure 8.4 r,s) is yet different to that of nitrogen and helium. The weak temporal dependence of the 777nm emission pattern suggests that $O(^3\Sigma_P)$ is mainly populated by collisions among long-lived heavy particles. Work underpinning the mechanisms leading to these different emission patterns is still ongoing. Here it is only noted that experimental and computational data suggest that helium emission at 706nm in He discharges with a small concentration of impurities can be used to indicate the presence of energetic electrons ($\varepsilon>20\text{eV}$), and thereby the 706nm emission pattern is closely related to that of the sheaths.

As the gap size is reduced, it is clear that the bulk plasma shrinks and the sheaths extend across a larger portion of the gap (Figure 8.4 k-n). This corroborates earlier computer simulation results. As a result of the shrinking of the bulk plasma, the bright emission layers observed above each electrode in the 2mm gap discharge start to get closer together and eventually overlap with each other in space (Figure 8.4 a-d). It is interesting to note, however, that as the gap decreases not only the emission pattern associated with each sheath approach each other, but a shift of dominant species also takes place. Whereas in the 1-2 mm gap discharges the overall emission was clearly dominated by nitrogen (see the pattern similarity between Figure 8.4 c,d and h,i), in the 300-500\text{\mu m} discharges the pattern of the overall emission agrees with that of helium (see Figure 8.4 a,b and 2k,l). This is also supported by the emission spectrum
(Figure 8.6) that shows a decrease in nitrogen emission and an increase of helium lines.

![Graph showing OES intensity versus wavelength with peaks at 391 nm (N₂⁺) and 777 nm (O⁺)]

**Figure 8.6** Optical emission of the discharge with 0.5mm gap. The discharge conditions are the same as those of Figure 8.4(b).

Figure 8.4 also corroborates the theoretical prediction regarding the presence of electron avalanches crossing the discharge gap and reaching the opposite electrode (compare Figure 8.4 k,l and note how 706nm emission extends across the discharge gap as the gap size is reduced). Although we have not measured the electron energy of electrons impinging on the electrodes, Ref. 113 suggested that up to 50% of the electrons could have energies above 5eV.

Another theoretical prediction made in Ref. 109 and 113 was that rf microdischarges can only operate in the γ-mode, i.e. the discharge is sustained mainly by ionization avalanches in the sheaths. This prediction was based on 1-dimensional analyses and therefore did not address the possible radial constriction of the discharge. It is normally believed that operation in the γ-mode at atmospheric pressure leads to a constriction of the discharge. However, the discharges described in this letter are diffuse and cover the whole electrode (unless otherwise noted). Therefore, the question of whether microdischarges
operate in the $\alpha$-mode against theoretical predictions in 109 and 113 or in a diffuse (rather than the typical constricted) $\gamma$-mode arises.

The emission pattern at 706nm (Figure 8.4 k-n) indicates that electron avalanches as those needed to sustain the discharge in the $\gamma$-mode actually exist in microdischarges but does not prove that the avalanches are the main ionization mechanism of the discharge. In fact emission at 706nm is also recorded in the sheaths of mm-gap discharges yet they operate in the $\alpha$-mode. It is noted, however, that in large (~2mm) constricted $\gamma$ discharges the emission pattern also agrees with that at 706nm (Figure 8.4 e,j,o,t), suggesting that microdischarges operate in a diffuse $\gamma$ mode because their emission is also dominated by He (compare Figure 8.4 a,b and i,j). Since electron generation cannot be measured directly, computer simulations are used to probe this further.

Figure 8.7d-f shows the 706nm emission pattern in small (500$\mu$m) and large (2mm) gaps ($\alpha$ and $\gamma$ mode) predicted by computer simulations. The simulation results agree well with the experimental data shown in Figure 8.4 k-o. Furthermore, simulations can predict the spatio-temporal evolution of the electron generation rate and this is shown in Figure 8.7 a and e. It can be seen that in the 2mm gap the emission at 706nm and the electron generation rate are different, i.e. avalanches in the sheaths are responsible for the excitation of helium atoms but ionization is governed by bulk electrons interacting with the oscillating sheaths in the $\alpha$ mode.\(^{109}\) On the other hand, avalanches inside the sheath is responsible for the excitation of He atom and ionization inside the sheath in the $\gamma$ mode. In small gaps (Figure 8.7c,f), however, the emission at 706nm and the electron generation rate present a very similar pattern indicating that avalanches in the sheaths are responsible for the ionization of the gas, which is same as the constricted $\gamma$ mode of 2mm(Figure 8.7b,e), i.e. small gaps operate in the $\gamma$-mode. Therefore we conclude that rf microdischarges operate in the $\gamma$-mode as theoretically predicted.
in Ref. 109 and 113 and furthermore, that rf microdischarges present a diffused $\gamma$
mode and only at high power they transit into a radically constricted discharge.
The reason for the radial constriction could be thermal (section 8.1) but it remains unclear.

Figure 8.7 Simulated spatio-temporal evolution of the (a,b,c) electron generation rate and
(d,e,f) 706nm He optical emission in (a,b) 2mm and (c) 500 nm rf He+0.04%N2 discharges.

### 8.3 Frequency and gap size

In the previous section we saw that in microdischarges the sheaths extend
over a larger fraction of the discharge gap. Similar effect is observed by varying
the rf excitation frequency while keeping the gap size constant. This is shown in
Figure 8.8. Decreasing the rf excitation frequency has a similar effect to the
reduction in the gap size, i.e. the sheaths extends over a larger portion of the
discharge gap. Nonetheless, the discharges obtained by changing the excitation
frequency and by reducing the gap size are not necessarily the same.
The qualitative behaviour described for discharges driven at 6.78 MHz in section 8.2 is also applicable to discharges driven at higher frequencies. The transition into a diffused $\gamma$ mode, however, will require a smaller gap size.

Figure 8.8 Spatio-temporal evolution of the optical emission of (a,d,g,j) 6.78 MHz, (b,e,h,k) 13.56 MHz, (c,f,i,l) 27.12 MHz discharges drive at 9 W: (a-c) wavelength-integrated, (d-f) N2 + 391 nm, (g-i) He 706 nm and (j-l) O 777 nm. White lines indicate the estimated sheath region based on the emission pattern of 706 nm and are shown to guide the eye. Images (a-l) are not normalized to highlight their pattern rather than their relative intensity. The 3 pictures on the top are taken with 1 ms exposure time and normalised to the maximum emission intensity at 6.78 MHz.
Figure 8.9 shows the breakdown voltage and the operation window in the diffused discharge mode as a function of the gap size for discharges driven at 6.78 and 13.56MHz. As discussed in section 6.1 the breakdown voltage decreases with frequency and the diffused operation window increases. For a given frequency this operation window remains relatively constant for large gaps but it rapidly increases when the gap is reduced below ~500μm for our experimental conditions. This increase is attributed to the appearance of a stable diffused γ mode that is not observed in large gaps.

Figure 8.9 Breakdown voltage and current range of 6.78MHz and 13.56MHz at different electrode gaps.

8.4 Summary

Microplasmas have been considered for a wide range of applications including bio-medical applications, displays, radiation sources, micro-chemical analysis systems, portable gas analyzers, photodetectors, microlasers, dynamic millimetre and microwave devices and microreactors. As shown in this chapter,
microplasmas involved not only a reduction in size but also a change in the physics at play.

Experimental and computational results suggest that emission at 706 nm from helium rf discharges with admixtures of air indicates the presence of high energy electrons and can be used to estimate the sheath width. Furthermore, experimental data support the theoretical predictions of energetic electron avalanches transiting across the discharge gap and the absence of an \( \alpha \)-mode in small microdischarges. Instead of an \( \alpha \) mode, experimental and simulation data suggest operation in a diffuse glow-like \( \gamma \) mode at low input power levels. Finally, the transition from a standard APGD to a micro-APGD is frequency dependent.
Chapter 9  Conclusions

Radio frequency atmospheric pressure glow discharges (rf-APGD) offer an interesting alternative to conventional low-pressure discharges and are being explored for a wide range of applications. While geometrically similar to conventional low-pressure discharges used in the semiconductor industry for decades, atmospheric pressure plasma present new physics that require investigation.

In this thesis, we present an experimental and computational study of helium rf-APGDs and make a contribution to the current understanding of these discharges. In particular, 10 international journal publications capture different aspects of this thesis and highlight the timely interest in and novelty of our findings. Basic characteristics of and deep insights into the governing mechanisms of rf-APGD including electron trapping, electron heating, influence of the rf excitation frequency, chemistry due to impurities, and shrinkage of APGDs down to microplasmas, have been obtained.

With the knowledge we have gained from this thesis, our rf-APGD can be readily used for a wide-range of applications including microbial inactivation, decontamination and portable gas analyzers.
Appendix

A: Plasma power and current-voltage phase analysis

Due to the different length of current and voltage probe wire, and non-synchronized oscilloscope channels, the calculated discharge power and current-voltage phase difference based on these measurements are inaccurate. A Matlab program is developed to solve this problem. By measuring the current and voltage through the standard resistor, we can estimate the time delay between voltage and current signals at different frequencies. This time delay can be checked through analysing the discharge condition in the pre-breakdown period. This is due to the capacitor being like a gas gap with a 90° current-voltage phase difference and zero dissipated power in the pre-breakdown period. Finally, the plasma power and current-voltage phase difference can be obtained by means of this accurately estimated time delay. The flow chart and the program code are shown as below.
Figure 10.1 Flow chart of the power and current-voltage phase analysis program.

Matlab Code:

```matlab
% Appendix

close all;
clear all;
data=load('C:\All.csv');
t=data(:,1);
t=t*1e9; % change timescale to ns
c=data(:,3);
v=data(:,2)*1000;
RMS_C=std(c*1000)
RMS_V=std(v)
i=2;
while ((t(i)-t(1))<=1 % voltage probe is 6.0ns later
    i=i+1;
end
Pow=trapz(t1,p1)/(t1(n-i)-t(1))
R0=max(v1)/max(c1)

% PHASE computation

% Sampling frequency
Ts=1/(2)-1(1);
Fs = 1/Ts;
% Time vector of 1 second
% t = 0:10000/Fs:1;
% load data
x=c1;
NFFT=2^nextpow2(length(x)));

% TAKE FFT, padding with zeroes so the length of fft(x) equals to NFFT
FFTX=fft(x,NFFT);
```
% Calculate the number of unique points
NumUniquePts = ceil((NFFT + 1)/2);
% FFT is symmetric and throw away the second half
FFTX = FFTX(1:NumUniquePts);
% Take the magnitude of fft of x.
MX = abs(FFTX).^2;
% Scale the fft so that it is not a function of the
% length of x.
MX = MX/length(x);
p = unwrap(angle(FFTX));
% Multiply by 2 to because you
% threw out the second half of FFTX above
MX = MX*2;
% DC Component should be unique.
MX(1) = MX(1)/2;
% Nyquist component should also be unique.
if rem(NFFT,2)
    % Here NFFT is even; therefore, Nyquist point is included.
    MX(end) = MX(end)/2;
end
% This is an evenly spaced frequency vector with
% NumUniquePts points.
f = (0:NumUniquePts-1)*Fs/NumUniquePts;
p = rad2deg(p);
plot(f,MX),ylabel('Power Magnitude');
plot(f,p),ylabel('Phase'),xlabel('Frequency (Hz)');
[mag,index] = max(MX);
% power = mag;
% pos = index;
fA = 0.5*(index-1)*Fs/NumUniquePts;
pA = p(index);

%----------------- Second Channel ------------------------------
%----------------- Second Channel ------------------------------
%----------------- Second Channel ------------------------------
% Load data
x1 = v1;
NFFT1 = 2^(nextpow2(length(x1)));%
% TAKE FFT, padding with zeroes so the length of fft(x) equals to NFFT
FFTX1 = fft(x1,NFFT1);
% Calculate the number of unique points
NumUniquePts1 = ceil((NFFT1 + 1)/2);
% FFT is symmetric and throw away the second half
FFTX1 = FFTX1(1:NumUniquePts1);
% Take the magnitude of fft of x.
MX1 = abs(FFTX1).^2;
% Scale the fft so that it is not a function of the
% length of x.
MX1 = MX1/length(x1);
p1 = unwrap(angle(FFTX1));
% Multiply by 2 to because you
% threw out the second half of FFTX above
MX1 = MX1*2;
% DC Component should be unique.
MX1(1) = MX1(1)/2;
% Nyquist component should also be unique.
if rem(NFFT1,2)
    % Here NFFT is even; therefore, Nyquist point is included.
    MX1(end) = MX1(end)/2;
end
% This is an evenly spaced frequency vector with
% NumUniquePts points.
f1 = (0:NumUniquePts1-1)*Fs/NumUniquePts1;
p1 = rad2deg(p1);
**B: Plasma images analysis**

Instead of a group of plasma images, a space and time resolved plasma image obtained by this matlab program is used to indicate the rf discharge evolution. The plasma images saved in " .dat" format are loaded into matlab in sequence. After cutting the area without plasma, the plasma area is integrated in a radial direction. These results are recollated to construct the discharge evolution.

**Figure 10.2 Flow chart for the plasma evolution image**

Matlab code:

```matlab
no_files=0;
input_path=fileparts(filename);
if isempty(input_path)
    input_path='.';
end
z(1:t0,:)=0;
```
```matlab
% t(1:t0)=1:t0;
aux=[t' x];
aux=sortrows(aux,1);
t=aux(:,1)';
t=t/74.6;
z=aux(:,2:end);
mean_z=mean(z)

[y,x]=size(z);
h=surf(1:x)*2,t-1,z);
view(0,90);
set(h, 'facecolor', 'interp');
set(h, 'linestyle', 'none');
title('Position (mm)', 'fontsize',26);
ylabel('Time (ns)', 'fontsize',20);
xlabel('Cycles', 'fontsize',26);
set(gca, 'fontsize', 20);

x_position=(1:x-1)*2/(x-1)

for i=1:x
   z1(:,i)=z(1,x+1-i);
end

figure;
h=surf((1:x-1)/(x-1)*2,t,z1);
view(0,90);
set(h, 'facecolor', 'interp');
set(h, 'linestyle', 'none');
title('Time (ns)', 'fontsize',20);
xlabel('Position (mm) ', 'fontsize',20);
ylabel('Cycles', 'fontsize',20);

C: 1 dimensional fluid code

The code for one dimensional fluid APGD simulation is divided into several files. Figure 3 shows the main files and their dependence. The program get executed by running F1_he.f90. After loading the input parameters in the "*.inp" file and source type in the "pource.f90" file, the electric field, the density of each species, and the electron energy are calculated in "electricfield.f90", "particlebalance.f90" and "energy.f90" files respectively. Finally, the simulation results are saved by the "output.f90" file, when the simulation reaches steady state.
Appendix

Figure 10.3 Main files and their dependency

A flow chart of the algorithm is shown in Figure 4. The current, voltage and power can call be the input controlling conditions. The program starts acquiring input parameters, estimates the electric field value, calculates density of each species, current and electron energy, and finally output the simulation results when the program reach the steady state. The difference ratio of the sum of each species maximum density between 2 cycles must be less than $10^{-5}$ is the steady state criteria. It usually takes at least 8 hours for the program reach steady state.
Appendix

Figure 10.4 Flow chart of the fluid code

FORTRAN CODE

**************************************************************
**************  f1_he.f90  ****************************************
**************************************************************

Program f1_he
use global
Implicit none
Integer::Narg,dp,dmp_flag,RF_cycle_max
Integer:: t0(t),tl(t)
Character(len=512)::cmd
Real:: Del_period,dx_2,double_dx
Logical::Flag_steadystate
Real::Max_ne,Max_nHep,Max_nHe2p,Max_nHem,Max_nHe2m
Real::Max_Max_ne,Max_Max_nHep,Max_Max_nHe2p,Max_Max_nHem,Max_Max_nHe2m
Integer:: step_h, step_t, RF_cycle, RF_cycle_Start,Esign_LHS,Esign_RHS,S_i=1
Character (len=512):: filename

Narg=command_argument_count()
call get_command(cmd) !Get command line
call command_parser(Narg,cmd,dmp_flag,dp,RF_cycle_max) !Parse command line

call version ! Display version
call start(RF_cycle_max) !Read input file, allocate memory, initialize variables
call date_and_time(values=t0) ! Initiate timer
call grid_array(double_dx) ! Create grid arrays

! Initialize electric field assuming that Efield is zero at the center
Efield(hh,1)=0


Efield(1:hh-l,1) = Efield(2:hh,1) - dx_array(1:hh-l) * q_eps * (n_Hep(1:hh-l,1)+n_He2p(1:hh-l,1)+n_Np(1:hh-l,1)+n_N2p(1:hh-l,1)-n_e(1:hh-l,1))
Efield(hh+1:Size_h,1) = Efield(hh:Size_h-1,1) + dx_array(hh:Size_h-l) * q_eps * (n_Hep(hh+1:Size_h,1)+n_He2p(hh+1:Size_h,1)+n_Np(hh+1:Size_h,1)+n_N2p(hh+1:Size_h,1)-n_e(hh+1:Size_h,1))

if (Efield(2,1)<0) then; Esign_LHS=1; else; Esign_LHS=0
end if

! Restore dump file if given
if (dmp_flag==1) then
    call restore(RF_cycle_start)
else
    RF_cycle_start=1
end if

write("","Simulation started...")
write("","")

Del_period = 2*Tol
! Simulate a maximum of RF_cycle_max RF cycles
do RF_cycle=1,RF_cycle_max

! Reset the maxima during 1 RF cycle
Max_ne=0; Max_Max_nHep=0; Max_Max_nHe2p=0; Max_Max_nHem=0; Max_Max_nHe2m=0;
if (RF_cycle>1) then
    Flux_p_l(1)=Flux_p_l(Size_t+1)
    Flux_p_sh(1)=Flux_p_sh(Size_t+1)
    FluxB_e_l(1)=FluxB_e_l(Size_t+1)
    FluxB_e_sh(1)=FluxB_e_sh(Size_t+1)
    Voltage(1)=Voltage(Size_t+1)
end if

! Check is steady state has been reached
Flag_steadystate=.FALSE.
if (((Del_period<Tol).AND.(RF_cycle>1000)).OR.(RF_cycle == RF_cycle_max)) then
    Flag_steadystate=.TRUE.
endif

! Simulate one RF
do step_t=1,Size_t

! Value of the power supply
    call power_source(RF_cycle,RF_cycle_start,step_t,voltage,current,power)
    call estimate_Efield(step_t,double_dx,Esign_LHS,Esign_RHS)
    call reaction_rates()
    if (grid_type==0) then
        call part_bal_uniform(step_t)
    else
        call part_bal(step_t)
    end if

Max_ne=maxval(n_e(:,2)); ! Maximum at this time step
Max_Max_ne=max(Max_ne,Max_Max_ne); !Maximum in this RF cycle
Max_nHep=maxval(n_Hep(:,2)); ! Maximum at this time step
Max_Max_nHep=max(Max_nHep,Max_Max_nHep); !Maximum in this RF cycle
Max_He2p=maxval(n_He2p(:,2)); ! Maximum at this time step
Max_Max_He2p=max(Max_He2p,Max_Max_He2p); !Maximum in this RF cycle
Max_nHem=maxval(n_Hem(:,2)); ! Maximum at this time step
Max_Max_nHem=max(Max_nHem,Max_Max_nHem); !Maximum in this RF cycle
Max_He2m=maxval(n_He2m(:,2)); ! Maximum at this time step
Max_Max_He2m=max(Max_He2m,Max_Max_He2m); !Maximum in this RF cycle

! Write the results
write("","step_t","part_balance")

! Calculate the electric field
do step_h=hh-1,1,-1
    Efield(step_h,2)=Efield(step_h+1,2) - x(step_h) * q_eps * (n_Hep(step_h,2)+n_He2p(step_h,2)+n_Np(step_h,2)+n_N2p(step_h,2)-n_e(step_h,2))
end do

do step_h=hh+1,Size_h
Appendix

\[
\begin{align*}
E_{\text{field}}(\text{step } h, 2) &= E_{\text{field}}(\text{step } h-1, 2) + (x(\text{step } h) - x(\text{step } h-1))^* q_{\text{eps}}*(n_{\text{He}}(\text{step } h, 2) + n_{\text{He}^2p}(\text{step } h, 2) + n_{\text{Np}}(\text{step } h, 2) + n_{\text{N}^2p}(\text{step } h, 2) - n_{\text{e}}(\text{step } h, 2)) \\
\end{align*}
\]

end do

! Current calculation
if (grid_type == 0)
    call currents_and_fluxes_uniform(step_t, Esign_LHS, Esign_RHS)
else
    call currents_and_fluxes(step_t, Esign_LHS, Esign_RHS)
end if

V_{\text{oltage}}(\text{step } t) = 0
if (grid_type == 0) then
    dx_2 = (x(2) - x(1)) / 2
    do step_h = 2, Size_h
        V_{\text{oltage}}(\text{step } t) = V_{\text{oltage}}(\text{step } t) + (E_{\text{field}}(\text{step } h, 1) + E_{\text{field}}(\text{step } h-1, 1)) * dx_2
    end do
else
do step_h = 2, Size_h
    V_{\text{oltage}}(\text{step } t) = V_{\text{oltage}}(\text{step } t) + (E_{\text{field}}(\text{step } h, 1) + E_{\text{field}}(\text{step } h-1, 1)) / 2 * (x(\text{step } h) - x(\text{step } h-1))
end do
end if

P_{\text{ower}}(\text{step } t) = I_{\text{current}}(\text{step } t) * V_{\text{oltage}}(\text{step } t)

! Energy equation
if (grid_type == 0)
    call energy_eq_uniform()
else
    call energy_eq(x, energy, field, energy, n_{\text{He}}, n_{\text{e}}, n_{\text{He}^2p}, n_{\text{He}^2m}, K_L_{\text{elastic}})
end if

if (Flag_{steady state}) then
    if ((S_{i} < Npoints.AND. step_{t} = 1 + (S_{i} - 1) * Size_{t}/Npoints).OR. (S_{i} == Npoints.AND. step_{t} == Size_{t})) then
        energy_S(:, S_{i}) = energy(:, 2)
        n_{e} S(:, S_{i}) = n_{e}(:, 2)
        E_{\text{field}} S(:, S_{i}) = E_{\text{field}}(:, 2)
        n_{\text{He}^2p} S(:, S_{i}) = n_{\text{He}^2p}(:, 2)
        n_{\text{He}^2m} S(:, S_{i}) = n_{\text{He}^2m}(:, 2)
        n_{\text{He}} S(:, S_{i}) = n_{\text{He}}(:, 2)
        n_{\text{He}^2m} S(:, S_{i}) = n_{\text{He}^2m}(:, 2)
        n_{\text{He}^2p} S(:, S_{i}) = n_{\text{He}^2p}(:, 2)
        n_{\text{He}^2m} S(:, S_{i}) = n_{\text{He}^2m}(:, 2)
        n_{\text{Np}} S(:, S_{i}) = n_{\text{Np}}(:, 2)
        n_{\text{N}_2p} S(:, S_{i}) = n_{\text{N}_2p}(:, 2)
        n_{\text{N}_2p} S(:, S_{i}) = n_{\text{N}_2p}(:, 2)
        n_{\text{N}} S(:, S_{i}) = n_{\text{N}}(:, 2)
    end if
end if
endif

enddo!
for step_t, 1 RF cycle completed

! History of maxima in each RF cycle
hist_max_ne(RF_cycle)=Max_max_ne
hist_max_nHep(RF_cycle)=Max_max_nHep
hist_max_nHe2p(RF_cycle)=Max_max_nHe2p
hist_max_nHem(RF_cycle)=Max_max_nHem
hist_max_nHe2m(RF_cycle)=Max_max_nHe2m

! Change between consecutive RF cycles
if (RF_cycle>1) then
  !Filter Del_period to prevent accidental termination of the program
  Del_period=Del_period+(abs(hist_max_ne(RF_cycle)-hist_max_ne(RF_cycle-1)))/hist_max_ne(RF_cycle)+abs((hist_max_nHep(RF_cycle)-hist_max_nHep(RF_cycle-1)))/hist_max_nHep(RF_cycle)+abs((hist_max_nHe2p(RF_cycle)-hist_max_nHe2p(RF_cycle-1)))/hist_max_nHe2p(RF_cycle)+abs((hist_max_nHem(RF_cycle)-hist_max_nHem(RF_cycle-1)))/hist_max_nHem(RF_cycle)+abs((hist_max_nHe2m(RF_cycle)-hist_max_nHe2m(RF_cycle-1)))/hist_max_nHe2m(RF_cycle)-Del_period)/5
endif

! Display progress and save time traces
! Diagnostic to monitor the progress of the simulation
call save_traces(t0,RF_cycle,RF_cycle_start,RF_cycle_max,Del_period)
if(S_i>Npoints) exit

!Dump file?
if (mod(RF_cycle,dp).EQ.0) then
call dump(RF_cycle) ! Dump file
endif
enddo! for RF_cycle_max, Simulation finished!
call dump(RF_cycle) ! Dump file
call savedata(t0) ! Output diagnostics - Save files

END PROGRAM f1_he

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subroutine saveld_float(filename, nn, var, n)
implicit none
Integer::i, n, nn
Character(len=nn)::filename
Real, dimension(n)::var
open (1, FILE = filename)
do i=1,n
write(*,*) i, var(i)
end do
close (1);
end subroutine saveld_float(filename, nn, var, n)

subroutine saveld_double(filename, nn, var, n)
implicit none
Integer::i, n, nn
Character(len=nn)::filename
Real(8), dimension(n)::var
open (1, FILE = filename)
do i=1,n
write(*,*) i, var(i)
end do
close (1);
end subroutine saveld_double(filename, nn, var, n)

subroutine save2d_double(filename, nn, var, n, m)
implicit none
Integer::i, j, n, m, nn
Character(len=nn)::filename
Real(8), dimension(n, m)::var
open (1, FILE = filename)
do i=1, n
do j=1, m
write(*, '(1E15.5)', advance='no') var(i, j)
end do
write(*, '()')
end do
close (1);
end subroutine save2d_double(filename, nn, var, n, m)

function rms(v, n) result (rms_v)
implicit none
Integer::i, n
Real, dimension(n)::v
Real::rms_v
rms_v=0
do i=1, n
rms_v=rms_v+(v(i)**2)
enddo
rms_v=SQRT(rms_v/n)
end function rms(v, n) result (rms_v)

subroutine bound(v, ZERO, n, nonfinite)
implicit none
Integer:: nonfinite
Integer::i, n
Real(8), dimension(n, 2)::v
Real(8)::ZERO
do i=1, n
if (v(i, 2)<0.0) then
  v(i, 2)=v(i, 1)
end if
end do
if (v(1, 2)>v(2, 2)) then
  v(1, 2)=v(1, 1)
end if
if (v(n, 2)>v(n, 2)) then
  v(n, 2)=v(n, 1)
end if

subroutine grid_array(double_dx)
use global
Implicit none
Real:: double_dx
Integer:: i
! Grid array
if (grid_type==l) then
! Non-uniform grid
do i=1,(Size_h-1)/2+1
x(i)=Height/2*(2*(i-1)/(Size_h-1))**2
end do
else
! Uniform grid
do i=1,Size_h
x(i)=(i-1.0)/(Size_h-1)*Height
end do
end if
do i=1,Size_h-1
dx_array(i)=x(i+1)-x(i);
end do
hh=(Size_h+1)/2
double_dx=x(hh+1)-x(hh-1)
end

subroutine run_number()
use global
Implicit none
Integer:: ios, rn
Character(len=512) :: buffer
do rn=1,999
write(buffer,'(A,13.3,A)') trim(ID)///_",rn,"_voltage_rms_t.txt"
open(123, file=buffer,iostat=ios,status="OLD")
if (ios/=0 .OR. rn.EQ.999) then
    exit
else
    close(123)
end if
end do
write(ID,' (A,I3.3) ') trim(ID)//_",rn
end

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%%%%%misc.f90
!*******************************************************************************
! UNIFORM GRID
!*******************************************************************************
subroutine currents_and_fluxes_uniform(step_t,Esign_LHS,Esign_RHS)
use global
implicit none
Integer:: step_t,step_h,Esign_LHS,Esign_RHS
Real:: q_mu, dx

dx=x(2)-x(1)
q_mu=q*mu_e
do step_h=2,Size_h
Diff_Current_e(step_h,2)=q_mu*(energy(step_h-1,1)+energy(step_h,1))/3.0*(n_e(step_h,2)-n_e(step_h-1,2))/dx
Drift_Current_e(step_h,2)=q*mu_e*(n_e(step_h,2))*field(step_h,2)
Current_e(step_h,2)=Diff_Current_e(step_h,2)+Drift_Current_e(step_h,2)
end do

end subroutine currents_and_fluxes_uniform
do step_h=2,Size_h
Current_Hep(step_h,2)=q* (-D_Hep* (n_Hep(step_h,2)-n_Hep(step_h-1,2))/dx+mu_Hep*n_Hep(step_h,2)*Efield(step_h,2))
end do

do step_h=2,Size_h
Current_Np(step_h,2)=q* (-D_Np* (n_Np(step_h,2)-n_Np(step_h-1,2))/dx+mu_Np*n_Np(step_h,2)*Efield(step_h,2))
end do

do step_h=2,Size_h
Current_N2p(step_h,2)=q*(-D_N2p*(n_N2p(step_h,2)-n_N2p(step_h-1,2))/dx+mu_N2p*n_N2p(step_h,2)*Efield(step_h,2))
end do

end do - - - -

Current_N2p(step_h,2)=q*(-D_N2p*(n_N2p(step_h,2)-n_N2p(step_h-1,2))/dx+mu_N2p*n_N2p(step_h,2)*Efield(step_h,2))

Current_n_e(step_h,2)=-q*(-quarter_vth_e*n_e(step_h,2)+Esign_LHS*mu_e*n_e(step_h,2)*Efield(step_h,2))

!”

---

Flux_B_e_sh(step_t+l)=quarter_vth_e*n_e(Size_h,2)+Esign_RHS*mu_e*n_e(Size_h,2)*Efield(Size_h,2)

Current_N2p(Size_h,2)=q*(-D_N2p*(n_N2p(Size_h,2)-n_N2p(Size_h-1,2))/dx+mu_N2p*n_N2p(Size_h,2)*Efield(Size_h,2))

Current_N2p(Size_h,2)=q*(-D_N2p*(n_N2p(Size_h,2)-n_N2p(Size_h-1,2))/dx+mu_N2p*n_N2p(Size_h,2)*Efield(Size_h,2))

Current_n_e(step_h,2)=q*(-quarter_vth_e*n_e(step_h,2)+Esign_LHS*mu_e*n_e(step_h,2)*Efield(step_h,2))

!”

Flux_p_sh(step_t+1)=quarter_vth_he2*n_he2p(Size_h,2)+Esign_RHS*mu_he2p*n_he2p(Size_h,2)*Efield(Size_h,2)
subroutine currents_and_fluxes(step_t,Esign_LHS,Esign_RHS)
  use global
  implicit none
  Integer::step_t,step_h,Esign_LHS,Esign_RHS
  do step_h=2,Size_h
    Current_e(step_h,2)=-q*(-mu_e*(energy(step_h-1,1)+energy(step_h,1))/x(step_h)-x(step_h-1)) &
    *(11594.0/(2.0*17406.0))*(n_e(step_h,2)-n_e(step_h-1,2))/(x(step_h)-x(step_h-1))
    Diff_Current_e(step_h,2)=-q*(-mu_e*(energy(step_h-1,1)+energy(step_h,1)) &
    *(11594.0/(2.0*17406.0))*(n_e(step_h,2)-n_e(step_h-1,2))/(x(step_h)-x(step_h-1))
    Drift_Current_e(step_h,2)=-q*(-mu_e*n_e(step_h,2)*Efield(step_h,2))
  end do
  do step_h=2,Size_h
    Current_N2p(step_h,2)=q*(-mu_Np*(n_N2p(step_h,2)-n_N2p(step_h-1,2)) &
    /(x(step_h)-x(step_h-1))+(mu_Np*n_Np(step_h,2)*Efield(step_h,2))
  end do
  do step_h=2,Size_h
    Current_N2p(1,2)=q*(-mu_Np*(n_N2p(1,2) &
    /x(1,2)+mu_Np*n_Np(1,2)*Efield(2,2))
  end do
  do step_h=2,Size_h
    Current_e(1,2)=-q*(-mu_e*(n_e(1,2)-&
    Efield(2,2))
  end do
  do step_h=2,Size_h
    Flux_Hem_l(step_t+1)=-n_Hem(l,2)*quarter_vth_Hem
    Flux_Hem_sh(step_t+1)=n_Hem(1,2)*quarter_vth_Hem
  end do
  do step_h=2,Size_h
    Flux_Hem_l(step_t+1)=-n_Hem(1,2)*quarter_vth_Hem
    Flux_Hem_sh(step_t+1)=n_Hem(1,2)*quarter_vth_Hem
  end do
  do step_h=2,Size_h
    Flux_Hem_l(step_t+1)=-n_Hem(l,2)*quarter_vth_Hem
    Flux_Hem_sh(step_t+1)=n_Hem(1,2)*quarter_vth_Hem
  end do
end subroutine currents_and_fluxes
Appendix

\[
\begin{align*}
\text{Flux}_p(l+1) &= \text{quarter} \ v_{th} \ \text{He}_2 \ n_{e}(1,2) + \text{Esign} \ \mu_He_2p \ n_{He_2p}(1,2) \times \text{Efield}(2,2) \quad &
\text{quarter} \ v_{th} \ \text{He}_2p \ n_{He_2p}(1,2) + \text{Esign} \ \mu_He_2p \ n_{He_2p}(1,2) \times \text{Efield}(2,2) \\
\text{FluxB}_p(l+1) &= \text{quarter} \ v_{th} \ \text{He}_2 \ n_{He_2p}(1,2) + \text{Esign} \ \mu_He_2p \ n_{He_2p}(1,2) \times \text{Efield}(2,2) \\
\text{Fluxp}_{sh}(l+1) &= \text{quarter} \ v_{th} \ \text{He}_2p \ n_{He_2p}(1,2) + \text{Esign} \ \mu_He_2p \ n_{He_2p}(1,2) \times \text{Efield}(2,2) \\
\text{FluxB}_{p_sh}(l+1) &= \text{quarter} \ v_{th} \ \text{He}_2p \ n_{He_2p}(1,2) + \text{Esign} \ \mu_He_2p \ n_{He_2p}(1,2) \times \text{Efield}(2,2) \\
\text{Current}_{He_2}(l+1,2) &= \text{quarter} \ v_{th} \ \text{He}_2 \ n_{He_2p}(1,2) + \text{Esign} \ \mu_He_2p \ n_{He_2p}(1,2) \times \text{Efield}(2,2) \\
\text{Current}_{He_{2p}}(l+1,2) &= \text{quarter} \ v_{th} \ \text{He}_2p \ n_{He_2p}(1,2) + \text{Esign} \ \mu_He_2p \ n_{He_2p}(1,2) \times \text{Efield}(2,2) \\
\text{Current}_{N_2}(l+1,2) &= \text{quarter} \ v_{th} \ N_2 \ n_{N_2p}(1,2) + \text{Esign} \ \mu_N2p \ n_{N_2p}(1,2) \times \text{Efield}(2,2) \\
\text{Current}_{Np}(l+1,2) &= \text{quarter} \ v_{th} \ Np \ n_{Np}(1,2) + \text{Esign} \ \mu_Np \ n_{Np}(1,2) \times \text{Efield}(2,2) \\
\text{Current}_{e}(l+1,2) &= \text{quarter} \ v_{th} \ e \ n_{e}(1,2) + \text{Esign} \ \mu_e \ n_{e}(1,2) \times \text{Efield}(2,2) \\
\end{align*}
\]
Appendix

```
Diff_e_sh = mu_e*(energy(Size_h-1,1) + energy(Size_h,1)) / 3.0
Ind_e_sh = muridad_2 * Diff_e_sh * (Efield(Size_h-1,2) + Efield(Size_h,2))
call coeff(Ind_e_sh, a1, b1)
A(Size_h) = (b1 * Diff_e_sh + dx) * (quarter_vth_e + Esign_RHS -
1) * mu_e * Efield(Size_h, 2)) * 2 * dx2 + 1.0
B(Size_h) = 0
C(Size_h) = 2 * a1 * Diff_e_sh * dx2
D(Size_h) = energy_e((Size_h, 1) + R(4, Size_h) + R(5, Size_h) + R(7, Size_h)
+ R(10, Size_h) &
R(11, Size_h) - R(12, Size_h) - R(6, Size_h) &
R(34, Size_h) + R(37, Size_h) + R(38, Size_h) &
R(13, Size_h) + R(14, Size_h) + R(15, Size_h) - R(21, Size_h) - R(22, Size_h) - R(23, Size_h) &
R(25, Size_h) + R(26, Size_h) + R(28, Size_h) &
+ Esign_RHS * sec * Flux_p_sh(step_t) * dx2) * Del_t

n_e(1, 2) = TDMA(A, B, C, D, Size_h)
call bound(n_e, 1e-3, Size_h, nonfinite) ! Remove negative values

Density - He ions
mcurity_2 = mu_e * dx2 / 2.0
do step_h = 2, Size_h - 1
Index_Hep(step_h) = mcurity_2 / D_Hep * (Efield(step_h, 2) + Efield(step_h-1, 2))
Index_Hep(step_h+1) = mcurity_2 / D_Hep * (Efield(step_h+1, 2) + Efield(step_h, 2))
call coeff(Index_Hep(step_h), a1, b1)
call coeff(Index_Hep(step_h+1), a2, b2)
A(step_h) = D_Hep * a2 + D_Hep * b2)
B(step_h) = D_Hep * b2 * dt2 -
C(step_h) = D_Hep * a2 * dt2
D(step_h) = n_Hep(step_h, 1) + (R(3, step_h) + R(4, step_h) + R(7, step_h) -
1) * Del_t
end do

Density - He ions - LHS boundary
Ind_Hep_2 = mcurity_2 / D_Hep * (Efield(1, 2) + Efield(2, 2))
call coeff(Ind_Hep_2, a1, b1)
A(1) = (a1 * D_Hep + dx) * (quarter_vth_e - Esign_LHS * mu_e * Efield(2, 2)) * dt2 + 1.0
B(1) = 2 * b1 * D_Hep * dt2
C(1) = 0
D(1) = n_Hep(1, 1) + (R(3, 1) + R(4, 1) + R(7, 1) - R(9, 1)) &
1
& R(37, 1) + R(38, 1) &
& R(16, 1) - R(17, 1)) * Del_t

Density - He ions - RHS boundary
Ind_Hep_sh = mcurity_2 / D_Hep * (Efield(Size_h-1, 2) + Efield(Size_h, 2))
call coeff(Ind_Hep_sh, a1, b1)
A(Size_h) = (b1 * D_Hep + dx) * (quarter_vth_e + Esign_RHS * mu_e * Efield(Size_h, 2)) * dt2 + 1.0
B(Size_h) = 0
C(Size_h) = 2 * a1 * D_Hep * dt2
D(Size_h) = n_Hep(Size_h, 1) + (R(3, Size_h) + R(4, Size_h) + R(7, Size_h) -
1) * Del_t
& R(37, Size_h) + R(38, Size_h) &
& R(16, Size_h) - R(17, Size_h)) * Del_t
n_Hep(:, 2) = TDMA(A, B, C, D, Size_h)
call bound(n_Hep, 1e-3, Size_h, nonfinite) ! Remove negative values

Density - He dimer ions
mcurity_2 = mu_e2p * dx2 / 2.0
do step_h = 2, Size_h - 1
```

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Index_{He2p}(step_h)=mudx_2*D_{He2p}^*(Efield(step_h,2)+Efield(step_h\_1,2))
Index_{He2p}(step_h+l)=mudx_2*D_{He2p}^*(Efield(step_h+l,2)+Efield(step_h,2))
call coeff(Index_{He2p}(step_h),a1,b1)
call coeff(Index_{He2p}(step_h+l),a2,b2)
A(step_h)=(D_{He2p}^*a2+D_{He2p}^*b1)*dt_{dx2}^2+1.0
B(step_h)=D_{He2p}^*b2*dt_{dx2}
C(step_h)=D_{He2p}^*a1*dt_{dx2}
D(step_h)=n_{He2p}(step_h,1)+R(5,step_h)+R(9,step_h)+R(10,step_h)&
-R(11,step_h)-R(12,step_h)-R(6,step_h)
|-----------------------------------|
&+R(34,step_h)
&+********************N
&+R(34,step_h)
&+********************N
&+R(18,step_h)-R(19,step_h)*Del_t
end do

Density - He dimer ions - LHS boundary
Ind_{He2p}_2=mudx_2*D_{He2p}^*(Efield(1,2)+Efield(2,2))
call coeff(Ind_{He2p}_2,al,b1)
A(1)=(a1^*D_{He2p}^*dx^*(quarter_vth_{He2}-Esign_{LHS}*mu_{He2p}*Efield(2,2)))*dt_{dx2}^2+1.0
B(1)=2*b1^*D_{He2p}^*dt_{dx2}
C(1)=0
D(1)=n_{He2p}(1,1)+R(5,1)+R(9,1)+R(10,1)-R(11,1)-R(12,1)-R(6,1)
|-----------------------------------|
&+R(34,1)
&+********************N
&+R(18,1)-R(19,1))*Del_t

Density - He dimer ions - RHS boundary
Ind_{He2p}_sh=mudx_2*D_{He2p}^*(Efield(Size_h-1,2)+Efield(Size_h,2))
call coeff(Ind_{He2p}_sh,al,b1)
A(Size_h)=(b1^*D_{He2p}^*dx^*(quarter_vth_{He2}+Esign_{RHS}*mu_{He2p}*Efield(Size_h,2)))*dt_d^2+1.0
B(Size_h)=2*b1^*D_{He2p}^*dt_dx2
C(Size_h)=0
D(Size_h)=n_{He2p}(Size_h,1)+R(5,Size_h)+R(9,Size_h)+R(10,Size_h)
-R(11,Size_h)-R(12,Size_h)-R(6,Size_h)
|-----------------------------------|
&+R(34,Size_h)
&+********************N
&+R(18,Size_h)-R(19,Size_h)*Del_t
n_{He2p}(1:,2)=TDMA(A,B,C,D,Size_h)
call bound(n_{He2p},1e-3,Size_h,nonfinite) !Remove negative values

Density - He metastable do step_h=2,Size_h-1
A(step_h)=D_{He33}^*dt_{dx2}^2+1.0
B(step_h)=D_{He33}^*dt_{dx2}
C(step_h)=D_{He33}^*dt_dx2
D(step_h)=n_{He33}(step_h,1)+R(6,step_h)+R(8,step_h)
-R(2,step_h)-R(4,step_h)-2*R(7,step_h)-R(8,step_h)
|-----------------------------------|
&+D1_{He_338}
&+********************N
&+R(13,step_h)-R(14,step_h)-R(39,step_h)-R(41,step_h)+R(33,step_h))*Del_t
! D1 He_338
D1(step_h)=n_{He_338}(step_h,1)+R(29,step_h)-R(34,step_h)-R(35,step_h)-
2*R(37,step_h)-R(39,step_h)
&+R(40,step_h)-R(32,step_h)*Del_t
! D2 He_338
D2(step_h)=n_{He_338}(step_h,1)+R(30,step_h)-R(32,step_h)-R(31,step_h)-
R(36,step_h)-2*R(38,step_h)-R(40,step_h)
&+R(41,step_h)-R(33,step_h))*Del_t
end do

Density - He metastable - LHS boundary
A(1)=2*D_{He33}^*dx^*(quarter_vth_{He})*dt_{dx2}^2+1.0
B(1)=2*D_{He33}^*dt_{dx2}
C(1)=0
D(1)=n_{He33}(1,1)+R(6,1)+R(8,1)-R(2,1)-R(4,1)-2*R(7,1)-R(8,1)
|-----------------------------------|
&+D1_{He_338}
D1(1)=n_{He_338}(1,1)+R(29,1)-R(34,1)-R(35,1)-2*R(37,1)+R(39,1)

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&R(40,1)-R(32,1)*Del_t
D2(1)=&n_He_23p(1,1)+R(30,1)+R(32,1)-R(31,1)-R(36,1)-2*R(38,1)-R(40,1)
&+R(41,1)-R(33,1)*Del_t

! Density - He metastable - RHS Boundary
A(Size_h)=2*(D_He^2m+dx*quarter_vth_He)*dt_dx2+1.0
B(Size_h)=0
C(Size_h)=2*D_He^2m*dt_dx2
D(Size_h)=n_He^2m(Size_h,1)+(R(1,Size_h)+R(6,Size_h)
-R(2,Size_h)-R(4,Size_h)-2*R(7,Size_h)-R(8,Size_h)
&+R(13,Size_h)-R(14,Size_h)-R(39,Size_h)-R(41,Size_h)+R(33,Size_h))*Del_t
D1(Size_h)=n_He_33s(Size_h,1)+(R(29,Size_h)-R(34,Size_h)-R(35,Size_h)
-2*R(37,Size_h)+R(39,Size_h)
&+R(40,Size_h)-R(32,Size_h))*Del_t
D2(Size_h)=n_He_23p(Size_h,1)+(R(30,Size_h)+R(32,Size_h)-R(31,Size_h)
-R(36,Size_h)-2*R(38,Size_h)-R(40,Size_h)
&+R(41,Size_h)-R(33,Size_h))*Del_t
n_He_m(:,2)=TDMA(A,B,C,D,Size_h)
n_He_33s(:,2)=TDMA(A,B,C,D1,Size_h)
n_He_23p(:,2)=TDMA(A,B,C,D2,Size_h)
call bound(n_He_m,le-3,Size_h,nonfinite) !Remove negative values
call bound(n_He_33s,le-3,Size_h,nonfinite) !Remove negative values
call bound(n_He_23p,le-3,Size_h,nonfinite) !Remove negative values

! Density - He dimer metastable
do step_h=2,Size_h-1
A(step_h)=D_He^2m*2*dt_dx2+1.0
B(step_h)=D_He^2m*dt_dx2
C(step_h)=D_He^2m*dt_dx2
D(step_h)=n_He^2m(step_h,1)+(R(8,step_h)-2*R(10,step_h)-R(5,step_h)
&+R(37,step_h)-R(15,step_h))*Del_t
end do

! Density - N dimer ions
mudx=mu N2p*dx/2.0
do step_h=2,Size_h-1
Index_N2p(step_h)=mudx_Z/D_N2p*(Efield(step_h(2)+Efield(step_h-1,Z»
Index=N2p(step_h+1)=mudx_Z/D_N2p*(Efield(step_h+1,2)+Efield(step_h,Z»
call coeff(Index_N2p(step_h),a1,b1)
call coeff(Index_N2p(step_h+1),a2,b2)

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A(step_h) = (D_N2p*a2 + D_N2p*b1)*dt_dx2 + 1.0
B(step_h) = D_N2p*b2*dt_dx2
C(step_h) = D_N2p*a1*dt_dx2

D(step_h) = n_N2pb(step_h, 1) + R(13, step_h) * BranchRatio_6 + R(14, step_h) * BranchRatio_7 +
R(15, step_h) * BranchRatio_8 +
R(18, step_h) * BranchRatio_4 + R(19, step_h) * BranchRatio_5 + R(20, step_h) -
R(21, step_h) * R(28, step_h) + R(27, step_h) * Del_t

D(1) = n_N2pb(1, 1) + R(13, 1) * BranchRatio_6 + R(14, 1) * BranchRatio_7 + R(15, 1) * BranchRatio_8 +
R(18, 1) * BranchRatio_4 + R(19, 1) * BranchRatio_5 + R(20, 1) -
R(21, 1) * R(28, 1) + R(27, 1) * Del_t

D(1) = n_N2px(1, 1) + R(13, 1) * BranchRatio_6 + R(14, 1) * BranchRatio_7 + R(15, 1) * BranchRatio_8 +
R(18, 1) * BranchRatio_4 + R(19, 1) * BranchRatio_5 + R(20, 1) -
R(21, 1) * R(28, 1) + R(27, 1) * Del_t

end do

! Density - N dimers ions - LHS boundary
Ind_N2p_LHS = mudx_2/D_N2p*Efield(1,2)*Efield(2,2)
call coeff(Ind_N2p_LHS, a1, b1)
A(1) = (a1*D_N2p + dx*(quarter_vth_N2 - Ensign_LHS*mu_N2p*Efield(2,2))) * dt_dx2 + 1.0
B(1) = b1*D_N2p*dt_dx2
C(1) = 0

D(1) = n_N2pb(1, 1) + R(13, 1) * BranchRatio_6 + R(14, 1) * BranchRatio_7 + R(15, 1) * BranchRatio_8 +
R(18, 1) * BranchRatio_4 + R(19, 1) * BranchRatio_5 + R(20, 1) -
R(21, 1) * R(28, 1) + R(27, 1) * Del_t

! Density - N dimers ions - RHS boundary
Ind_N2p_RHS = mudx_2/D_N2p*Efield(1,2)*Efield(2,2)
call coeff(Ind_N2p_RHS, a1, b1)
A(1) = (a1*D_N2p + dx*(quarter_vth_N2 - Ensign_RHS*mu_N2p*Efield(2,2))) * dt_dx2 + 1.0
B(1) = b1*D_N2p*dt_dx2
C(1) = 0

D(1) = n_N2pb(1, 1) + R(13, 1) * BranchRatio_6 + R(14, 1) * BranchRatio_7 + R(15, 1) * BranchRatio_8 +
R(18, 1) * BranchRatio_4 + R(19, 1) * BranchRatio_5 + R(20, 1) -
R(21, 1) * R(28, 1) + R(27, 1) * Del_t

n_N2pb(:,2) = TDMA(A, B, C, D, Size_h)
n_N2px(:,2) = TDMA(A, B, C, D, Size_h)
call bound(n_N2pb, -3, Size_h, nonfinite) !Remove negative values
call bound(n_N2px, -3, Size_h, nonfinite) !Remove negative values
n_N2p(:,2) = n_N2pb(:,2) + n_N2px(:,2)

! Density - N metastable - LHS Boundary
A(1) = 2*D_N2p + dx*(quarter_vth_N2)*dt_dx2 + 1.0
B(1) = 2*D_N2p*dt_dx2
C(1) = 0

D(1) = n_N1(1, 1) + R(16, 1) * BranchRatio_2 + R(17, 1) * BranchRatio_3 +
R(21, 1) + R(22, 1) + R(23, 1) + R(24, 1) * Del_t

end do

! Density - N metastable - RHS Boundary
A(1) = 2*D_N2p + dx*(quarter_vth_N2)*dt_dx2 + 1.0
B(1) = 2*D_N2p*dt_dx2
C(1) = 0

D(1) = n_N1(1, 1) + R(16, 1) * BranchRatio_2 + R(17, 1) * BranchRatio_3 +
R(21, 1) + R(22, 1) + R(23, 1) + R(24, 1) * Del_t

end do
Appendix

D(Size_h)=n N(Size h)\times BranchRatio_{2}+R(17,Size_h)\times BranchRatio_{3} & 
\vdots +2\times R(21,Size_h)\times R(22,Size_h)\times R(23,Size_h)\times R(24,Size_h)\times R(25,Size_h)\times Del_t

call bound(n_N,le-3,Size_h,nonfinite) !Remove negative values

!! Density - N2
!!
!! do step_h=2,Size_h-1
!! N(step_h)=D_N2*dt_dx2+1.0
!! B(step_h)=D_N2*dt_dx2
!! C(step_h)=D_N2*dt_dx2
!! D(step_h)=n N2(step_h,1)+(-R(13,step_h)-(14,step_h)-(15,step_h)-(16,step_h)-
!! (17,step_h)-(18,step_h)-(19,step_h)-(20,step_h)+
!! (21,step_h)-(22,step_h)-R(23,step_h))\times Del_t
!!
!! Density - N2 - LHS Boundary
!! A(1)=2*(D_N2*dx*quarter_vth_N2)*dt_dx2+1.0
!! B(1)=2*D_N2*dt_dx2
!! C(1)=0
!! D(1)=0
!!
!! Density - N2 metastable - RHS Boundary
!! A(1)=2*(D_N2*dx*quarter_vth_N2)*dt_dx2+1.0
!! B(1)=0
!! C(1)=0
!! D(1)=0
!!
!! Density - electrons - LHS boundary
!! Del_k=x(2)-x(1)
!!
!!********************************************

else
!write(*,*), "No N2"
 !n_Np(:,2)=0
 !n_N2p(:,2)=0
 !n_N2p(:,2)=0
 !n_Np(:,2)=0
 !n_N(:,2)=0
endif

end subroutine part_bal(step_t)

use global
use m_tdma
implicit none

Integer::nonfinite=0
Real(B):: a1,b1,a2,b2
Real(B):: D_e_1,D_e_2
Real(B):: Diff_e_2,Ind_e_2,Del_e_1,Del_a_1,Diff_e_1,Ind_e_1,Ind_Hep_2,Ind_Hep_1,Ind_Hep_2p,Ind_Hep_1p,Ind_Np_2,Ind_Np_1,Ind_Np_2p,Ind_Np_1p
Integer:: step_h, step_t, Esign_LHS, Esign_RHS
Real:: Del_k, Del_k_1, Del_avg_k

if(Efield(2,2)<0) then
  Esign_LHS=1
else
  Esign_LHS=0
end if
if(Efield(Size_h,2)>0 then
  Esign_RHS=1
else
  Esign_RHS=0
end if

!! Density - electrons - LHS boundary
Del_k=x(2)-x(1)
\[\begin{align*}
\text{Del}_a &= \text{Del}_a / 2 \\
\text{Diff}_e &= \mu_e \left(\text{engy}(1,1) + \text{engy}(2,1)\right) / 3.0 \\
\text{Ind}_e &= \mu_e \text{Diff}_e \left(\text{Efield}(1,2) + \text{Efield}(2,2)\right) / 2 \times \text{Del}_t \\
\text{call coeff(Ind}_e, 31, b1) \\
\text{R}(1) &= (a1 \times \text{Diff}_e / \text{Del}_a + \text{quarter_vth_e} \times (\text{Esign}\_\text{LHS} - 1)) / \mu_e \times \text{Efield}(2,2) / \text{Del}_a + 1.0 \\
\text{B}(1) &= b1 \times \text{Diff}_e / \text{Del}_a / \text{Del}_a + 1.0 \\
\text{C}(1) &= 0 \\
\text{D}(1) &= n_e(1,1) + R(3,1) + R(4,1) + R(5,1) + R(7,1) + R(10,1) \\
&- R(11,1) - R(12,1) - R(6,1) + 6 \\
\text{Density - electrons - RHS boundary} \\
\text{Ind}_e &= \mu_e / \text{Diff}_e \left(\text{Efield}(1,2) + \text{Efield}(2,2)\right) / 2 \times \text{Del}_t \\
\text{call coeff(Ind}_e, a1, b1) \\
\text{A}(\text{Size}_h) &= (b1 \times \text{Diff}_e / \text{Del}_a + \text{quarter_vth_e} \times (\text{Esign}\_\text{LHS} - 1)) / \mu_e \times \text{Efield}(2,2) / \text{Del}_a + 1.0 \\
\text{B}(\text{Size}_h) &= b1 / \text{Diff}_e / n_e(1,1) / \text{Del}_a + 1.0 \\
\text{C}(\text{Size}_h) &= 0 \\
\text{D}(\text{Size}_h) &= n_e(1,1) + \left(R(3) + R(4) + R(7) + R(10)\right) \\
&- \left(R(11) - R(12) - R(6)\right) + 6 \\
\text{Density - He ions - RHS boundary} \\
\text{Ind}_e &= \mu_e / \text{Diff}_e \left(\text{Efield}(1,2) + \text{Efield}(2,2)\right) / 2 \times \text{Del}_t \\
\text{call coeff(Ind}_e, a1, b1) \\
\text{A}(\text{Size}_h) &= (b1 \times \text{Diff}_e / \text{Del}_a + \text{quarter_vth_e} \times (\text{Esign}\_\text{RHS} - 1)) / \mu_e / \text{Efield}(2,2) / \text{Del}_a + 1.0 \\
\text{B}(\text{Size}_h) &= b1 / \text{Diff}_e / \text{Del}_a + 1.0 \\
\text{C}(\text{Size}_h) &= 0 \\
\text{D}(\text{Size}_h) &= n_e(1,1) + \left(R(3) + R(4) + R(7) + R(10)\right) \\
&- \left(R(11) - R(12) - R(6)\right) + 6 \\
\text{Density - He ions - LHS boundary} \\
\text{Ind}_e &= \mu_e / \text{Diff}_e \left(\text{Efield}(1,2) + \text{Efield}(2,2)\right) / 2 \times \text{Del}_t \\
\text{call coeff(Ind}_e, a1, b1) \\
\text{A}(1) &= a1 \times \text{Diff}_e / \text{Del}_a + \text{quarter_vth_he} - \text{Esign}\_\text{LHS} \times \mu_e \text{Diff}_e / \text{Del}_a + 1.0 \\
\text{B}(1) &= b1 \times \text{Diff}_e / \text{Del}_a / \text{Del}_a + 1.0 \\
\text{C}(1) &= 0 \\
\text{D}(1) &= n_e(1,1) + R(3,1) + R(4,1) + R(7,1) + R(9,1) \\
&- R(11,1) - R(12,1) - R(6,1) + 6 \\
\text{Density - He ions - LHS boundary} \\
\text{Ind}_e &= \mu_e / \text{Diff}_e \left(\text{Efield}(1,2) + \text{Efield}(2,2)\right) / 2 \times \text{Del}_t \\
\text{call coeff(Ind}_e, a1, b1) \\
\text{A}(\text{Size}_h) &= (b1 \times \text{Diff}_e / \text{Del}_a + \text{quarter_vth_he} - \text{Esign}\_\text{RHS} \times \mu_e \text{Diff}_e / \text{Del}_a + 1.0 \\
&- \text{Del}_t + 1.0 \\
\text{B}(\text{Size}_h) &= 0 \\
\text{C}(\text{Size}_h) &= a1 \times \text{Diff}_e / \text{Del}_a / \text{Del}_a + 1.0 \\
\text{Density - He ions - LHS boundary} \\
\text{Ind}_e &= \mu_e / \text{Diff}_e \left(\text{Efield}(1,2) + \text{Efield}(2,2)\right) / 2 \times \text{Del}_t \\
\text{call coeff(Ind}_e, a1, b1) \\
\text{A}(\text{Size}_h) &= (b1 \times \text{Diff}_e / \text{Del}_a + \text{quarter_vth_he} - \text{Esign}\_\text{RHS} \times \mu_e \text{Diff}_e / \text{Del}_a + 1.0 \\
&- \text{Del}_t + 1.0 \\
\text{B}(\text{Size}_h) &= 0 \\
\text{C}(\text{Size}_h) &= a1 \times \text{Diff}_e / \text{Del}_a / \text{Del}_a + 1.0 \\
\end{align*}\]
Appendix

D(Size_h)=n_Hep(Size_h,1)+(R(3,Size_h)+R(4,Size_h)+R(7,Size_h)+R(9,Size_h))

\[D.(Size_h)=n_Hep.(Size_h,1)+R(3,Size_h)+R(4,Size_h)+R(7,Size_h)+R(9,Size_h)\]

\[\text{call bound}(n_Hep,1,Size_h) \text{ Remove negative values}\]

!Density - He dimer ions

\[D.(Size_h)=n_Hep.(Size_h,1)+R(3,Size_h)+R(4,Size_h)+R(7,Size_h)+R(9,Size_h)\]

\[\text{call bound}(n_Hep,1,Size_h) \text{ Remove negative values}\]

!Density - He dimer ions

\[D.(Size_h)=n_Hep.(Size_h,1)+R(3,Size_h)+R(4,Size_h)+R(7,Size_h)+R(9,Size_h)\]

\[\text{call bound}(n_Hep,1,Size_h) \text{ Remove negative values}\]

!Density - He dimer ions

\[D.(Size_h)=n_Hep.(Size_h,1)+R(3,Size_h)+R(4,Size_h)+R(7,Size_h)+R(9,Size_h)\]

\[\text{call bound}(n_Hep,1,Size_h) \text{ Remove negative values}\]

!Density - He dimer ions

\[D.(Size_h)=n_Hep.(Size_h,1)+R(3,Size_h)+R(4,Size_h)+R(7,Size_h)+R(9,Size_h)\]

\[\text{call bound}(n_Hep,1,Size_h) \text{ Remove negative values}\]

!Density - He dimer ions

\[D.(Size_h)=n_Hep.(Size_h,1)+R(3,Size_h)+R(4,Size_h)+R(7,Size_h)+R(9,Size_h)\]

\[\text{call bound}(n_Hep,1,Size_h) \text{ Remove negative values}\]

!Density - He dimer ions

\[D.(Size_h)=n_Hep.(Size_h,1)+R(3,Size_h)+R(4,Size_h)+R(7,Size_h)+R(9,Size_h)\]

\[\text{call bound}(n_Hep,1,Size_h) \text{ Remove negative values}\]

!Density - He dimer ions

\[D.(Size_h)=n_Hep.(Size_h,1)+R(3,Size_h)+R(4,Size_h)+R(7,Size_h)+R(9,Size_h)\]

\[\text{call bound}(n_Hep,1,Size_h) \text{ Remove negative values}\]

!Density - He dimer ions

\[D.(Size_h)=n_Hep.(Size_h,1)+R(3,Size_h)+R(4,Size_h)+R(7,Size_h)+R(9,Size_h)\]

\[\text{call bound}(n_Hep,1,Size_h) \text{ Remove negative values}\]
D2(step_h)=n_He_23p(step_h,1)+(R(30,step_h)+R(32,step_h)-R(31,step_h) - R(36,step_h)-2*R(38,step_h)-R(40,step_h) & +R(41,step_h)-R(33,step_h)*Del_t
end do

! Density - He metastable - LHS Boundary
A(1)=D_Hem/Del_1*quarter_vth_He/|Del_a_1|*Del_t+1.0
B(1)=D_Hem/Del_1/|Del_a_1|*Del_t
C(1)=0
D(1)=n_Hem(1,1)+(R(1,1)+R(6,1)-R(2,1)-R(4,1)-2*R(7,1)-R(8,1) & +R(13,1)-R(14,1)-R(39,1)-R(41,1)+R(33,1)*Del_t
! DI He_33s
D(1)=n_He_33s(1,1)+(R(29,1)-R(34,1)-R(35,1)-2*R(37,1)+R(39,1) & +R(40,1)-R(32,1)))*Del_t
! D2 He_23p
D2(1)=n_He_23p(1,1)+(R(30,1)+R(32,1)-R(31,1)-R(36,1)-2*R(38,1)-R(40,1) & +R(41,1)-R(33,1))*Del_t

! Density - He metastable - RHS Boundary
A(Size_h)=(D_Hem/Del_1*quarter_vth_He)/|Del_a_1|*Del_t+1.0
B(Size_h)=0
C(Size_h)=D_Hem/Del_1/|Del_a_1|*Del_t
D(Size_h)=n_He(1,1)+(R(1,1)-R(2,1)-R(4,1)-2*R(7,1)-R(8,1) & +R(13,1)-R(14,1)-R(39,1)-R(41,1)+R(33,1)*Del_t
! DI He_33s
D1(1)=n_He_33s(1,1)+(R(29,1)-R(34,1)-R(35,1)-2*R(37,1)+R(39,1) & +R(40,1)-R(32,1)*Del_t
! D2 He_23p
D2(1)=n_He_23p(1,1)+(R(30,1)+R(32,1)-R(31,1)-R(36,1)-2*R(38,1)-R(40,1) & +R(41,1)-R(33,1))*Del_t

Density - He dimer metastable
A(1)=(D_Hem/Del_1+quarter_vth_He)/|Del_a_1|*Del_t+1.0
B(1)=D_Hem/Del_1/|Del_a_1|*Del_t
C(1)=0
D(1)=n_He(1,1)+(R(1,1)-2*R(10,1)-R(5,1) & +R(31,1)-R(15,1))*Del_t
end do

Density - He dimer metastable - LHS Boundary
A(1)=(D_Hem/Del_1+quarter_vth_He)/|Del_a_1|*Del_t+1.0
B(1)=D_Hem/Del_1/|Del_a_1|*Del_t
C(1)=0
D(1)=n_He(1,1)+(R(8,1)-2*R(10,1)-R(5,1) & +R(31,1)-R(15,1))*Del_t

Density - He dimer metastable - RHS Boundary
A(Size_h)=(D_Hem/Del_1+quarter_vth_He)/|Del_a_1|*Del_t+1.0
B(Size_h)=0
C(Size_h)=D_Hem/Del_1/|Del_a_1|*Del_t
D(Size_h)=n_He(1,1)+(R(8,1)-2*R(10,1)-R(5,1) & +R(31,1)-R(15,1))*Del_t
n_He(:,2)=TDMA(A,B,C,D,Size_h)
call bound(n_He,le-3,Size_h,nonfinite) !Remove negative values
n_He_33s(:,2)=TDMA(A,B,C,D,Size_h)
call bound(n_He_33s,le-3,Size_h,nonfinite) !Remove negative values
n_He_23p(:,2)=TDMA(A,B,C,D,Size_h)
call bound(n_He_23p,le-3,Size_h,nonfinite) !Remove negative values

Density - N ions
A(1)=(D_He2m/Del_1+quarter_vth_He2)/|Del_a_1|*Del_t+1.0
B(1)=D_He2m/Del_1/|Del_a_1|*Del_t
C(1)=0
D(1)=n_He2m(1,1)+(R(8,1)-2*R(10,1)-R(5,1) & +R(31,1)-R(15,1))*Del_t
end do
Appendix

\[ \text{Del}_k = x(\text{step}_h + 1) - x(\text{step}_h) \]
\[ \text{Del}_\text{avg}_k = (\text{Del}_k + \text{Del}_{k+1}) / 2.0 \]
\[ \text{Index}_Np(\text{step}_h) = \text{mu}_Np / D_Np * (\text{Efield}(\text{step}_h, 2) + \text{Efield}(\text{step}_h-1, 2)) / 2.0 * \text{Del}_k \]
\[ \text{call coeff} (\text{Index}_Np(\text{step}_h), a1, b1) \]
\[ \text{call coeff} (\text{Index}_Np(\text{step}_h+1), a2, b2) \]
\[ A(\text{step}_h) = (\text{D}_Np * a2 / \text{Del}_k + \text{D}_Np / \text{Del}_k * b1) / \text{Del}_\text{avg}_k * \text{Del}_t + 1.0 \]
\[ B(\text{step}_h) = \text{D}_Np / \text{Del}_k * b2 / \text{Del}_\text{avg}_k * \text{Del}_t \]
\[ C(\text{step}_h) = \text{D}_Np / \text{Del}_k / \text{Del}_\text{avg}_k * \text{Del}_t * a1 \]

\[ \text{D}(\text{step}_h) = \text{N}_p(\text{step}_h, 1) + (R(16, \text{step}_h) * \text{BranchRatio}_2 + R(17, \text{step}_h) * \text{BranchRatio}_3 - R(23, \text{step}_h)) * \text{Del}_t \]

\[ \text{end do} \]

<table>
<thead>
<tr>
<th>Density - N ions</th>
<th>LHS boundary</th>
</tr>
</thead>
</table>
| \[ \text{Ind}_Np(\text{step}_h) = \text{mu}_Np / D_Np * (\text{Efield}(\text{step}_h, 2) + \text{Efield}(\text{step}_h-1, 2)) / 2.0 * \text{Del}_1 \]
| \[ \text{call coeff}(\text{Ind}_Np(\text{step}_h), a1, b1) \] |
| \[ A(1) = (a1 * \text{D}_Np / \text{Del}_1 + \text{quarter}_vth_N * \text{Esign}_LHS * \text{mu}_Np * \text{Efield}(2, 2)) / \text{Del}_a_1 * \text{Del}_t + 1.0 \]
| \[ B(1) = b1 * \text{D}_Np / \text{Del}_1 / \text{Del}_a_1 * \text{Del}_t \]
| \[ C(1) = 0 \]
| \[ \text{D}(1) = \text{N}_p(1, 1) + (R(16, 1) * \text{BranchRatio}_2 + R(17, 1) * \text{BranchRatio}_3 - R(23, 1)) * \text{Del}_t \]

\[ \text{Density - N dimer ions \ do step}_h=2, \text{Size}_h-1 \]
\[ \text{Del}_k = x(\text{step}_h) - x(\text{step}_h-1) \]
\[ \text{Del}_\text{avg}_k = (\text{Del}_k + \text{Del}_{k+1}) / 2.0 \]
\[ \text{Index}_N2p(\text{step}_h) = \text{mu}_N2p / D_N2p * (\text{Efield}(\text{step}_h, 2) + \text{Efield}(\text{step}_h-1, 2)) / 2.0 * \text{Del}_k \]
\[ \text{call coeff} (\text{Index}_N2p(\text{step}_h), a1, b1) \]
\[ \text{call coeff} (\text{Index}_N2p(\text{step}_h+1), a2, b2) \]
\[ A(\text{step}_h) = (\text{D}_N2p * a2 / \text{Del}_k + \text{D}_N2p / \text{Del}_k * b1) / \text{Del}_\text{avg}_k * \text{Del}_t + 1.0 \]
\[ B(\text{step}_h) = \text{D}_N2p / \text{Del}_k * b2 / \text{Del}_\text{avg}_k * \text{Del}_t \]
\[ C(\text{step}_h) = \text{D}_N2p / \text{Del}_k / \text{Del}_\text{avg}_k * \text{Del}_t * a1 \]

\[ \text{D}(\text{step}_h) = \text{N}_2p(\text{step}_h, 1) + (R(13, \text{step}_h) * \text{BranchRatio}_6 + R(14, \text{step}_h) * \text{BranchRatio}_7 + R(15, \text{step}_h) * \text{BranchRatio}_8 - R(18, \text{step}_h) * \text{BranchRatio}_9 + R(19, \text{step}_h) * \text{BranchRatio}_10 - R(20, \text{step}_h) * \text{BranchRatio}_11 + R(21, \text{step}_h) * \text{BranchRatio}_12 - R(22, \text{step}_h) * \text{BranchRatio}_13 - R(23, \text{step}_h) * \text{BranchRatio}_14 + R(24, \text{step}_h) * \text{BranchRatio}_15 - R(25, \text{step}_h) * \text{BranchRatio}_16) * \text{Del}_t \]

\[ \text{end do} \]

<table>
<thead>
<tr>
<th>Density - N dimer ions</th>
<th>RHS boundary</th>
</tr>
</thead>
</table>
| \[ \text{Ind}_N2p(\text{step}_h) = \text{mu}_N2p / D_N2p * (\text{Efield}(\text{step}_h, 2) + \text{Efield}(\text{step}_h-1, 2)) / 2.0 * \text{Del}_1 \]
| \[ \text{call coeff}(\text{Ind}_N2p(\text{step}_h), a1, b1) \] |
| \[ A(1) = (a1 * \text{D}_N2p / \text{Del}_1 + \text{quarter}_vth_N * \text{Esign}_RHS * \text{mu}_N2p * \text{Efield}(2, 2)) / \text{Del}_a_1 * \text{Del}_t + 1.0 \]
| \[ B(1) = b1 * \text{D}_N2p / \text{Del}_1 / \text{Del}_a_1 * \text{Del}_t \]
| \[ C(1) = 0 \]
| \[ \text{D}(1) = \text{N}_2p(1, 1) + (R(13, 1) * \text{BranchRatio}_6 + R(14, 1) * \text{BranchRatio}_7 + R(15, 1) * \text{BranchRatio}_8 - R(18, 1) * \text{BranchRatio}_9 + R(19, 1) * \text{BranchRatio}_10 - R(20, 1) * \text{BranchRatio}_11 + R(21, 1) * \text{BranchRatio}_12 - R(22, 1) * \text{BranchRatio}_13 - R(23, 1) * \text{BranchRatio}_14 + R(24, 1) * \text{BranchRatio}_15 - R(25, 1) * \text{BranchRatio}_16) * \text{Del}_t \]

\[ \text{Density - N dimer ions \ call bound(n_Np, le-3, Size_h-1, nonfinite) \ Remove negative values} \]
Ind_N2p_sh=mu_N2p/D_N2p*(Efield(Size_h,1,2)+Efield(Size_h,2))/2.0*Del_1
call coeff(Ind_N2p_sh,al,b1)
A(Size_h)=bl*D_N2p/Del_1+quarter_vth*2*Sign_RHS*mu_N2p*Efield(Size_h,2)/Del_a_1*Del_t+1.0
B(Size_h)=0
C(Size_h)=al*D_N2p/Del_1/1*Del_a_1*Del_t
D(Size_h)=-N2p(Size_h,1)+(R(13,Size_h)*BranchRatio_6+R(14,Size_h)*BranchRatio_7+
                R(15,Size_h)*BranchRatio_8)*Del_t
Dl(Size_h)=(N2p*(Size_h,1)+R(15,Size_h)*BranchRatio_6+R(14,Size_h)*BranchRatio_7+
                R(16,Size_h)*BranchRatio_8)*Del_t
Dl(Size_h)*=N2px*(Size_h,1)+(R(13,Size_h)*I/BranchRatio_6+R(14,Size_h)*I/BranchRatio_7+
                R(15,Size_h)*I/BranchRatio_8)*Del_t
n_N2p(:,2)="TDMA(A,B,C,D,Size_h)"- TDMA(A,B,C,D,Size_h)
end do
!
Density - N metastable - LHS Boundary
A(1)=(D_N/Del_1+quarter_vth_N)/Del_a_1*Del_t+1.0
B(1)=(D_N/1/1+D_N/1)*Del_t
C(1)=0
D(1)=n_N(1,1)+(R(16,1)*BranchRatio_2+R(17,1)*BranchRatio_3+R(21,1)+2*R(22,1)+R(24,1)-R(25,1))*Del_t
!
Density - N metastable - RHS Boundary
A(1)=(D_N/1/1+quarter_vth_N)/Del_a_1*Del_t+1.0
B(1)=(D_N/1/1+D_N/1)*Del_t
C(1)=0
D(1)=n_N(1,1)+(R(16,1)*BranchRatio_2+R(17,1)*BranchRatio_3+R(21,1)+2*R(22,1)+R(24,1)-R(25,1))*Del_t
end do
!
Density - N metastable - LHS Boundary
A(1)=(D_N/2/1+quarter_vth_N)/Del_a_1*Del_t+1.0
B(1)=(D_N/2/1+D_N/2)*Del_t
C(1)=0
D(1)=n_N2(1,1)+(-R(13,1)-R(14,1)-R(15,1)-R(16,1)-R(17,1)-R(18,1)-R(19,1)-R(24,1)+
                R(25,1)-R(26,1))*Del_t
end do
!
Density - N metastable - RHS Boundary
A(1)=(D_N2/2/1+quarter_vth_N)/Del_a_1*Del_t+1.0
B(1)=(D_N2/2/1+D_N2/2)*Del_t
C(1)=0
D(1)=n_N2(1,1)+(-R(13,1)-R(14,1)-R(15,1)-R(16,1)-R(17,1)-R(18,1)-R(19,1)-R(24,1)+
                R(25,1)-R(26,1))*Del_t
end do
!
Density - N2 - LHS Boundary
A(1)=(D_N2/1/1+quarter_vth_N2)/Del_a_1*Del_t+1.0
B(1)=(D_N2/1/1+D_N2/1)*Del_t
C(1)=0
D(1)=n_N2(1,1)+(-R(13,1)-R(14,1)-R(15,1)-R(16,1)-R(17,1)-R(18,1)-R(19,1)-R(24,1)+
                R(25,1)-R(26,1))*Del_t
end do
!
Density - N2 - RHS Boundary
A(1)=(D_N2/1/1+quarter_vth_N2)/Del_a_1*Del_t+1.0
B(1)=(D_N2/1/1+D_N2/1)*Del_t
C(1)=0
D(1)=n_N2(1,1)+(-R(13,1)-R(14,1)-R(15,1)-R(16,1)-R(17,1)-R(18,1)-R(19,1)-R(24,1)+
                R(25,1)-R(26,1))*Del_t
end do
!
Density - N metastable - LHS Boundary
A(1)=(D_N/2/1+quarter_vth_N)/Del_a_1*Del_t+1.0
B(1)=(D_N/2/1+D_N/2)*Del_t
C(1)=0
D(1)=n_N2(1,1)+(-R(13,1)-R(14,1)-R(15,1)-R(16,1)-R(17,1)-R(18,1)-R(19,1)-R(24,1)+
                R(25,1)-R(26,1))*Del_t
end do
!
Appendix

call bound(n_N2,le-3,Size_h,nonfinite) !Remove negative values

else
n_Np(:,2)=0
n_N2p(:,2)=0
n_N2pb(:,2)=0
n_N2px(:,2)=0
n_N(:,2)=0
n_N2(:,2)=0
endif
end

start.f90

subroutine start(RF_cycle_max)
use global
implicit none
Integer::i,read_flag,RF cycle max,ios=0
Real::initial
engy=0.5
Real (B) ::n He-initial,n e initial,n H2p initial,n He3p initial,n He2
m initial,
6n_N2p initial,n_N2pb initial,n_N2px initial,n_Np initial,n_N initial,n_He_33s
initial,n_He_23p initial
Character(512)::buffer,prev line=' 

call exit(1)
end if

read_flag=0
read (1,'(A)',ioeat=ios) buffer !Read one line
if (ios<0) then
write(*,*) "Error reading the input file. Wrong format!"
call exit(1)
end if
if ((buffer(1:1)==0).AND.buffer(1:1)<='9') .AND. (len_trim(buffer)>0)) then !If
a data line, read it
!Format line for reading - separate numbers by only one space
i=index(trim(buffer),')
do while (i>0)
buffer=buffer(1:i)//trim(buffer(i+2:))
i=index(trim(buffer),')
dode
end do
!Now read
! !
DEC$
if DEBUG
!write (*,*) trim(buffer)
!DEC$
endif

read_flag=0
read (1,'(A)',ioeat=ios) buffer !Read one line
if (ios<0) then
write(*,*) "Error reading the input file. Wrong format!"
call exit(1)
end if
if ((buffer(1:1)==0').AND.buffer(1:1)<='9') .AND. (len_trim(buffer)>0)) then !If
a data line, read it
!Format line for reading - separate numbers by only one space
i=index(trim(buffer),')
do while (i>0)
buffer=buffer(1:i)//trim(buffer(i+2:))
i=index(trim(buffer),')
dode
!Now read
!!DEC$ if DEBUG
!write (*,*) trim(buffer)
!!DEC$ endif
read (buffer,*) Nreactions, seec, Npoints

!!DEC$ if DEBUG
   write ('(*)',*) trim(prev_line)
   write ('(*)',*) Nreactions, seec, Npoints
!!DEC$ endif
 end if
prev_line=buffer
end do

read_flag=0
do while(read_flag==0)
 read (1,'(A)',iostat=ios) buffer !Read one line
 if (ios<0) then
   write('(*,*) trim(buffer)
   write('(*,*) "Error reading the input file. Wrong format!"
   call exit(1)
 endif
 buffer=trim(adjustl(buffer)) !Remove leading and trailing blank spaces
 if ((buffer(1:1)>'0').AND. buffer(1:1)<='9') .AND. (len_trim(buffer)>0)) then ! If a data line, read it:
   !Format line for reading - separate numbers by only one space
   i=index(trim(buffer), ' ')
   do while (i>0)
      buffer=buffer(1:i)/trim(buffer(i+2:))
      i=index(trim(buffer), ' ')
   end do
   !Now read
   !!DEC$ if DEBUG
   !write ('(*)',*) trim(buffer)
   !!DEC$ endif
   read (buffer,*) amplitude, frequency, source_type
   !!DEC$ if DEBUG
   write ('(*)',*) trim(prev_line)
   write ('(*)',*) amplitude, frequency, source_type
   !!DEC$ endif
   read_flag=1
 endif
 prev_line=buffer
end do

read_flag=0
do while(read_flag==0)
 read (1,'(A)',iostat=ios) buffer !Read one line
 if (ios<0) then
   write('(*,*) trim(buffer)
   write('(*,*) "Error reading the input file. Wrong format!"
   call exit(1)
 endif
 buffer=trim(adjustl(buffer)) !Remove leading and trailing blank spaces
 if ((buffer(1:1)>'0').AND. buffer(1:1)<='9') .AND. (len_trim(buffer)>0)) then ! If a data line, read it:
   !Format line for reading - separate numbers by only one space
   i=index(trim(buffer), ' ')
   do while (i>0)
      buffer=buffer(1:i)/trim(buffer(i+2:))
      i=index(trim(buffer), ' ')
   end do
   !Now read
   !!DEC$ if DEBUG
   !write ('(*)',*) trim(buffer)
   !!DEC$ endif
   read (buffer,*) P,Tg
   !!DEC$ if DEBUG
   write ('(*)',*) P,Tg
   !!DEC$ endif
   read_flag=1
 endif
 prev_line=buffer
end do
read_flag=0
do while(read_flag==0)
read (i,'(A)',iostat=ios) buffer  !Read one line
if (ios<0) then
   write(*,*),trim(buffer)
   write(*,*),"Error reading the input file. Wrong format!
   call exit(1)
end if
buffer=trim(adjustl(buffer)) !Remove leading and trailing blank spaces
if ((buffer(1:1)>='0'.AND.buffer(1:1)<='9') .AND. (len_trim(buffer)>0)) then !If a data line, read it
   !Format line for reading - separate numbers by only one space
   i=index(trim(buffer),',')
   do while (i>0)
      buffer=buffer(1:i+1)/trim(buffer(i+2:))
      i=index(trim(buffer),',')
   end do
   !Now read
   !!DEC$ if DEBUG
   !write(*,*) trim(buffer)
   !!DEC$ endif
   n_e_initial,n_N2_initial,n_H2p_initial,n_N2m_initial,n_N2m_initial
   !!DEC$ if DEBUG
   write(*,*),trim(prev_line)
   write(*,*)
   !!DEC$ endif
   !!DEC$ end if
   read_flag=1
endif
prev_line=buffer
end do
read_flag=0
do while(read_flag==0)
read (i,'(A)',iostat=ios) buffer  !Read one line
if (ios<0) then
   write(*,*),trim(buffer)
   write(*,*),"Error reading the input file. Wrong format!
   call exit(1)
end if
buffer=trim(adjustl(buffer)) !Remove leading and trailing blank spaces
if ((buffer(1:1)>='0'.AND.buffer(1:1)<='9') .AND. (len_trim(buffer)>0)) then !If a data line, read it
   !Format line for reading - separate numbers by only one space
   i=index(trim(buffer),',')
   do while (i>0)
      buffer=buffer(1:i+1)/trim(buffer(i+2:))
      i=index(trim(buffer),',')
   end do
   !Now read
   !!DEC$ if DEBUG
   !write(*,*) trim(buffer)
   !!DEC$ endif
   read (buffer,*) per_He,per_N2,Bolsig
   !!DEC$ if DEBUG
   write(*,*),trim(prev_line)
   write(*,*),per_He,per_N2,Bolsig
   !!DEC$ endif
   read_flag=1
endif
prev_line=buffer
end do
read_flag=0
do while(read_flag==0)
read (i,'(A)',iostat=ios) buffer  !Read one line
if (ios<0) then
   write(*,*),trim(buffer)
   write(*,*),"Error reading the input file. Wrong format!
   call exit(1)
Appendix

```verbatim
end if
buffer=trim(adjustl(buffer)) ! Remove leading and trailing blank spaces
if ((buffer(1:1)='0'.AND.buffer(1:1)<='9') .AND. (len(trim(buffer))>0)) then
   if a data line, read it
      i=index(trim(buffer),',')
   do while (i>0)
      buffer=buffer(1:i)//trim(buffer(i+2:))
      i=index(trim(buffer),',')
   end do
   ! Now read
   ! DECS if DEBUG
   write ('*',*) trim(buffer)
   ! DECS endif
   n_N2p_initial,n_N2pb_initial,n_N2px_initial,n_Np_initial,n_N_initial,n_He_33s_initial,n_He_23p_initial
   ! DECS if DEBUG
   write ('*',*) prev_line
   write ('*',*)
   n_N2p_initial,n_N2pb_initial,n_N2px_initial,n_Np_initial,n_N_initial,n_He_33s_initial,n_He_23p_initial
   ! DECS endif
   endif
   prev_line=buffer
   end do
Size_t=1.0/(Frequency*Del_t)
! DECS if DEBUG
write ('*',*) Size_t,Del_t
! DECS endif
call allocate_memory(RF_cycle_max) ! Allocate memory
*************David
n_He=n_He_initial
n_He2p=n_He2p_initial
n_He2m=n_He2m_initial
*************David
n_N=n_N_initial
n_Np=n_Np_initial
n_N2p=n_N2p_initial
n_N2pb=n_N2pb_initial
n_N2px=n_N2px_initial
n_He_33s=n_He_33s_initial
n_He_23p=n_He_23p_initial
*************David
mu_E=1132*760/P*Tg/300 ! [cm^2/V-s] Y.P.Raizer, Gas Discharge Physics, Springer, Berlin 1991, pp 11 & 211
mu_He2p=24.03*760/P*Tg/300 ! [cm^2/V-s] L.M.Chanin, M.A.Biondi, Phys.Rev. 106, 473 (1957)
quarter_vth_e=0.25*4.733e7
quarter_vth_He=0.25*sqrt(8*Tg*KB/pi/Mass_He) ! [cm/s]
quarter_vth_He2=0.25*sqrt(8*Tg*KB/pi/(2*Mass_He)) ! [cm/s]
D_He=4.116*760/P*Tg/300
D_He2p=0.10026*760/P*Tg/300 ! [cm^2/sec]
D_He2m=0.116*760/P*Tg/300
D_He2m=2.029*760/P*Tg/300 ! [cm^2/sec]
*************David
mu_Np=28.63*760/P
mu_N2p=29.93*760/P
D_Np=0.971*760/P
D_N2p=1.015*760/P
```

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D_N = 1.955 × 10^6 / P
D_N2 = 1.075 × 10^6 / P
quarter_Vth_N = 0.25 × 6.714 × 10^4
quarter_Vth_N2 = 0.25 × 4.7454 × 10^4;

! Set initial conditions
! engy = initial_engy;
schias(l) = 0
pci(l) = 0
FK(l) = 1e-3
Perror_avg(l) = 0
Efield_mid = 0
Efield = 0
Flux_e = 0
Flux_Hep = 0
Flux_He2p = 0
Flux_Np = 0
Flux_N2p = 0
Flux_p_j = 0
Flux_p_sh = 0
Flux_e_l = 0
Flux_e_sh = 0
Current = 0
Voltage = 0
Power = 0
Current_ds = 0
Current_Hep = 0
Current_He2p = 0
Current_Np = 0
Current_N2p = 0
Current_e = 0
end

Appendix

output.f90

subroutine version
write(*,*)
write(*,*) "FI-He: 1-dimensional fluid model of He plasmas"
write(*,*) "Plasma and Pulsed Power Group - P3G"
write(*,*) "Dept. Electronic and Electrical Engineering"
write(*,*) "Loughborough University, UK"
write(*,*) "Send bugs/comments to:
write(*,*) "Felipe Iza"
write(*,*) "f.iza@lboro.ac.uk"
write(*,*) "Developers: J.J. Shi, D.W. Liu"
write(*,*)
end

subroutine save_traces(t0, RF_cycle, RF_cycle_start, RF_cycle_max, Del_period)
use global
use m rms
implicit none
Real:: rms_V, DC_V, rms_I, Pavg
Real:: Del_period
Integer:: RF_cycle_max
Character (len=512):: filename
Integer:: t0(8), t1(8)
Integer:: RF_cycle, RF_cycle_Start

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call date_and_time(values=t1)
DC v=sum(Voltage(l:Size t))/Size t 
rms_v=rms(Voltage(l:Size t),Size t) 
rms_I=rms(Current(l:Size t),Size t) 
Pavg=sum(Power(l:Size t))/Size t

!Display summary
write(*, '(A)') trim(ID) 
write(*, '(A,I6,A,IG,A,ES8.2) ') "RF cycle:",RF cycle start+RF cycle-I," of ",RF cycle_start+RF cycle_max-1," - Delta="Del_period
write(*, '(A,I4.4,A,12.2,A,12.2,A,12.2,A,12.2,A,12.2)') "Simulation started on ",t0(1),"-",t0(2),"-",t0(3)," at ",t0(5),"-",t0(6),":",t0(7)
write(*, '(A,I4.4,A,12.2,A,12.2,A,12.2,A,12.2,A,12.2)') "Current date/time is ",t1(1),"-",t1(2),"-",t1(3)," at ",t1(5),":",t1(6),":",t1(7)
Pavg, "W"
write(*, '*')

!Save traces
if (RF_cycle==1) then !Generate new files
  write(filename,*),trim(ID),"_difference_t.txt"; open(1001,file=filename)
  write(filename,*),trim(ID),"_voltage_rms_t.txt"; open(1002,file=filename)
  write(filename,*),trim(ID),"_power_t.txt"; open(1003,file=filename)
  write(filename,*),trim(ID),"_ne_t.txt"; open(1004,file=filename)
  write(filename,*),trim(ID),"_nHe_t.txt"; open(1005,file=filename)
  write(filename,*),trim(ID),"_nHe2p_t.txt"; open(1006,file=filename)
  write(filename,*),trim(ID),"_nHem_t.txt"; open(1007,file=filename)
  write(filename,*),trim(ID),"_run_info.txt"; open(1008,file=filename)
  write(filename,*),"Gap: ",Height," cm" 
  write(filename,*),"Pressure: ",P," Torr" 
  write(filename,*),"Source: ",amplitude," ,source_type 
  write(filename,*),"Frequency: ",Frequency," Hz" 
  write(filename,*),"Seed: ",seed 
  write(filename,*),"Grid points (Size_h):",Size_h 
  write(filename,*),"Steps per rf cycle (Size_t):",Size_t 
  write(filename,*),"Simulation started on ",t0(1),"-",t0(2),"-",t0(3)," at ",t0(5),",",t0(6),":",t0(7)
close(1009)
else !Append to existing files
  write(filename,*),trim(ID),"_difference_t.txt";open(1001,file=filename,access="append")
  write(filename,*),trim(ID),"_voltage_rms_t.txt";open(1002,file=filename,access="append")
  write(filename,*),trim(ID),"_power_t.txt";open(1003,file=filename,access="append")
  write(filename,*),trim(ID),"_ne_t.txt";open(1004,file=filename,access="append")
  write(filename,*),trim(ID),"_nHe_t.txt";open(1005,file=filename,access="append")
  write(filename,*),trim(ID),"_nHe2p_t.txt";open(1006,file=filename,access="append")
  write(filename,*),trim(ID),"_nHem_t.txt";open(1007,file=filename,access="append")
  write(filename,*),"Gap: ",Height," cm" 
  write(filename,*),"Pressure: ",P," Torr" 
  write(filename,*),"Source: ",amplitude," ,source_type 
  write(filename,*),"Frequency: ",Frequency," Hz" 
  write(filename,*),"Seed: ",seed 
  write(filename,*),"Grid points (Size_h):",Size_h 
  write(filename,*),"Steps per rf cycle (Size_t):",Size_t 
  write(filename,*),"Simulation started on ",t0(1),"-",t0(2),"-",t0(3)," at ",t0(5),",",t0(6),":",t0(7)
  ! 100 format (A,12.2,A,12.2,A,12.2,A,12.2) 
end if

write(1001, '(I7,I5.5)') RF_cycle_start+RF_cycle=1,Del_period
write(1002, '(I7,I5.5)') RF_cycle_start+RF_cycle=1,rms_V 
write(1010, '(I7,I5.5)') RF_cycle_start+RF_cycle=1,rms_I 
write(1003, '(I7,I5.5)') RF_cycle_start+RF_cycle=1,Pavg
write(1004, '(I7,I5.5)') RF_cycle_start+RF_cycle=1,hist_Max_ne(RF_cycle)
write(1005, '(I7,I5.5)') RF_cycle_start+RF_cycle=1,hist_Max_nHe(RF_cycle)
write(1006, '(I7,I5.5)') RF_cycle_start+RF_cycle=1,hist_Max_nHe2p(RF_cycle)
write(1007, '(I7,I5.5)') RF_cycle_start+RF_cycle=1,hist_Max_nHem(RF_cycle)
write(1008, '(I7,I5.5)') RF_cycle_start+RF_cycle=1,hist_Max_nHe2m(RF_cycle)
subroutine savedata(t0)
use global
implicit none
character (len=512):: filename
integer:: t0(8), t1(8)
write(*,*) "Saving simulation results"
write(filename,*) trim(ID), '_grid.txt'
call save1d_float(filename,len_trim(filename),x,Size_h)
write(filename,*) trim(ID), '_voltage_t.txt'
call save1d_float(filename,len_trim(filename),Voltage,Size_t)
write(filename,*) trim(ID), '_current_t.txt'
call save1d_float(filename,len_trim(filename),Current,Size_t)
write(filename,*) trim(ID), '_power_t.txt'
call save1d_float(filename,len_trim(filename),Power,Size_t)
write(filename,*) trim(ID), '_engy_t_x.txt'
call save2d_double(filename,len_trim(filename),engy_S,Size_h,Npoints)
write(filename,*) trim(ID), '_ne_t_x.txt'
call save2d_double(filename,len_trim(filename),n_e_S,Size_h,Npoints)
write(filename,*) trim(ID), '_nHe_t_x.txt'
call save2d_double(filename,len_trim(filename),n_He_S,Size_h,Npoints)
write(filename,*) trim(ID), '_nHe2p_t_x.txt'
call save2d_double(filename,len_trim(filename),n_He2p_S,Size_h,Npoints)
write(filename,*) trim(ID), '_nHe3p_t_x.txt'
call save2d_double(filename,len_trim(filename),n_He_23p_S,Size_h,Npoints)
write(filename,*) trim(ID), '_nHe3s_t_x.txt'
call save2d_double(filename,len_trim(filename),n_He_33s_S,Size_h,Npoints)
write(filename,*) trim(ID), '_nN2_t_x.txt'
call save2d_double(filename,len_trim(filename),n_N2_S,Size_h,Npoints)
write(filename,*) trim(ID), '_nN2pb_t_x.txt'
call save2d_double(filename,len_trim(filename),n_N2pb_S,Size_h,Npoints)
write(filename,*) trim(ID), '_nN2px_t_x.txt'
call save2d_double(filename,len_trim(filename),n_N2px_S,Size_h,Npoints)
write(filename,*) trim(ID), '_nN_t_x.txt'
call save2d_double(filename,len_trim(filename),n_N_S,Size_h,Npoints)
write(filename,*) trim(ID), '_nNp_t_x.txt'
call save2d_double(filename,len_trim(filename),n_Np_S,Size_h,Npoints)
write(filename,*) trim(ID), 'Efield_t_x.txt'
call save2d_double(filename,len_trim(filename),Efield_S,Size_h,Npoints)
write(filename,*) trim(ID), 'current_net_t_x.txt'
call save2d_double(filename,len_trim(filename),Current_S,Size_h,Npoints)
write(filename,*) trim(ID),'_current_e_t_x.txt'
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call save2d_double(filename,len_trim(filename),Current_e_S,Size_h,Npoints)
write(filename,*) trim(ID),'Current_e_t_.txt'
call save2d_double(filename,len_trim(filename),Current_Hep_e_S,Size_h,Npoints)
write(filename,*) trim(ID),'Current_Hep_e_t_.txt'
call save2d_double(filename,len_trim(filename),Current_Hep_s,Size_h,Npoints)
write(filename,*) trim(ID),'Current_Hep_s_t_.txt'
call save2d_double(filename,len_trim(filename),Current_Np_e_S,Size_h,Npoints)
write(filename,*) trim(ID),'Current_Np_e_t_.txt'
call save2d_double(filename,len_trim(filename),Current_Np_s,Size_h,Npoints)
write(filename,*) trim(ID),'Current_Np_s_t_.txt'
call save2d_double(filename,len_trim(filename),Current_ds_S,Size_h,Npoints)
write(filename,*) trim(ID),'Current_ds_t_.txt'
call save2d_double(filename,len_trim(filename),Drift_Current_e_S,Size_h,Npoints)
write(filename,*),trim(ID),'Drift_Current_e_t_.txt'
call save2d_double(filename,len_trim(filename),Diff_Current_e_S,Size_h,Npoints)
write(filename,*),trim(ID),'Diff_Current_e_t_.txt'
call save2d_double(filename,len_trim(filename),R1,Size_h,Npoints)
write(filename,*),trim(ID),'R1_t_.txt'
call save2d_double(filename,len_trim(filename),R2,Size_h,Npoints)
write(filename,*),trim(ID),'R2_t_.txt'
call save2d_double(filename,len_trim(filename),R3,Size_h,Npoints)
write(filename,*),trim(ID),'R3_t_.txt'
call save2d_double(filename,len_trim(filename),R4,Size_h,Npoints)
write(filename,*),trim(ID),'R4_t_.txt'
call save2d_double(filename,len_trim(filename),R5,Size_h,Npoints)
write(filename,*),trim(ID),'R5_t_.txt'
call save2d_double(filename,len_trim(filename),R6,Size_h,Npoints)
write(filename,*),trim(ID),'R6_t_.txt'
call save2d_double(filename,len_trim(filename),R7,Size_h,Npoints)
write(filename,*),trim(ID),'R7_t_.txt'
call save2d_double(filename,len_trim(filename),R8,Size_h,Npoints)
write(filename,*),trim(ID),'R8_t_.txt'
call save2d_double(filename,len_trim(filename),R9,Size_h,Npoints)
write(filename,*),trim(ID),'R9_t_.txt'
call save2d_double(filename,len_trim(filename),R10,Size_h,Npoints)
write(filename,*),trim(ID),'R10_t_.txt'
call save2d_double(filename,len_trim(filename),R11,Size_h,Npoints)
write(filename,*),trim(ID),'R11_t_.txt'
call save2d_double(filename,len_trim(filename),R12,Size_h,Npoints)
write(filename,*),trim(ID),'R12_t_.txt'
call save2d_double(filename,len_trim(filename),R13,Size_h,Npoints)
write(filename,*),trim(ID),'R13_t_.txt'
call save2d_double(filename,len_trim(filename),R14,Size_h,Npoints)
write(filename,*),trim(ID),'R14_t_.txt'
call save2d_double(filename,len_trim(filename),R15,Size_h,Npoints)
write(filename,*),trim(ID),'R15_t_.txt'
call save2d_double(filename,len_trim(filename),R16,Size_h,Npoints)
write(filename,*),trim(ID),'R16_t_.txt'

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write(filename,*) trim(ID), '_R17_t_x.txt'
call save2d_double(filename, len_trim(filename), R17, Size_h, Npoints)

write(filename,*) trim(ID), '_R18_t_x.txt'
call save2d_double(filename, len_trim(filename), R18, Size_h, Npoints)

write(filename,*) trim(ID), '_R19_t_x.txt'
call save2d_double(filename, len_trim(filename), R19, Size_h, Npoints)

write(filename,*) trim(ID), '_R20_t_x.txt'
call save2d_double(filename, len_trim(filename), R20, Size_h, Npoints)

write(filename,*) trim(ID), '_R21_t_x.txt'
call save2d_double(filename, len_trim(filename), R21, Size_h, Npoints)

write(filename,*) trim(ID), '_R22_t_x.txt'
call save2d_double(filename, len_trim(filename), R22, Size_h, Npoints)

write(filename,*) trim(ID), '_R23_t_x.txt'
call save2d_double(filename, len_trim(filename), R23, Size_h, Npoints)

write(filename,*) trim(ID), '_R24_t_x.txt'
call save2d_double(filename, len_trim(filename), R24, Size_h, Npoints)

write(filename,*) trim(ID), '_R25_t_x.txt'
call save2d_double(filename, len_trim(filename), R25, Size_h, Npoints)

write(filename,*) trim(ID), '_R26_t_x.txt'
call save2d_double(filename, len_trim(filename), R26, Size_h, Npoints)

write(filename,*) trim(ID), '_R27_t_x.txt'
call save2d_double(filename, len_trim(filename), R27, Size_h, Npoints)

write(filename,*) trim(ID), '_R28_t_x.txt'
call save2d_double(filename, len_trim(filename), R28, Size_h, Npoints)

write(filename,*) trim(ID), '_R29_t_x.txt'
call save2d_double(filename, len_trim(filename), R29, Size_h, Npoints)

write(filename,*) trim(ID), '_R30_t_x.txt'
call save2d_double(filename, len_trim(filename), R30, Size_h, Npoints)

write(filename,*) trim(ID), '_R31_t_x.txt'
call save2d_double(filename, len_trim(filename), R31, Size_h, Npoints)

write(filename,*) trim(ID), '_R32_t_x.txt'
call save2d_double(filename, len_trim(filename), R32, Size_h, Npoints)

write(filename,*) trim(ID), '_R33_t_x.txt'
call save2d_double(filename, len_trim(filename), R33, Size_h, Npoints)

write(filename,*) trim(ID), '_R34_t_x.txt'
call save2d_double(filename, len_trim(filename), R34, Size_h, Npoints)

write(filename,*) trim(ID), '_R35_t_x.txt'
call save2d_double(filename, len_trim(filename), R35, Size_h, Npoints)

write(filename,*) trim(ID), '_R36_t_x.txt'
call save2d_double(filename, len_trim(filename), R36, Size_h, Npoints)

write(filename,*) trim(ID), '_R37_t_x.txt'
call save2d_double(filename, len_trim(filename), R37, Size_h, Npoints)

write(filename,*) trim(ID), '_R38_t_x.txt'
call save2d_double(filename, len_trim(filename), R38, Size_h, Npoints)

write(filename,*) trim(ID), '_R39_t_x.txt'
call save2d_double(filename, len_trim(filename), R39, Size_h, Npoints)

write(filename,*) trim(ID), '_R40_t_x.txt'
call save2d_double(filename, len_trim(filename), R40, Size_h, Npoints)
write(filename,*), trim(ID), '_Flux_R41_t_x.txt'
call saveld_double(filename,len_trim(filename),R41,Size_h,Npoints)

!******************************
write(filename,*), trim(ID), '_Re_t_x.txt'
call saveld_double(filename,len_trim(filename),Re,Size_h,Npoints)
write(filename,*), trim(ID), '_tave_elastic_engy_x.txt'
call saveld_double(filename,len_trim(filename),Ren_elastic,Size_h)
write(filename,*), trim(ID), '_tave_inelastic_engy_x.txt'
call saveld_double(filename,len_trim(filename),Ren_inelastic,Size_h)
write(filename,*), trim(ID), '_tave_Joule_heating_x.txt'
call saveld_double(filename,len_trim(filename),Ren_field,Size_h)
write(filename,*), trim(ID), '_Flux_LHS_Hem_t.txt'
call saveld_double(filename,len_trim(filename),Flux_Hem_l_S,Npoints)
write(filename,*), trim(ID), '_Flux_RHS_Hem_t.txt'
call saveld_double(filename,len_trim(filename),Flux_Hem_sh_S,Npoints)
write(filename,*), trim(ID), '_Flux_LHS_He2m_t.txt'
call saveld_double(filename,len_trim(filename),Flux_He2m_l_S,Npoints)
write(filename,*), trim(ID), '_Flux_RHS_He2m_t.txt'
call saveld_double(filename,len_trim(filename),Flux_He2m_sh_S,Npoints)
write(filename,*), trim(ID), '_Flux_LHS_Hep_t.txt'
call saveld_double(filename,len_trim(filename),Flux_Hep_l_S,Npoints)
write(filename,*), trim(ID), '_Flux_RHS_Hep_t.txt'
call saveld_double(filename,len_trim(filename),Flux_Hep_sh_S,Npoints)
write(filename,*), trim(ID), '_Flux_LHS_e_t.txt'
call saveld_double(filename,len_trim(filename),Flux_e_l_S,Npoints)
write(filename,*), trim(ID), '_Flux_RHS_e_t.txt'
call saveld_double(filename,len_trim(filename),Flux_e_sh_S,Npoints)
write(filename,*), trim(ID), '_run_info.txt'
open(1008,file=filename,access=",append")
write(1008,*), "Simulation finished on ", t1(1),"-",t1(2),"-",t1(3)," at ",t1(5),":",t1(6),":",t1(7)
close(1008)
write(*,'(A,I4.4,A,I2.2,A,I2.2,A,I2.2,A,I2.2,A,I2.2)') "Simulation started on ",t0(1),"-",t0(2),"-",t0(3)," at ",t0(5),"-",t0(6),":",t0(7)
write(*,'(A,I4.4,A,I2.2,A,I2.2,A,I2.2,A,I2.2,A,I2.2)') "Simulation finished on ",t1(1),"-",t1(2),"-",t1(3)," at ",t1(5),":",t1(6),":",t1(7)
end

---------------------------------------------------------------

%---------------------------------------------------------------

tDMA.f90

!Subfunction of TDMA - Tridiagonal matrix
!A x_i= B x_i+1 + C x_i-1 + D

Function TDMA(A,B,C,D,n) Result(TDMA_Result)
Implicit None
Integer::n
Real(8),Intent(in),Dimension(1:n):: A,B,C,D
Real(8),Dimension(1:n)::TDMA_result, P, Q
Integer::step_h

Do step_h=1,n
if (step_h==1) then
  P(step_h)=B(step_h)/A(step_h)
  Q(step_h)=D(step_h)/A(step_h)
else
  P(step_h)=B(step_h)/(A(step_h)-C(step_h)*P(step_h-1))
  Q(step_h)=(D(step_h)+C(step_h)*Q(step_h-1))/(A(step_h)-C(step_h)*P(step_h-1))
end if
end do
Do step_h=n,1,-1
if (step_h==n) then
  P(step_h)=0
  TDMA_Result(step_h)=Q(step_h)
else
  TDMA_Result(step_h)=P(step_h)*TDMA_Result(step_h+1)+Q(step_h)
end if
end do
TDMA_Result=abs(TDMA_Result)
end Function TDMA

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

parser.f90

subroutine command_parser(Narg,command_line,dmp_flag,dp,RF_cycle_Max)
use global
implicit none
Integer:: pos1,pos2,Narg,dp
Integer::dmp_flag
Integer::RF_cycle_Max
Integer,parameter::RF_cycle_Max_default=25000 ! Number of rf cycles
Character(len=512):: command_line
Character(len=512):: filename

!Check that an even number of parameters are given
if (Narg==0 .OR. mod(Narg,2).NE.0) then
  write(*,*:"Usage: fl_he -i <input_file> [-d <dump_file>]"
  call exit(1)
end if

!INPUT FILE NAME
-----------------
!Find input file name location
pos1=index(command_line,' -i ')
if (pos1.EQ.0) then
  write(*,*:"Usage: fl_he -i <input_file> [-d <dump_file>]"
  call exit(1)
end if

!Read input file name

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pos2=index(command_line(pos1+4:),' ',
if (pos1+pos2>len_trim(command_line)) pos2=len_trim(command_line)-pos1-2 
filename=command_line(pos1+4:pos1+pos2+2) 
Add inp extension if needed 
if (index(trim(filename),'inp')==0) then 
filename=trim(filename)/'.inp' 
end if 
ID_inp=filename 
%Initialize the variable ID to identify output files
ID=filename(1:len(trim(filename))-4) //ID=filename(1:len(trim(filename))-4) 
call run_number(ID) !Get run ID

[!DUMP FILE NAME
-------------]
!Find dump file name location
pos1=index(command_line,' -d ') 
if (pos1==0) then ! No dump file provided 
ID_dump=trim(ID) //'.dmp' 
dmp_flag=0 
else 
!Read dump file name 
pos2=index(command_line(pos1+4:),' ',
if (pos1+pos2>len_trim(command_line)) pos2=len_trim(command_line)-pos1-2 
filename=command_line(pos1+4:pos1+pos2+2) 
!Initialize the variable ID to identify output files 
ID_dump=trim(filename) 
dmp_flag=1 
end if 

[!DUMP PERIOD
-------------]
!Find dump period location
pos1=index(command_line,' -dp ') 
if (pos1==0) then ! No dump file provided 
dp=dp_default 
else 
!Read dump period 
pos2=index(command_line(pos1+5:),' ',
if (pos1+pos2>len_trim(command_line)) pos2=len_trim(command_line)-pos1-3 
filename=command_line(pos1+5:pos1+pos2+3) 
read(filename,*l dp 
end if 

[!MAX. NUMBER OF RF CYCLES
------------------------]
!Find location of max. # rf cycles 
pos1=index(command_line,' -s ') 
if (pos1==0) then ! Max. # of rf cycles not specified 
RF_cycle_Max=RF_cycle_Max_default 
else 
!Read max # of rf cycles 
pos2=index(command_line(pos1+4:),' ',
if (pos1+pos2>len_trim(command_line)) pos2=len_trim(command_line)-pos1-2 
filename=command_line(pos1+4:pos1+pos2+2) 
read(filename,*l RF_cycle_Max 
end if 
if (RF_cycle_Max>RF_cycle_Max_default) then 
write(*,*) "Error: The number of rf cycles to be simulated has to be
less than RF_cycle_max_default." 
write(*,*) "Increase RF_cycle_max_default in the input file!" 
call exit(1) 
end if 
end

efield.f90

subroutine estimate_Efield(step_t, double_dx, Esign_LHS, ESign_RHS)
use global 
use m_flux 
implicit none
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Integer, parameter:: criteria_Efield_max=20 !!Max. number of iterations
Integer, parameter:: criteria_tol=1e-6
Integer:: criteria_Efield
Real:: double dx
Real(8) :: De-1, De2
Integer:: step_h, step_t, Esign_LHS, Esign_RHS
Real:: D_e_k, D_e_k_l, Del_avg_k, Del_Efield_f, Del_Efield_mid, voltage_ds
Real:: fne, fnHe, fnHe2p, fnHep, fnNp, fnN2p
Real:: Del_k, Del_k_l, Del_avg_k

if ((source_type=="v") or (source_type=="V") ) then

D_e_1=mu_e*(energy(step_h-1,1)+energy(step_h,1))/3.0
D_e_2=mu_e*(energy(step_h,1)+energy(step_h+1,1))/3.0

Index_e(step_h)=mu_e/D_e_1*Efield_mid(step_h,2)*Del_k
Flux_e(step_h)=flux(Index_e(step_h),D_e_1/De_k_l,n_e(step_h-1,1),n_e(step_h,1))
Index_Hep(step_h)=mu_Hep/D_Hep*Efield_mid(step_h,2)*Del_k
Flux_Hep(step_h)=flux(Index_Hep(step_h),D_Hep/De_k_l,n_Hep(step_h-1,1),n_Hep(step_h,1))
Index_He2p(step_h)=mu_He2p/D_He2p*Efield_mid(step_h,2)*Del_k
Flux_He2p(step_h)=flux(Index_He2p(step_h),D_He2p/De_k_l,n_He2p(step_h-1,1),n_He2p(step_h,1))

Index_Np(step_h)=mu_Np/D_Np*Efield_mid(step_h,2)*Del_k
Flux_Np(step_h)=flux(Index_Np(step_h),D_Np/De_k_l,n_Np(step_h-1,1),n_Np(step_h,1))

Index_Efield_mid(step_h+1,2)=Efield_mid(step_h+1,1)
end if

! criteria_Efield=0; Del_Efield_f=0
!

do while (criteria_Efield==0)
criteria_Efield=criteria_Efield+1;
criteria_Efield=1; Del_Efield_f=0

do while (criteria_Efield>0)
criteria_Efield=criteria_Efield+1
if (criteria_Efield==2) then

Efield_mid(step_h+1,2)=Efield_mid(step_h+1,1)
end if

Index_e(step_h+1)=mu_e/D_e_2*Efield_mid(step_h+1,2)*Del_k
Flux_e(step_h+1)=flux(Index_e(step_h+1),D_e_2/De_k_l,n_e(step_h+1,1),n_e(step_h+1,1))
fne=-(flux_e(step_h+1)-flux_e(step_h))/Del_avg_k
Index_Hep(step_h+1)=mu_Hep/D_Hep*Efield_mid(step_h+1,2)*Del_k
Flux_Hep(step_h+1)=flux(Index_Hep(step_h+1),D_Hep/De_k_l,n_Hep(step_h+1,1),n_Hep(step_h+1,1))
fHep=-(flux_Hep(step_h+1)-flux_Hep(step_h))/Del_avg_k
Index_He2p(step_h+1)=mu_He2p/D_He2p*Efield_mid(step_h+1,2)*Del_k
Flux_He2p(step_h+1)=flux(Index_He2p(step_h+1),D_He2p/De_k_l,n_He2p(step_h+1,1),n_He2p(step_h+1,1))
fHe2p=-(flux_He2p(step_h+1)-flux_He2p(step_h))/Del_avg_k

Index_Np(step_h+1)=mu_Np/D_Np*Efield_mid(step_h+1,2)*Del_k
Flux_Np(step_h+1)=flux(Index_Np(step_h+1),D_Np/De_k_l,n_Np(step_h+1,1),n_Np(step_h+1,1))
fNp=-(flux_Np(step_h+1)-flux_Np(step_h))/Del_avg_k
Index_N2p(step_h+1)=mu_N2p/D_N2p*Efield_mid(step_h+1,2)*Del_k
Flux_N2p(step_h+1)=flux(Index_N2p(step_h+1),D_N2p/De_k_l,n_N2p(step_h+1,1),n_N2p(step_h+1,1))
fN2p=-(flux_N2p(step_h+1)-flux_N2p(step_h))/Del_avg_k

Del_Efield_mid=Del_avg_k*q_eps*(n_Hep(step_h,1)+Del_t*fHep+ &
n_He2p(step_h,1)+Del_t*fnHe2p+ &
n_Np(step_h,1)+Del_t*fnNp+ &
n_N2p(step_h,1)+Del_t*fnN2p-(n_e(step_h,1)+Del_t*fne)
if (abs((Del Efield_mid-Del Efield_f)/Efield_mid(step_h+1,2))<criteria_tol .OR. criteria_Efield>criteria_Efield_max) then
    criteria_Efield=0
end if
if (abs((Del Efield_mid-Del Efield_f)/Efield_mid(step_h+1,2))<criteria_tol .OR. criteria_Efield>criteria_Efield_max) then
    if (criteria_Efield>criteria_Efield_max) then
        write("*",") "WARNING: Maximum number of iterations reached -
    end if
    criteria_Efield=-1
end if
Del Efield_f=Del Efield_mid
end do
Efield(step_h+1,2)=2.0*Efield_mid(step_h+1,2)-Efield_mid(step_h,2)
end do
do step_h=hh,2,-1
    Del k=x(step_h)-x(step_h-1)
    Del_k=x(step_h+1)-x(step_h)
    Del_avg_k=(Del_k+Del_k_l)/2.0
    D_e=mu e*(engy(step_h-1,1)+engy(step_h,1))/3.0
    D_e=mu e*(engy(step_h,1)+engy(step_h+1,1))/3.0
    Index_e(step_h+1)=mu e/D_e*Efield_mid(step_h,2)*Del_k
    Flux e(step_h+1)=flux(Index_e(step_h+1),D_e/Del_k_l,n_e(step_h-1,1),n_e(step_h,1),n_e(step_h+1,1))
    Index_Hep(step_h+1)=mu Hep/D Hep*Efield_mid(step_h,2)*Del_k
    Flux Hep(step_h+1)=flux(Index_Hep(step_h+1),D Hep/Del_k_l,n Hep(step_h,1),n Hep(step_h+1,1))
    Index He2p(step_h+1)=mu He2p/D He2p*Efield_mid(step_h,2)*Del_k
    Flux He2p(step_h+1)=flux(Index He2p(step_h+1),D He2p/Del_k_l,n He2p(step_h,1),n He2p(step_h+1,1))
    !*******************************************
    Index Np(step_h+1)=mu Np/D Np*Efield_mid(step_h+1,2)*Del k
    Flux Np(step_h+1)=flux(Index Np(step_h+1),D Np/Del_k_l,n Np(step_h,1),n Np(step_h+1,1))
    Index N2p(step_h+1)=mu N2p/D N2p*Efield_mid(step_h,2)*Del k
    Flux N2p(step_h+1)=flux(Index N2p(step_h+1),D N2p/Del_k_l,n N2p(step_h,1),n N2p(step_h+1,1))
    !*******************************************
end do
if (Del_Efield_f=Del_Efield_mid) then
    !do while (criteria_Efield=0)!
    !criteria_Efield=criteria_Efield+1
    !criteria_Efield=1; Del_Efield_f=0;
    !do while (criteria_Efield>0)
    !criteria_Efield=criteria_Efield+1
end if
if (criteria_Efield=2) then
    Efield_mid(step_h+1,1,Efield_mid(step_h,1,1))
end if

Appendix

\[
\text{fnHe2p} = \frac{\text{Flux}_{\text{He2p}}(\text{step}_h+1) - \text{Flux}_{\text{He2p}}(\text{step}_h)}{\text{Del}_{\text{avg}}}
\]

\[
\text{Index}_{\text{Np}}(\text{step}_h) = \frac{\mu_{\text{Np}}}{D_{\text{Np}}} \cdot \text{Efield}_{\text{mid}}(\text{step}_h) \cdot \text{Del}_{k_1}
\]

\[
\text{Flux}_{\text{Np}}(\text{step}_h) = \text{flux}(-\text{Index}_{\text{Np}}(\text{step}_h), D_{\text{Np}}/\text{Del}_{k_1}, n_{\text{Np}}(\text{step}_h, 1))
\]

\[
\text{fnNp} = \frac{\text{Flux}_{\text{Np}}(\text{step}_h+1) - \text{Flux}_{\text{Np}}(\text{step}_h)}{\text{Del}_{\text{avg}}}
\]

\[
\text{Index}_{\text{N2p}}(\text{step}_h) = \frac{\mu_{\text{N2p}}}{D_{\text{N2p}}} \cdot \text{Efield}_{\text{mid}}(\text{step}_h, 2) \cdot \text{Del}_{k_1}
\]

\[
\text{Flux}_{\text{N2p}}(\text{step}_h) = \text{flux}(-\text{Index}_{\text{N2p}}(\text{step}_h), D_{\text{N2p}}/\text{Del}_{k_1}, n_{\text{N2p}}(\text{step}_h, 1))
\]

\[
\text{fnN2p} = \frac{\text{Flux}_{\text{N2p}}(\text{step}_h+1) - \text{Flux}_{\text{N2p}}(\text{step}_h)}{\text{Del}_{\text{avg}}}
\]

\[
\text{Del}_{\text{Efield}_{\text{mid}}} = \text{Del}_{\text{avg}} \cdot \varepsilon \cdot \left( n_{\text{HeNp}}(\text{step}_h, 1) + \text{Del}_{t} \cdot \text{fnHeNp} + \text{Del}_t \cdot \text{HeNp} + \text{Del}_t \cdot \text{fnNp} + \text{Del}_t \cdot \text{fnNp} + \text{Del}_t \cdot \text{HeNp} + \text{Del}_t \cdot \text{Np} \right)
\]

\[
\text{Efield}_{\text{mid}}(\text{step}_h, 2) = \text{Efield}_{\text{mid}}(\text{step}_h, 2) - \text{Del}_{\text{Efield}_{\text{mid}}}
\]

if \((\text{abs}(\text{Del}_{\text{Efield}_{\text{mid}}} - \text{Del}_{\text{Efield}_{\text{f}}})/\text{Efield}_{\text{mid}}(\text{step}_h, 2)) < 1e-8 \) OR. \( \text{criteria}_{\text{Efield}} > \text{criteria}_{\text{Efield}_{\text{max}}}) \) then

criteria_{Efield}=0

end if

\[
\text{Del}_{\text{Efield}_{\text{f}}} = \text{Del}_{\text{Efield}_{\text{mid}}}
\]

end do

\[
\text{Efield}(\text{step}_h, 2) = 2 \cdot \text{Efield}_{\text{mid}}(\text{step}_h, 2) - \text{Efield}(\text{step}_h, 2)
\]

end do

Reactions.f90

subroutine reaction_rates()
use global
implicit none
integer :: i

! Electron elastic collisions
\[
E(0,:) = 1.6E-16/(\text{engy}(:,1)+10.0)**1.0 \cdot (2.0*1.6E-19*\text{engy}(:,1)/\text{Mass}_e)**0.5 \cdot 100.0
\]
\[
R(0,:) = K(0,:) \cdot n_e(:,1) \cdot n_{\text{He}}(:,1)
\]
\[
\text{Del}_{\text{engy}}(0) = 3.0 \cdot \text{Mass}_e/\text{Mass}_{\text{He}}
\]

! Ground state ionization: e + He -> He^+ + e \([1,2]\]
\[
K(3,:) = 1.5E-9 \cdot \left( \text{two-thirds} \cdot \text{engy}(:,1) \right)^{0.68} \cdot \exp(-24.6/(\text{two-thirds} \cdot \text{engy}(:,1)))
\]
\[
R(3,:) = K(3,:) \cdot n_e(:,1) \cdot n_{\text{He}}(:,1)
\]
\[
\text{Del}_{\text{engy}}(3) = 24.6
\]

! Step ionization: e + He^+ -> He^2+ + e \([1,2]\]
\[
K(4,:) = 1.28E-7 \cdot \left( \text{two-thirds} \cdot \text{engy}(:,1) \right)^{0.68} \cdot \exp(-4.78/(\text{two-thirds} \cdot \text{engy}(:,1)))
\]
\[
R(4,:) = K(4,:) \cdot n_e(:,1) \cdot n_{\text{He}}(:,1)
\]
\[
\text{Del}_{\text{engy}}(4) = 4.78
\]

! Superelastic ionization: e + He2m -> He2p + 2e \([1]\]
\[
K(5,:) = 9.75E-10 \cdot \left( \text{two-thirds} \cdot \text{engy}(:,1) \right)^{0.71} \cdot \exp(-3.4/(\text{two-thirds} \cdot \text{engy}(:,1)))
\]
\[
R(5,:) = K(5,:) \cdot n_e(:,1) \cdot n_{\text{He2m}}(:,1)
\]
\[
\text{Del}_{\text{engy}}(5) = 3.4
\]

! Dissociative recombination: e + He2p -> He^+ + He \([1]\]
\[
R(6,:) = 5.002E-9 \cdot \left( \text{two-thirds} \cdot \text{engy}(:,1) \right)^{-0.5}
\]
\[ R(6, :) = K(6, :) \cdot n_{e(1, :1)} \cdot n_{He2p(1, :1)} \]
\[ \text{Del_engy}(6) = 0.0 \]

1. Metastable pooling: \( \text{Hem} + \text{Hem} \rightarrow \text{He} + \text{He} + e \) [1]
\[ K(7, :) = 2.7E-10 \]
\[ R(7, :) = K(7, :) \cdot n_{\text{Hem}(1, :1)} \cdot n_{\text{He}(1, :1)} \]
\[ \text{Del_engy}(7) = -15.0 \]

1. Three body Hem quenching: \( \text{Hem} + 2\text{He} \rightarrow \text{He} + \text{He} + \text{e} \) [1]
\[ K(8, :) = 1.3E-33 \]
\[ R(8, :) = K(8, :) \cdot n_{\text{Hem}(1, :1)} \cdot n_{\text{He}(1, :1)} \cdot n_{\text{He}(1, :1)} \]
\[ \text{Del_engy}(8) = 0.0 \]

1. Ton conversion: \( \text{Hep} + 2\text{He} \rightarrow \text{He} + \text{He} + e \) [1]
\[ K(9, :) = 1.5E-9 \]
\[ R(9, :) = K(9, :) \cdot n_{\text{Hep}(1, :1)} \cdot n_{\text{He}(1, :1)} \cdot n_{\text{He}(1, :1)} \]
\[ \text{Del_engy}(9) = 0.0 \]

1. Dimer metastable pooling: \( \text{He} + \text{He} \rightarrow \text{Hep} + \text{He} + e \) [3]
\[ K(10, :) = 1.0E-8 \]
\[ R(10, :) = K(10, :) \cdot n_{\text{He}(1, :1)} \cdot n_{\text{He}(1, :1)} \cdot n_{\text{He}(1, :1)} \]
\[ \text{Del_engy}(10) = 0.0 \]

1. Electron recombination: \( e + \text{He} \rightarrow 2\text{He} \) [4]
\[ K(11, :) = 2.0E-27 \]
\[ R(11, :) = K(11, :) \cdot n_{\text{e}(1, :1)} \cdot n_{\text{He}(1, :1)} \cdot n_{\text{He}(1, :1)} \]
\[ \text{Del_engy}(11) = 0.0 \]

1. Three body electron recombination: \( e + \text{He} \rightarrow 3\text{He} \) [4]
\[ K(12, :) = 2.0E-27 \]
\[ R(12, :) = K(12, :) \cdot n_{\text{e}(1, :1)} \cdot n_{\text{He}(1, :1)} \cdot n_{\text{He}(1, :1)} \]
\[ \text{Del_engy}(12) = 0.0 \]

if (per_N2 > 0.0) then

1. \( \text{He}^{23S} + \text{N}2 \rightarrow (1-r9)\text{N}2+(\text{B}2\text{u}) + (1-r9)\text{N}2+(\text{X}2\text{g}) + \text{He} + e \) \( r9 = 0.5 \) [5]
\[ K(13, :) = 7.6E-11 \]
\[ R(13, :) = K(13, :) \cdot n_{\text{He}(1, :1)} \cdot n_{\text{N}2(1, :1)} \]
\[ \text{Del_engy}(13) = 0.0 \]

1. \( \text{He}^{23S} + \text{He} + \text{Ne} \rightarrow (1-r7)\text{N}2+(\text{B}2\text{u}) + (1-r7)\text{N}2+(\text{X}2\text{g}) + 2\text{He} + e \) \( r7 = 0.5 \) [5]
\[ K(14, :) = 3.3E-30 \]
\[ R(14, :) = K(14, :) \cdot n_{\text{He}(1, :1)} \cdot n_{\text{N}2(1, :1)} \]
\[ \text{Del_engy}(14) = 0.0 \]

1. \( \text{He} + \text{N}2 \rightarrow (1-r4)\text{N}2+(\text{X}2\text{g}) + (1-r4)\text{N}2+(\text{X}2\text{g}) + 2\text{He} + e \) \( r4 = 0.5 \) [5]
\[ K(16, :) = 1.2E-9 \]
\[ R(16, :) = K(16, :) \cdot n_{\text{He}(1, :1)} \cdot n_{\text{N}2(1, :1)} \]
\[ \text{Del_engy}(16) = 0.0 \]

1. \( \text{He} + \text{N}2 + \text{He} \rightarrow (1-r3)\text{N}2+(\text{X}2\text{g}) + (1-r3)\text{N}2+(\text{X}2\text{g}) + 2\text{He} + e \) \( r3 = 0.5 \) [5]
\[ K(17, :) = 2.2E-29 \]
\[ R(17, :) = K(17, :) \cdot n_{\text{He}(1, :1)} \cdot n_{\text{N}2(1, :1)} \]
\[ \text{Del_engy}(17) = 0.0 \]

1. \( \text{He}^{2+} + \text{N}2 \rightarrow (r9)\text{N}2+(\text{B}2\text{u}) + (1-r9)\text{N}2+(\text{X}2\text{g}) + 2\text{He} + e \) \( r9 = 0.5 \) [From raja]
\[ K(15, :) = 7.0E-11 \]
\[ R(15, :) = K(15, :) \cdot n_{\text{He}^{2+}(1, :1)} \cdot n_{\text{N}2(1, :1)} \]
\[ \text{Del_engy}(15) = 0.0 \]

1. \( \text{He} + \text{H} + \text{N}2 \rightarrow (1-r4)\text{N}2+(\text{X}2\text{g}) + (1-r4)\text{N}2+(\text{X}2\text{g}) + 2\text{He} + e \) \( r4 = 0.5 \) [5]
\[ K(18, :) = 1.1E-9 \]
\[ R(18, :) = K(18, :) \cdot n_{\text{He}(1, :1)} \cdot n_{\text{N}2(1, :1)} \]
\[ \text{Del_engy}(18) = 0.0 \]

1. \( \text{He}^{2+} + \text{N}2 \rightarrow (r5)\text{N}2+(\text{B}2\text{u}) + (1-r5)\text{N}2+(\text{X}2\text{g}) + 3\text{He} + e \) \( r5 = 0.75 \) [5]
\[ K(19, :) = 1.36E-29 \]
\[ R(19, :) = K(19, :) \cdot n_{\text{He}^{2+}(1, :1)} \cdot n_{\text{N}2(1, :1)} \]
\[ \text{Del_engy}(19) = 0.0 \]

1. \( \text{N}2+(\text{B}2\text{u}) \rightarrow \text{N}2+(\text{X}2\text{g}) + hv \) [5]
\[ K(20, :) = 1.5E7 \]
\[ R(ZQ) = K(20,:) \cdot n_{N2pb(:,1)} \]

\[ \text{Del_engy}(20) = 0.0 \]

\[ \text{N2} + (B2U) + e \rightarrow 2N \quad [5] \]

\[ R(21,:) = 1.0e^{-7} \]

\[ \text{Del_engy}(21) = 0.0 \]

\[ \text{N2} + (X2g) + e \rightarrow 2N \quad [5] \]

\[ R(22,:) = 1.0e^{-7} \]

\[ \text{Del_engy}(22) = 0.0 \]

\[ \text{N} + e \rightarrow N \quad [7] \]

\[ K(23,:) = 5.0e^{-9} \]

\[ R(23,:) = K(23,:) \cdot n_{Np(:,1)} \cdot n_e(:,1) \]

\[ \text{Del_engy}(23) = 0.0 \]

\[ \text{N2} + e \rightarrow 2N + e \quad [7] \]

\[ K(24,:) = 2.7976E^{-9} \cdot (2.0/3.0 \cdot \text{engy(:,1)})^{-0.7} \cdot \exp(-9.757/(2.0/3.0 \cdot \text{engy(:,1)})) \]

\[ R(24,:) = K(24,:) \cdot n_{N2x(:,1)} \cdot n_e(:,1) \]

\[ \text{Del_engy}(24) = 9.757 \]

\[ e + N \rightarrow N + 2e \quad [7] \]

\[ K(25,:) = 8.401E^{-5} \cdot \exp(-14.5/(2.0/3.0 \cdot \text{engy(:,1)})) \]

\[ R(25,:) = K(25,:) \cdot n_{Np(:,1)} \cdot n_e(:,1) \]

\[ \text{Del_engy}(25) = 14.5 \]

\[ e + \text{N2} \rightarrow \text{N2} + (X2g) + 2e \quad [7] \]

if (Bolsig == "n" OR Bolsig == "N")

\[ K(26,:) = 2.705E^{-6} \cdot (2.0/3.0 \cdot \text{engy(:,1)})^{-0.3} \cdot \exp(-15.6/(2.0/3.0 \cdot \text{engy(:,1)})) \]

else

\[ K(26,:) = 1.0e^{-6} \cdot \exp(-26.38 - 0.7135 \cdot \log(\text{engy(:,1)}) - 68.94/\text{engy(:,1)} + 120.3/(\text{engy(:,1)} \cdot \text{engy(:,1)}) \]

\& \text{133.9}/(\text{engy(:,1)} \cdot \text{engy(:,1)} \cdot \text{engy(:,1)}) \]

endif

\[ R(26,:) = K(26,:) \cdot n_{N2px(:,1)} \cdot n_e(:,1) \]

\[ \text{Del_engy}(26) = 15.6 \]

\[ e + N2 \rightarrow N2 + (X2g) + e \quad [8] \]

if (Bolsig == "n" OR Bolsig == "N")

\[ K(27,:) = 1.3E^{-1} \cdot (2.0/3.0 \cdot \text{engy(:,1)})^{-0.65} \cdot \exp(-3.17/(2.0/3.0 \cdot \text{engy(:,1)})) \]

else

\[ K(27,:) = 1.0e^{-6} \cdot \exp(-27.8 - 0.8933 \cdot \log(\text{engy(:,1)}) - 71.35/\text{engy(:,1)} + 119/\text{engy(:,1)} \cdot \text{engy(:,1)} \]

\& \text{136.6}/(\text{engy(:,1)} \cdot \text{engy(:,1)} \cdot \text{engy(:,1)}) \]

endif

\[ R(27,:) = K(27,:) \cdot n_{N2px(:,1)} \cdot n_e(:,1) \]

\[ \text{Del_engy}(27) = 3.17 \]

else

\[ K(13:28,:) = 0 \]

R(13:28,:) = 0

endif

\[ e + He \rightarrow He*(339) + e \quad [11] \]

if (Bolsig == "n" OR Bolsig == "N")

\[ K(29,:) = 9.7E^{-10} \cdot (2.0/3.0 \cdot \text{engy(:,1)})^{-0.31} \cdot \exp(-22.7/(2.0/3.0 \cdot \text{engy(:,1)})) \]

else

\[ K(29,:) = 1.0e^{-6} \cdot \exp(-5.936 - 7.663 \cdot \log(\text{engy(:,1)}) - \text{108.2}/\text{engy(:,1)} + 339.4/(\text{engy(:,1)} \cdot \text{engy(:,1)}) \]

\& 311.6/(\text{engy(:,1)} \cdot \text{engy(:,1)} \cdot \text{engy(:,1)}) \]

endif

\[ R(29,:) = K(29,:) \cdot n_{He(:,1)} \cdot n_e(:,1) \]
Appendix

\begin{verbatim}
Del_engy(29)=22.7
He + He => He*(23P) + e \[11\]
if (Solsig=='n' .OR. Bolsig=='N') then
  K(30,:)=7.7E-10*(2.0/3.0*engy(:,1))**(0.31)*exp(-20.9/(2.0/3.0*engy(:,1))
else
  K(30,:)=1.0e6*exp(-9.931-6.199*log(engy(:,1)) &
  -294.5/(engy(:,1)*engy(:,1)*engy(:,1)))
endif
R(30,:)=K(30,:)*n_He(:,1)*n_e(:,1)
Del_engy(30)=20.9

He*(23P) + 2He => He2* + He \[11\]
R(31,:)=1.6e-32
R(31,:)=K(31,:)*n_He_23p(:,1)*n_He(:,1)*n_He(:,1)
Del_engy(31)=0

He*(23S) => He*(23S) + 706 \[11\]
K(32,:)=7.8e7
R(32,:)=K(32,:)*n_He_33s(:,1)
Del_engy(32)=0

He*(23P) => He*(23S) + 1083 \[11\]
K(33,:)=1.022e7
R(33,:)=K(33,:)*n_He_23p(:,1)
Del_engy(33)=0

He*(33S) + He => He2* + e \[11\]
K(34,:)=0.21e11
R(34,:)=K(34,:)*n_He_33s(:,1)*n_He(:,1)
Del_engy(34)=0

He*(33S) + e => He + e* \[11\]
K(35,:)=6.0e-10*(2.0/3.0*engy(:,1))**(0.31)
R(35,:)=K(35,:)*n_He_33s(:,1)*n_e(:,1)
Del_engy(35)=22.7

He*(23P) + e => He + e \[11\]
K(36,:)=4.0e-10*(2.0/3.0*engy(:,1))**(0.31)
R(36,:)=K(36,:)*n_He_23p(:,1)*n_e(:,1)
Del_engy(36)=20.9

He*(33S) + He*(33S) => He* + He + e \[11\]
K(37,:)=1.0e-9
R(37,:)=K(37,:)*n_He_33s(:,1)*n_He_33s(:,1)
Del_engy(37)=20.8

He*(23P) + He*(23P) => He* + He + e \[11\]
K(38,:)=1.0e-9
R(38,:)=K(38,:)*n_He_23p(:,1)*n_He_23p(:,1)
Del_engy(38)=17.2

He*+e=>He 335 + e
K(39,:)=4.8E-8*(2.0/3.0*engy(:,1))**(-0.2)*exp(-2.9/(2.0/3.0*engy(:,1)))
R(39,:)=K(39,:)*n_He_33s(:,1)*n_e(:,1)
Del_engy(39)=2.9

He 23P +e=>He 335 + e
K(40,:)=3.5E-8*(2.0/3.0*engy(:,1))**(-0.12)*exp(-1.8/(2.0/3.0*engy(:,1)))
R(40,:)=K(40,:)*n_He_23p(:,1)*n_e(:,1)
Del_engy(40)=1.8

He*+e=>He 23P + e
K(41,:)=1.1E-6*(2.0/3.0*engy(:,1))**(-0.05)*exp(-1.1/(2.0/3.0*engy(:,1)))
R(41,:)=K(41,:)*n_He(:,1)*n_e(:,1)
Del_engy(41)=1.1

end do
end if
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endi
!! UNIFORM GRID !******************************************************************************

subroutine energy_e_uniform()
use global
use m_tdma
implicit none
Real  :: dx, dx_2, dt, dx2, mudx, mu_dx
Real (B) :: al, a1, a2, b2
Real (B) :: D_e, D_e_2
Integer :: step_h

dx=x(2)-x(1)
dx_2=dx/2

dt=dx_2/2.0

& *Kengo(24,step_h)*+Kengo(25,step_h)*+Kengo(26,step_h)*+Kengo(27,step_h)*+Kengo(28,step_h)*
& *Kengo(29,step_h)*
& *Kengo(30,step_h)*+Kengo(35,step_h)*+Kengo(36,step_h)*+Kengo(37,step_h)*+Kengo(38,step_h)*
& *Kengo(39,step_h)*
& *Kengo(40,step_h)*+Kengo(41,step_h)*

! K_L_elastic(step_h) = 5.0*Mass_e/Mass_He*n_He(step_h,1)*n_e(step_h,1)*(2.0/3.0*energy(step_h,1)-393.0/11594.0)*D_e
end do

! LHS boundary
A(1)=1.0; B(1)=0; C(1)=0; D(1)=0.5

! RHS boundary
A(Size_h)=1.0; B(Size_h)=0; C(Size_h)=0; D(Size_h)=0.5

engy(:,2)=TOMA(A,B,C,D) call bound(engy,le-3,Size_h)
end

******************************************************************************

! NONUNIFORM GRID !******************************************************************************

subroutine energy_eq1()
use global
use m_tdma
implicit none
Real (B) :: D_e, D_e_2
Real  :: step_h
Real :: Del_k, Del_k_1, Del_k_avg

! Solution of the energy equation
coeff(Index_e(step_h+1),a1,a2)
Flux_e(step_h+1)=D_e_1*(a1*n_e(step_h,1)-b1*n_e(step_h,1))
Flux_e(step_h+1)=D_e_2*(a2*n_e(step_h,1)-b2*n_e(step_h,1))

K_L_elastic(step_h) = 85.0*16/(energy(step_h,1)+10.0)**1.1*(2.0*1.6E-19*energy(step_h,1)/Mass_e)**(0.5)*100.0

A(step_h)=(5.0/3.0*Flux_e(step_h+1)+2.0*D_e_1*n_e(step_h,1)+n_e(step_h,2))/2.0
&B(step_h)=(5.0/3.0*Flux_e(step_h+1)+2.0*D_e_1*n_e(step_h,1)+n_e(step_h,2))/2.0

A(step_h+1)=D_e_1*n_e(step_h,1)+n_e(step_h,2)
&B(step_h+1)=D_e_1*n_e(step_h,1)+n_e(step_h,2)

C(step_h)=(5.0/3.0*Flux_e(step_h)+2.0*D_e_1*n_e(step_h,1)+n_e(step_h,2))/2.0
&C(step_h+1)=D_e_1*n_e(step_h,1)+n_e(step_h,2)

end
\[
D(\text{step } h) = (n_e(\text{step } h, l) \times \text{energy}(\text{step } h, l) - \langle \text{Flux}_e(\text{step } h) \rangle / 4.0 & \\
+ \langle \text{Keny}(1, \text{step } h) \rangle + \langle \text{Keny}(2, \text{step } h) \rangle + \langle \text{Keny}(3, \text{step } h) \rangle + \langle \text{Keny}(4, \text{step } h) \rangle & \\
\langle \text{Keny}(5, \text{step } h) \rangle + \langle \text{Keny}(7, \text{step } h) \rangle & \\
+ \langle \text{Keny}(24, \text{step } h) \rangle + \langle \text{Keny}(25, \text{step } h) \rangle + \langle \text{Keny}(26, \text{step } h) \rangle + \langle \text{Keny}(27, \text{step } h) \rangle + \langle \text{Keny}(29, \text{step } h) \rangle & \\
\langle \text{Keny}(30, \text{step } h) \rangle + \langle \text{Keny}(35, \text{step } h) \rangle + \langle \text{Keny}(36, \text{step } h) \rangle + \langle \text{Keny}(37, \text{step } h) \rangle + \langle \text{Keny}(38, \text{step } h) \rangle & \\
\langle \text{Keny}(39, \text{step } h) \rangle & \\
+ \langle \text{Keny}(40, \text{step } h) \rangle + \langle \text{Keny}(41, \text{step } h) \rangle & \\
+ \langle K_L \text{ elastic}(\text{step } h) \rangle / 3.0 \times \text{Mass}_e / \text{Mass}_He \times n_He(\text{step } h, l) & \\
+ \langle n_e(\text{step } h, l) \rangle / (2.0 / 3.0 \times \text{energy}(\text{step } h, 1) - 333.0 / 11594.0) \times \text{Del}_t / n_e(\text{step } h, 2) & \\
\text{end do} & \\
| \text{LHS boundary} & \\
A(1) = 1.0; B(1) = 0; C(1) = 0; D(1) = 0.5; & \\
| \text{RHS boundary} & \\
A(\text{Size}_h) = 1.0; B(\text{Size}_h) = 0; C(\text{Size}_h) = 0; D(\text{Size}_h) = 0.5; & \\
\text{energy}(2) = \text{TDMA}(A, B, C, D, \text{Size}_h) & \\
call \text{bound(energy, le-3, Size}_h) & \\
\text{end} \\
\]
Appendix

Real, parameter :: two_thirds = 2.0/3.0, five_thirds = 5.0/3.0

Rea1, Dimension (:), allocatable :: hist_max: ne, hist max: nHe, hist max: nHe2p
Real (8), Dimension (:), allocatable :: nHe, n_e, n_Hep, n_He2p, n_Hem, n_He2m, n_He_23p, n_He_33s, n_N2, n_Np, n_He2p, n_N2px, n_N

Real (8), Dimension (:), allocatable :: enegy, Efield, Efield_mid, Current_dse, Diff_Current_e, Drift_Current_e

Real (8), Dimension (:), allocatable :: X, Kenvey, R

Real (8), Dimension (:), allocatable :: Del_energy

Real (8), Dimension (:), allocatable :: A, B, C, D, D1, D2

Real (8), Dimension (:), allocatable :: n_e_S, n_Hep_S, n_He2p_S, n_Hem_S, n_He2m_S, n_He_23p_S, n_He_33s_S, n_N2_S, n_Np_S, n_N2px_S, n_N_S

Real (8), Dimension (:), allocatable :: Re, R1, R2, R3, R4, R5, R6, R7, R8, R9, R10, R11, R12, R13, R14, R15, R16, R17, R18, R19, R20, R21, R22, R

Real (8), Dimension (:), allocatable :: n_He, n_e, n_Hem, n_He2p, n_He2m, n_He_23p, n_He_33s, n_N2, n_Np, n_N2px, n_N

Real (8), Dimension (:), allocatable :: Index_e, Index_Hep, Index_He2p, Index_Np, Index_N2p

Real (8), Dimension (:), allocatable :: Flux_e, Flux_Hep, Flux_He2p, Flux_Np, Flux_N2p

Real (8), Dimension (:), allocatable :: Prf, Peror, Power_avg, PK, pcci, acbias

Real (8), Dimension (:), allocatable :: Ren_inelastic, Ren_elastic, Ren_field

Real (8), Dimension (:), allocatable :: Flux_Hem_1_S, Flux_Hem_sh_S, Flux_He2m_1_S, Flux_He2m_sh_S, Flux_e_S, Flux_e_sh_S, Flux_N_1_S, Flux_N_sh_S, Flux_N2_1_S, Flux_N2_sh_S

Real (8), Dimension (:), allocatable :: Flux_Hep_1_S, Flux_Hep_sh_S, Flux_He2p_1_S, Flux_He2p_sh_S, Flux_Np_1_S, Flux_Np_sh_S, Flux_N2p_1_S, Flux_N2p_sh_S, All_Current_S

Real (8), Dimension (:), allocatable :: Voltage, Power, Current

Character (LEN=256) :: ID, ID_dump, ID_inp

end module global

module m_flux
#endif

Interface

Function flux(ind, D_dx, n1, n2) result (f)
Real (6) :: ind, D_dx, n1, n2
Real (6) :: f
end function flux

end interface

end module m_flux

module m_tdma
#endif

Interface

Function TDMA(A, B, C, D, n) result (TDMA_Result)
Integer :: n
Real (8), Dimension (1:n) :: A, B, C, D
Real (8), Dimension (1:n) :: TDMA_Result
end function TDMA

end interface

end module m_tdma

module m_rms
#endif

Interface

Function rms(v, n) result (rms_v)
Integer :: n
Real, dimension (n) :: v
Real :: rms_v
end function rms

end interface

end module m_rms

subroutine allocate_memory(RF_cycle_Max)
#endif

use global

- 170 -
Implicit none
Integer::RF_cycle_Max
allocate(hist_Max_ne(1:RF_cycle_Max))
allocate(hist_Max_nNep(1:RF_cycle_Max))
allocate(hist_Max_nHem(1:RF_cycle_Max))
allocate(hist_Max_nHemn(1:RF_cycle_Max))
allocate(hist_Max_nHem2n(1:RF_cycle_Max))
allocate(PFr(1:RF_cycle_Max))
allocate(Perror(1:RF_cycle_Max))
allocate(PK(1:RF_cycle_Max))
allocate(Perror_avg(1:RF_cycle_Max))
allocate(PK(1:RF_cycle_Max))
allocate(pci(1:RF_cycle_Max))
allocation(acbias(1:RF_cycle_Max))
allocation(n_N(1:Size_h,1:2))
allocation(n_e(1:Size_h,1:2))
allocation(n_R(1:Size_h,1:2))
allocation(n_Ne(1:Size_h,1:2))
allocation(n_Nem(1:Size_h,1:2))
allocation(n_Nem(1:Size_h,1:2))
allocate(R9(1:Size_h,1:Npoints))
allocate(R10(1:Size_h,1:Npoints))
allocate(R11(1:Size_h,1:Npoints))
allocate(R12(1:Size_h,1:Npoints))
******************************************************************************David
allocate(R13(1:Size_h,1:Npoints))
allocate(R14(1:Size_h,1:Npoints))
allocate(R15(1:Size_h,1:Npoints))
allocate(R16(1:Size_h,1:Npoints))
allocate(R17(1:Size_h,1:Npoints))
allocate(R18(1:Size_h,1:Npoints))
allocate(R19(1:Size_h,1:Npoints))
allocate(R20(1:Size_h,1:Npoints))
allocate(R21(1:Size_h,1:Npoints))
allocate(R22(1:Size_h,1:Npoints))
allocate(R23(1:Size_h,1:Npoints))
allocate(R24(1:Size_h,1:Npoints))
allocate(R25(1:Size_h,1:Npoints))
allocate(R26(1:Size_h,1:Npoints))
allocate(R27(1:Size_h,1:Npoints))
allocate(R28(1:Size_h,1:Npoints))
allocate(R29(1:Size_h,1:Npoints))
allocate(R30(1:Size_h,1:Npoints))
allocate(R31(1:Size_h,1:Npoints))
allocate(R32(1:Size_h,1:Npoints))
allocate(R33(1:Size_h,1:Npoints))
allocate(R34(1:Size_h,1:Npoints))
allocate(R35(1:Size_h,1:Npoints))
allocate(R36(1:Size_h,1:Npoints))
allocate(R37(1:Size_h,1:Npoints))
allocate(R38(1:Size_h,1:Npoints))
allocate(R39(1:Size_h,1:Npoints))
allocate(R40(1:Size_h,1:Npoints))
allocate(R41(1:Size_h,1:Npoints))
******************************************************************************
allocate(x(1:Size_h))
allocate(dx_array(1:Size_h))
allocate(engy_S(1:Size_h,1:Npoints))
allocate(Current_S(1:Size_h,1:Npoints))
allocate(Current_da_S(1:Size_h,1:Npoints))
allocate(Diff_Current_e_S(1:Size_h,1:Npoints))
allocate(Drift_Current_e_S(1:Size_h,1:Npoints))
allocate(Current_e_S(1:Size_h,1:Npoints))
allocate(Current_Hep_S(1:Size_h,1:Npoints))
allocate(Current_Np_S(1:Size_h,1:Npoints))
******************************************************************************
allocate(Current_e(1:Size_h+1,1:2))
allocate(Current_Hep(1:Size_h+1,1:2))
allocate(Current_Np(1:Size_h+1,1:Npoints))
******************************************************************************David
allocate(Ren_elastic(1:Size_h))
allocate(Ren_inelastic(1:Size_h))
allocate(Ren_field(1:Size_h))
allocate(K_L_elastic(1:Size_h))
allocate(Index_e(1:Size_h))
allocate(Index_Hep(1:Size_h))
allocate(Index_Np(1:Size_h))
allocate(Flux_e(1:Size_h))
allocate(Flux_Hep(1:Size_h))
allocate(Flux_Np(1:Size_h))
******************************************************************************
allocate(Flux_e_1_S(1:Npoints))
allocate(Flux_e_sh_S(1:Npoints))
allocate(Flux_Hep_1_S(1:Npoints))
allocate(Flux_Hep_sh_S(1:Npoints))
allocate(Flux_Np_1_S(1:Npoints))
allocate(Flux_Np_sh_S(1:Npoints))
allocate(\text{Flux}_{\text{He2m}}_{\text{sh}}(1:\text{Npoints}))
allocate(\text{Index}_{\text{Np}}(1:\text{Size}_{\text{h}}))
allocate(\text{Index}_{\text{N2p}}(1:\text{Size}_{\text{h}}))
allocate(\text{Flux}_{\text{Np}}(1:\text{Size}_{\text{h}}))
allocate(\text{Flux}_{\text{N2p}}(1:\text{Size}_{\text{h}}))
allocate(\text{Flux}_{\text{N1}}_{\text{S}}(1:\text{Npoints}))
allocate(\text{Flux}_{\text{N2}}_{\text{S}}(1:\text{Npoints}))
allocate(\text{Flux}_{\text{N1}}_{\text{sh}}_{\text{S}}(1:\text{Npoints}))
allocate(\text{Flux}_{\text{N2}}_{\text{sh}}_{\text{S}}(1:\text{Npoints}))
allocate(\text{Flux}_{\text{NP}}_{\text{l}}_{\text{S}}(1:\text{Npoints}))
allocate(\text{Flux}_{\text{N2p}}_{\text{sh}}_{\text{S}}(1:\text{Npoints}))
allocate(\text{Flux}_{\text{N2p}}_{\text{sh}}_{\text{S}}(1:\text{Npoints}))
allocate(\text{All}_{\text{Current}}_{\text{S}}(1:\text{Npoints}))
allocate(\text{Voltage}(1:\text{Size}_{\text{t}+1}))
allocate(\text{Power}(1:\text{Size}_{\text{t}+1}))
allocate(\text{Current}(1:\text{Size}_{\text{t}}))
allocate(\text{Flux}_{\text{p}}(1:\text{Size}_{\text{t}+1}))
allocate(\text{Flux}_{\text{p}}_{\text{sh}}(1:\text{Size}_{\text{t}+1}))
allocate(\text{Flux}_{\text{e}}_{\text{l}}(1:\text{Size}_{\text{t}+1}))
allocate(\text{Flux}_{\text{e}}_{\text{sh}}(1:\text{Size}_{\text{t}+1}))
allocate(\text{Flux}_{\text{He}}_{\text{l}}(1:\text{Size}_{\text{t}+1}))
allocate(\text{Flux}_{\text{He}}_{\text{sh}}(1:\text{Size}_{\text{t}+1}))
allocate(\text{Flux}_{\text{He2m}}_{\text{l}}(1:\text{Size}_{\text{t}+1}))
allocate(\text{Flux}_{\text{He2m}}_{\text{sh}}(1:\text{Size}_{\text{t}+1}))
end subroutine

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%%>%%%flux.f90
function flux(ind,D_dx,nl,n2) result(f)
implicit none
Real (8) :: ind,nl,n2,D_dx
Real (8) :: f,ca,cb
   call coeff(ind,ca,cb);
   f=D_dx*(ca*nl-cb*n2)
end

subroutine coeff(ind,ca,cb)
implicit none
Real (8) :: ca,cb
Real (8) : ind
if (\text{abs}(\text{ind}) \leq 1e-8) then
  ca=1
  cb=1
else if (\text{ind}=10) then
  ca=\text{ind}
  cb=0
else if (\text{ind}=-10) then
  ca=0
  cb=-\text{ind}
else
  \text{cb}=\text{ind}/(\text{exp}(\text{ind})-1)
  ca=\text{exp}(\text{ind})*\text{cb}
end if
end
References


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