Stable atmospheric glow discharges: computational study and applications

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Stable Atmospheric Glow Discharges: Computational Study and Applications

By

Xu Tao Deng

A Doctoral Thesis

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

May 2004

© Xu Tao Deng 2004
Dedicated to: My Family

&

My Fiancé
Abstract

This thesis describes a study of stable atmospheric pressure glow discharges through both a PC-based numerical simulation of their dynamics and exploratory experiments for establishing their decontamination efficacy. The numerical work is based on a one-dimensional fluid model with a commonly adopted hydrodynamic approximation that assumes electron equilibrium with the local electric field. Two gas systems are considered, namely pure helium and helium-nitrogen mixture, and our simulation results agree well with relevant experimental data. Also the numerical study establishes a specific frequency range within which stable helium atmospheric pressure dielectric-barrier glow discharges can be generated, and unravels two distinct plasma disruption mechanisms when the plasma excitation is outside the above mentioned frequency range. Further explored is possible plasma power saving that can be achieved by means of pulsed excitation. It is shown that significant power saving of up to 40% can be achieved by a combination of wave-shaping and pulse-width reduction. Finally through preliminary exploratory experiments, it is shown that atmospheric pressure glow discharge is biologically lethal to food-borne microorganisms and when further developed can form the basis for a novel food decontamination technology.

Key words: gas discharges, glow plasmas, atmospheric, fluid model, computational, decontamination.
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Last but certainly not least I would like to express my love to my parents, sister and brother for their support and love in various manners throughout my studies in the UK. I would not have the opportunity to study abroad without their support, and I would not be able to withstand every past challenge without their greatest love. My love also goes to my fiancé Mr Jinghua Zhang. His encouragement accompanies me through all the difficulties, and his love wipes away all my tears for the pressure these years and enables me face the future with a smile.


6. X. T. Deng and M. G. Kong, "Frequency range for stable generation of atmospheric glow discharges in He and N\textsubscript{2}" presented at 30th IEEE International Conference on Plasma Science, 5A06, Jeju, South Korea, June 2003.


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<thead>
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<th>Definition</th>
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<tbody>
<tr>
<td>$\alpha$</td>
<td>Townsend first ionization coefficient;</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>Townsend second ionization coefficient;</td>
</tr>
<tr>
<td>$\varepsilon_0$</td>
<td>Absolute permittivity;</td>
</tr>
<tr>
<td>$\varepsilon_r$</td>
<td>Relative permittivity;</td>
</tr>
<tr>
<td>$\eta$</td>
<td>Nitrogen percentage content;</td>
</tr>
<tr>
<td>$k$</td>
<td>Boltzmann's constant;</td>
</tr>
<tr>
<td>$\mu$</td>
<td>Mobility;</td>
</tr>
<tr>
<td>$\phi$</td>
<td>Particle flow;</td>
</tr>
<tr>
<td>$\tau$</td>
<td>Pulse width of Gaussian signal;</td>
</tr>
<tr>
<td>$C$</td>
<td>Capacitance;</td>
</tr>
<tr>
<td>$C_g$</td>
<td>Gas capacitance;</td>
</tr>
<tr>
<td>$C_{ds}$</td>
<td>Capacitance of the dielectric layer;</td>
</tr>
<tr>
<td>$d$</td>
<td>Thickness of the dielectric layer;</td>
</tr>
<tr>
<td>$D$</td>
<td>Diffusion coefficient;</td>
</tr>
<tr>
<td>$e$</td>
<td>Electron charge;</td>
</tr>
<tr>
<td>$E$</td>
<td>Electric field;</td>
</tr>
<tr>
<td>$f$</td>
<td>Frequency of the applied voltage source;</td>
</tr>
<tr>
<td>$i$</td>
<td>Discharge current;</td>
</tr>
<tr>
<td>$j$</td>
<td>Discharge current density;</td>
</tr>
<tr>
<td>$K$</td>
<td>Reaction rate;</td>
</tr>
<tr>
<td>$L$</td>
<td>Separation distance between two electrodes;</td>
</tr>
<tr>
<td>$m$</td>
<td>Particle mass;</td>
</tr>
<tr>
<td>$n$</td>
<td>Number density;</td>
</tr>
<tr>
<td>$N$</td>
<td>Number density of the background gas;</td>
</tr>
<tr>
<td>$N_i$</td>
<td>Number of microorganisms survived after the treatment;</td>
</tr>
<tr>
<td>$N_o$</td>
<td>Number of microorganisms on the original samples</td>
</tr>
<tr>
<td>$p$</td>
<td>Gas pressure;</td>
</tr>
<tr>
<td>$P$</td>
<td>Electric Power;</td>
</tr>
<tr>
<td>$q$</td>
<td>Electric charge of particles;</td>
</tr>
<tr>
<td>$Q$</td>
<td>Electric charge;</td>
</tr>
<tr>
<td>$s$</td>
<td>Electrode area;</td>
</tr>
<tr>
<td>$S$</td>
<td>Source of species production or loss;</td>
</tr>
<tr>
<td>$T$</td>
<td>Period of the applied source;</td>
</tr>
<tr>
<td>$T_{en}$</td>
<td>Temperature;</td>
</tr>
<tr>
<td>$\nu$</td>
<td>Collision frequency;</td>
</tr>
<tr>
<td>$\nu_m$</td>
<td>Momentum transfer frequency;</td>
</tr>
<tr>
<td>$V_a$</td>
<td>Applied voltage;</td>
</tr>
<tr>
<td>$V_b$</td>
<td>Breakdown voltage;</td>
</tr>
<tr>
<td>$V_{ds}$</td>
<td>Voltage on the dielectric layer;</td>
</tr>
<tr>
<td>$V_g$</td>
<td>Gap voltage;</td>
</tr>
<tr>
<td>$V_m$</td>
<td>Memory voltage;</td>
</tr>
<tr>
<td>$V_s$</td>
<td>Magnitude of the sinusoidal voltage;</td>
</tr>
<tr>
<td>$V_p$</td>
<td>Magnitude peak-levelled voltage;</td>
</tr>
<tr>
<td>$V_1$</td>
<td>Magnitude of Gaussian decay signal;</td>
</tr>
<tr>
<td>$V_{thc}$</td>
<td>Velocity caused by species' thermal agitation;</td>
</tr>
<tr>
<td>$\omega$</td>
<td>Radian frequency;</td>
</tr>
<tr>
<td>$\omega_p$</td>
<td>Plasma frequency;</td>
</tr>
<tr>
<td>$W$</td>
<td>Drift velocity;</td>
</tr>
<tr>
<td>$x_m$</td>
<td>Oscillation amplitude of a charged particle;</td>
</tr>
<tr>
<td>$e$ (subscript)</td>
<td>Variables relative to electron;</td>
</tr>
<tr>
<td>$i$ (subscript)</td>
<td>Variables relative to ion species;</td>
</tr>
<tr>
<td>$p$ (subscript)</td>
<td>Variables relative to positive ion species;</td>
</tr>
<tr>
<td>n (subscript)</td>
<td>Variables relative to negative ion species;</td>
</tr>
<tr>
<td>AC</td>
<td>Alternating Current;</td>
</tr>
<tr>
<td>APGD</td>
<td>Atmospheric Pressure Glow Discharge;</td>
</tr>
<tr>
<td>APPJ</td>
<td>Atmospheric Pressure Plasma Jet;</td>
</tr>
<tr>
<td>DBD</td>
<td>Dielectric Barrier Discharge;</td>
</tr>
<tr>
<td>DC</td>
<td>Direct Current;</td>
</tr>
<tr>
<td>EED</td>
<td>Electron Energy Distribution;</td>
</tr>
<tr>
<td>FCT</td>
<td>Flux-Corrected Transport (algorithm);</td>
</tr>
<tr>
<td>IED</td>
<td>Ion Energy Distribution;</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared;</td>
</tr>
<tr>
<td>LFA</td>
<td>Local Field Approximation;</td>
</tr>
<tr>
<td>MC</td>
<td>Monte Carlo (technique);</td>
</tr>
<tr>
<td>MRD</td>
<td>Maximum Recovery Diluent;</td>
</tr>
<tr>
<td>PIC</td>
<td>Particle-In-Cell;</td>
</tr>
<tr>
<td>RBD</td>
<td>Resistive Barrier Discharge;</td>
</tr>
<tr>
<td>RF</td>
<td>Radio Frequency;</td>
</tr>
<tr>
<td>TDMA</td>
<td>Tri-diagonal Matrix Algorithm;</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet;</td>
</tr>
<tr>
<td>V–I</td>
<td>Voltage-Current (characteristics);</td>
</tr>
</tbody>
</table>
1.1 Gas Plasmas: a Historical Review

Plasma, or ionized gas, is the most common form of matter as it makes up over 99% of the universe\textsuperscript{1}. In our daily life, plasma is widely utilised and one common example is fluorescent lamps. The topics on plasmas and plasma-activated phenomena have attracted a lot of interests from many research communities since man's first acquaintance with electric discharges dating back to 1600\textsuperscript{1,2}. The sub-subjects include plasma physics, plasma chemistry, plasma processing and plasma fabrications\textsuperscript{1,3}.

At the beginning of the 19\textsuperscript{th} century, the development of sufficiently powerful electric batteries allowed the discovery of the arc discharge. V. V. Petrov of Russia reported this discovery in 1803\textsuperscript{12}. In 1808, Sir Humphry Davy developed the steady state DC arc discharge\textsuperscript{13}. Since then, more intense scientific studies of plasma followed. About 20 years later, Michael Faraday and others developed the high voltage DC electric discharge tube at a pressure $p \sim 1\ \text{Torr}$\textsuperscript{12,13}. An English physicist, Sir William Crookes, firstly identified this state as the fourth state of matter in 1879\textsuperscript{1,4}, in order to differentiate it from the already-known states of matter: solid, liquid and gas.
Chapter 1

Beginning in 1900, J. S. E. Townsend discovered the laws which govern gas ionization in a uniform electric field\textsuperscript{1,2}. The gaseous discharge he discovered is now known as the Townsend discharge. His experimental work accumulated a great deal of information on cross sections of various electron-atom collisions, drift velocities of electrons and ions, and recombination coefficients. Townsend’s work laid down the foundation of the current gas discharge reference sources, without which no research in discharge physics would be possible\textsuperscript{1,2}. The word “PLASMA” was first used to describe ionized gases by Dr Irving Langmuir, an American chemist and physicist, in 1927\textsuperscript{1,4}. Also, Langmuir developed the probe techniques for plasma diagnostics that have subsequently found widespread uses for low-pressure gas discharges\textsuperscript{1,2}. During the 19\textsuperscript{th} century, the low-pressure arc and DC electrical discharge plasmas were extensively researched in scientific laboratories, but the only widespread application of plasmas in this era was illumination. From 1920’s to 1960’s, research concentrated on the development of plasmas in numerous frequency regions, and explored their possible applications in many industrial and domestic areas\textsuperscript{1,2,13}. Since 1970, plasmas have been extensively used in the microelectronics industry as an enabling tool for the deposition and dry etching processes necessary for the fabrication of microelectronic circuits\textsuperscript{1,3}. To minimise their thermal damage to microelectronic circuits, these gas discharges are typically generated in a vacuum chamber so that they are near or at room temperature and are significantly uniform for large-scale circuit fabrication.

The use of a vacuum chamber severely restricts the application range of cold gas discharges. Fundamentally it is desirable if uniform and near room-temperature gas plasmas can be generated in open-air without the vacuum chamber. Following a technology breakthrough in late 1980’s, it is now possible to generate cold atmospheric plasmas, also known as atmospheric pressure glow discharges (APGD), using alternative power sources typically in the frequency range of 1kHz-30MHz\textsuperscript{1,5}. It has been shown in the past 15 years that similar to vacuum gas plasmas, APGD are well suited for a wide range of material processing applications with the distinct advantage of open-air operation. Because of this, they have been attracting more and more interests.
particularly in the past 10 years. The current mainstream research of the field aims to produce stable glow discharges at atmospheric pressure of different volumes tailored for different applications\cite{16,17}. Many theoretical and computational works\cite{18,19} have also been undertaken to advance the understanding of this new type of gas discharges.

The most common type of atmospheric pressure glow discharges has two parallel-plate electrodes with at least one electrode insulated with a dielectric coating and a plasma excitation frequency in 1–100 kHz\cite{16,11}. The background gas is usually helium although other gases, such as nitrogen and argon, have also been used. This type of APGD is known as dielectric-barrier discharges (DBD), and is the subject of this PhD thesis. Since the stable generation of atmospheric dielectric-barrier discharge was reported by Kanazawa and co-workers in 1988\cite{11}, they have been studied by many research groups\cite{19,11,12,14} for its uniformity\cite{8} and stability\cite{9}. However dielectric barrier discharges are still not fully understood, and many important issues still need to be addressed. The present work aims to improve the knowledge of the physiochemical behaviour of atmospheric DBD primarily through numerical modelling supplemented by an experimental exploration of their capability for food decontamination. It is hoped that through the success of the intended study for this PhD thesis greater insight into APGD could be gained to help better design and interpret experimental works as well as exploration of their applications.

1.2 Brief Introduction to Gas Plasmas

1.2.1 Definition and generation of plasma

Plasmas are often known as a fourth state of matter in addition to solid, liquid and gas states. As it is well known, a solid can generally evolve into a liquid as the inner energy is increased to a certain level, and the further increase of energy can transfer the liquid into a gas. With the same mechanism, when the energy is increased to a sufficiently high level, the atoms in the gas state decompose into the freely moving
charged particles, including electrons and positive charged ions, and negatives charged ions in some cases. This is called the plasma state. This procedure is clearly illustrated in figure 1.1. In other words, plasma is a collection of charged particles that can move freely in random directions. On average gas plasma is electrically neutral and is considered quasi-neutral\textsuperscript{14}. 

<table>
<thead>
<tr>
<th>Solid</th>
<th>Liquid</th>
<th>Gas</th>
<th>Plasma</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecules or atoms are fixed on a crystal lattice</td>
<td>Molecules or atoms move freely without lattice, but still dense</td>
<td>Neutral molecules or atoms move freely in a larger space than liquid</td>
<td>Ions, electrons and excited atoms move freely independently in even larger space</td>
</tr>
</tbody>
</table>

Figure 1.1: Structures in the four states of matter.

The concentration of charged particles in the background neutral gas in the plasma is a criterion of the degree of ionization, which can be defined as\textsuperscript{1.1,14}.

\[
\text{Ionization degree} = \frac{n_i}{n_i + n}
\]  

(1.1)

where \( n_i \) is the density of ionized atoms and \( n \) that of neutral atoms. The plasma is weakly ionized when this figure is less than \( 10^{-2} \), and fully ionized when it is of the order of unity. For most gas discharges, the electron density varies within a very large range from \( 10^4 \text{cm}^{-3} \) to \( 10^{15} \text{cm}^{-3} \)\textsuperscript{13}.

Gas plasmas can be generated either by the assemblage of the constituent plasma particles, by, for example, injection of external electrons, or by ionising a neutral gas\textsuperscript{1.5}. Gas ionization can be realized by several means: 1) through an external source of radiation such as X-rays\textsuperscript{1.5}, electron beams\textsuperscript{1.16,1.17}, photo-ionizing radiation\textsuperscript{1.18}; 2) through a gas discharge\textsuperscript{1.2,1.18,1.19}. By far the second one is the most common approach\textsuperscript{1.5}. 

---

\text{Chapter 1}  

\text{Introduction}
1.2.2 Characteristics of glow discharges

This thesis is primarily concerned with the glow discharges because of their many desirable properties for material processing applications, and as such it is worth discussing some of their basic characteristics.

1.2.2.1 General electrical characteristics

In general, gas discharges can be classified into three broad categories: the Townsend discharge, the glow discharge and the arc\textsuperscript{1,18,1,20}. Figure 1.2 illustrates the typical voltage-current characteristics of these three types of gas discharges.

![Electrical characteristics of typical glow discharge](image)

Figure 1.2: Electrical characteristics of typical glow discharge\textsuperscript{1,20,1,21}.

It is not possible to distinguish them strictly and usually there is a transition regime between the Townsend and glow discharges and one between the glow and the arc. These two transition regimes are often known as Townsend-to-glow and glow-to-arc transitions respectively. Comparing the glow to Townsend discharges, the most important characteristic is that the glow discharge is visible to human's eyes while the Townsend discharge is not, because the current in the glow discharge is high enough to...
support sufficient optical emission\textsuperscript{1,20}. Comparing the glow discharge to the arc, the difference in electrical characteristics can be summarized specifically in table 1.1. The large cathode fall of potential in the glow discharge is of the order of a few hundred volts, while the arc cathode fall is only of the order of 10 volts\textsuperscript{121}. In a normal glow discharge, the current density is typically of the order of 10 mA/cm\textsuperscript{2}, while the current density ranges from 10\textsuperscript{2} –10\textsuperscript{7} A/cm\textsuperscript{2} in arc\textsuperscript{121}.

Table 1.1: Comparative characteristics of glow and arc discharges\textsuperscript{121}.

<table>
<thead>
<tr>
<th></th>
<th>Glow</th>
<th>Arc</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current density</td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td>Ionization density</td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td>Degree of ionization</td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td>Gas temperature</td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td>Electron drift velocity</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td>Column voltage gradient</td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td>Cathode fall of potential</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td>Cathode current density</td>
<td>Low</td>
<td>High</td>
</tr>
</tbody>
</table>

1.2.2.2 Visible phenomena of glow discharges

Light emission is usually associated with gas plasmas. Although most glow discharges appear to be uniform occupying the entire space between the two electrodes, there is in fact a variation in their light emission. The actual distribution of light in the glow discharge between the two electrodes is significant, and a typical example is illustrated in figure 1.3\textsuperscript{18,120}. Closest to the cathode, there is a very thin dark layer, called the Aston dark space. An adjacent thin layer of bright glow is called the cathode glow region, on the anode side of which there is a much darker region called the cathode dark space. The width of this layer increases as the gas pressure is reduced for any given current\textsuperscript{18}. Then follows another luminous region, which is
called the negative glow, and an almost completely dark region, the Faraday dark space. Towards the anode, this layer is next to a uniform glow region called the positive column, which expands to the anode. In many gases, whether the luminosity is uniform or not depends on the degree of gas purity. The end of the positive column which is close to the anode is sometimes brighter than elsewhere, so the name of the anode glow is given to this thin layer. Like the cathode, there is a very narrow dark space next to the anode and this region is known as the anode dark space. The dimensions of these layers depend on the nature of the gas and the discharge current. The colour and intensity of the glow depend on the composition and pressure of the gas, and increase with the current.

**Figure 1.3:** Spatial characteristics of typical glow discharge.

### 1.2.3 Applications of glow discharge

Because of their spatial uniformity and temporal stability, glow discharges have found an increasingly wide range of applications. Traditionally, the low-pressure glow discharge has been utilized for the lighting and materials processing. The most commonly known discharge light source is the fluorescent light, which produces colourful light via the discharges in a suitable gas or gas mixture. The plasma etching process takes the advantage of anisotropism over the isotropism in the conventional etching process. With the advent of open-air glow discharges at
atmospheric pressure, these applications can now be realized without the expensive vacuum system. New applications of atmospheric plasmas are emerging, such as plasma decontamination and sterilization\cite{1,24,25}. Although low-pressure plasmas are at present still the main engines for numerous applications, the removal of a vacuum system is a great advantage and is likely to drive rapid development of atmospheric plasma technology. Some particular applications, for example in-line sterilization processing, can only be done with atmospheric pressure plasmas\cite{15}. Other applications where atmospheric pressure operation is the only option are plasma modification of electromagnetic propagation and plasma aerodynamics\cite{13}. More close to our daily life, plasma display is another application of glow discharges.

1.3 Organization of Thesis

This thesis aims to report the achievements of this project, as well as the challenges and difficulties encountered during this study. The thesis consists of 8 chapters. Chapter 1 gives a general review of the research work on APGD, and some essential background knowledge is introduced for the purpose to lay the foundation for the current work. Because the major tool used in the study is computational simulation, Chapter 2 discusses the details of the physical model and the numerical algorithms for APGD. As a first example of APGD systems, APGD generated in pure helium is studied because of its simplicity and stability. Chapter 3 considers this pure helium case, and studies the general characteristics of atmospheric pressure glow discharges. Key quantities studied include the current-voltage characteristics, the spatial profile of densities of plasma species as well as the variation in plasma dynamics under different plasma operation conditions. Chapter 4 reports on a more realistic discharge model in helium-nitrogen mixture than that in pure helium. The addition of small amount of nitrogen introduces some important chemical reactions to plasma dynamics, for example the Penning reaction, which is shown to dominate plasma generation. This chapter aims to give a clear idea of the important role of gas composition and hence
plasma chemistry in APGD.

After the studies on the typical characteristics of APGD, we study some special issues to gain a deeper understanding on this topic. Chapter 5 raises the question of production efficiency of APGD and ways to improve the APGD production efficiency. A pulsed excitation is suggested and studied. This approach utilizes a pulsed voltage to drive the plasma system, and is shown to be capable of reducing up to 40% of the power consumed for plasma generation. This promising result is especially important for those applications where power consumption is an important issue. Chapter 6 considers the frequency range for stable generation of APGD. This study focuses on discharge behavior at the bounds of a frequency range within which they are stable, and on possible disruption mechanisms that lead to plasma instability. The generic frequency dependence obtained in this study is useful for system optimization of atmospheric DBD equipments. To confirm some of the desirable properties of APGD in reality, a series of exploratory experiment is reported in Chapter 7 with an emphasis on their decontamination capability for foodstuffs. Finally, Chapter 8 summarises all the findings reached in this project, and offers suggestions on the future research work of atmospheric pressure dielectric-barrier glow discharges.
Reference


Chapter 2

Mathematical APGD Model

2.1 Introduction

The characteristics of glow discharges have allowed their widespread use in industry and medicine. As discharge process is a complex synthesis of plasma physics, reaction chemistry and surface science, information gathered from plasma experiments is typically laced with multiple and interwound physiochemical processes and does not land itself easily to clear understanding of these plasma processes. To aid wider and improved applications of glow discharges, it is both desirable and essential to gain a fundamental understanding of their basic characteristics as well as key physical and chemical processes that underpin their generation and sustainment. This is particularly important for atmospheric pressure glow discharges, for which the current understanding remains largely an uncharted territory.

Theoretical study is an indispensable strategy in the endeavour towards a full fundamental understanding of glow discharges. Occasionally this can be approached analytically when different plasma processes can be treated separately and significant approximations can be justified to allow for necessary mathematical simplification. When an analytical approach is viable, the physical problem concerned usually has weak
coupling among relevant physical, chemical and surface based processes and its multidimensional effects are negligible. In reality such physical problems are relatively few and analytical models of plasma systems are often used as a first step towards a more realistic and mathematically more sophisticated model. Consequently the majority of theoretical studies of discharge plasmas are based on computer simulation.

For low-pressure glow discharges, there is a vast body of reported work on their computational studies. For example, Boeuf\textsuperscript{21} constructed an rf plasma model based on solution of the particle continuity and momentum transfer equations coupled with Poisson's equation by assuming local equilibrium between charged particle kinetics and the electric field. Lymberopoulos and Economou\textsuperscript{22,23} considered the nonequilibrium of electrons in the local electrical field by including the energy continuity equations. For atmospheric pressure glow discharges, one of the most comprehensive theoretical studies so far is that reported by Segur and Massines for dielectric-barrier discharges at audio frequencies\textsuperscript{24,25} with a local field approximation (LFA) and by Raja for discharges generated between two bare electrodes at radio frequency\textsuperscript{26,27} without LFA.

Most plasma models commonly use one of two basic approaches, either a kinetic scheme or a fluid treatment\textsuperscript{28,29}. The kinetic schemes, such as particle-in-cell (PIC) methods\textsuperscript{2,10,21}, solve at least some of the species' velocity or energy distribution functions in both time and space, for example the electron energy distribution (EED) and the ion energy distribution (IED)\textsuperscript{2,8}. The kinetic technique is capable of unravelling detailed information regarding the velocity or energy distribution functions of relevant plasma species at the expense of long computation time\textsuperscript{2,3,8}. The fluid treatment generally consists of subsets of the first several moments of the Boltzmann equation without resolving the particle distribution function\textsuperscript{3,23}. It often assumes local equilibrium between charged particle kinetics and the electric field\textsuperscript{2,1-24}. With the local equilibrium approximation, transport coefficients, including drift velocity, diffusion coefficients, ionization and attachment coefficients, are assumed to depend only on the local electric field rather than on the velocity or energy distribution function\textsuperscript{2,1-24}. Compared to the kinetic schemes, the fluid model offers less information but it is
simpler and more computationally efficient\textsuperscript{2,3,8}. The main purpose of fluid simulation is to provide a global insight into the profiles of plasma quantities\textsuperscript{2,12}, and the fluid models are usually more stable numerically than other models\textsuperscript{2,4,7,28}. Research shows that the local equilibrium approximation is not valid for the charged particles in very low-pressure discharges\textsuperscript{23}, whilst it is acceptably accurate for high pressure discharges for which the frequent collisions among plasma species accelerate the transient processes towards their equilibrium with the local electric field\textsuperscript{24}. Therefore, the fluid model is a reasonable choice for APGD simulation.

In this Chapter, the mathematical model of APGD is considered and developed based on a fluid treatment similar to those used by several APGD research groups\textsuperscript{2,4,27}. In section 2.2, a brief description of the proposed physical model is introduced, and the mathematical model is detailed. Two numerical methods commonly used for solving plasma problems are introduced in section 2.3. Finally, section 2.4 provides a general flow chart for the plasma simulation.

2.2 Model Description

2.2.1 Physical description of key discharge processes

Our simulation work is aimed at a viable computer code for gas discharges generated at atmospheric pressure. As shown in figure 2.1, the plasma reactor considered in this work consists simply of two parallel plane electrodes, an impedance matched power supply and the gas volume between two electrodes.

As suggested by Okazaki\textsuperscript{2,11}, in order to generate a stable and homogeneous discharge at atmospheric pressure at audio frequencies, one or both electrodes need to be coated with a thin layer of dielectric. The dielectric layers play an important role in stabilizing the generated atmospheric plasma. Similar to any gas discharge, the gas gap between the two dielectrically coated electrodes breaks down when the externally applied voltage raises the gap voltage above the breakdown voltage. This leads to gas
ionization and an avalanche of production of electrons and ions. These charged particles, under the electrical field set up by the gap voltage, move towards the two electrodes and start to accumulate on the electrodes upon their arrival there. Charged particles accumulating on the dielectric coatings set up an opposing voltage to the original gap voltage, and as a result the gap voltage is now reduced thus suppressing the growth of the avalanche. The dielectric barriers not only limit the discharge current, but also provide the surface to spread local micro-discharges thus preventing them from arcing\textsuperscript{2,14,15}. Different materials may be used as the coating layer, and values of their permittivity influence the plasma generation and sustainment. This will be studied in Chapter 3 and Chapter 4.

Both the two dielectric layers and the gas volume work as capacitors in the equivalent electric circuit of the discharge-power supply system and there are three capacitors in series as shown in figure 2.1.

![Figure 2.1: Schematic description of the discharge reactor.](image)

The capacitance of each capacitor may be approximated as:

$$C = \varepsilon_0 \varepsilon_r \frac{s}{L}$$  \hspace{1cm} (2.1)

where $\varepsilon_0$ is the absolute permittivity whose value is $8.85 \times 10^{-12}$ CV$^{-1}$m$^{-1}$; $\varepsilon_r$ is the
relative permittivity; \( s \) is the electrodes' area; and \( L \) is the separation distance of the two electrodes. The total capacitance of the dielectric layers coated on the electrodes is given by:

\[
\frac{1}{C_{ds}} = \frac{1}{C_{d1}} + \frac{1}{C_{d2}}
\]

(2.2)

For the case in which \( C_{d1} \) and \( C_{d2} \) are equal,

\[
C_{ds} = \frac{C_{d1}}{2}
\]

(2.3)

A voltage source supplies electrical energy to the plasma system, and the temporal variation of the voltage applied to the plasma, \( V_a \), is usually sinusoidal. By increasing the applied voltage, the voltage across the gas gap, \( V_g \), increases. The avalanche only occurs when \( V_g \) reach the breakdown voltage, \( V_b \), of the gas gap. Breakdown voltage is the minimal voltage required to induce gas breakdown. The avalanche is a result of several simultaneous processes including\(^{16,17}\):

1) Ions accelerated by the electric field strike the instantaneous cathode with sufficient energy to cause the emission of secondary electrons from the cathode surface;

2) Electrons created in ionizing collisions and by secondary emission move from the instantaneous cathode to the instantaneous anode by drift and diffusion, and in such movement they collide with neutral species to produce more electron-ion pairs as well as other plasma species. Some of them also recombine with positive ions.

As the generated charged particles arrive at the electrodes, they accumulate on the dielectric surfaces and this induces a memory voltage, \( V_m \), with a polarity opposing to the applied voltage. Therefore through controlling \( V_m \) the dielectric layers prevent the generated plasma from evolving into a thermal arc plasma. The increase of \( V_m \) leads to a rapid decrease of the gas voltage \( V_g \) till it becomes too small to sustain the generated plasma, and at this point the discharge starts to extinguish. In the next half
cycle of the applied voltage, the applied voltage and the memory voltage combine initially to increase the gas voltage and raise it gradually above the breakdown voltage. At this point a new discharge is initiated. Repetition of this plasma extinction and initiation leads to a periodic discharge. The periodicity is a major characteristic of APGD.

2.2.2 Mathematical model

The mathematical model of gas plasmas usually consists of a set of coupled non-linear differential equations. Solution to these equations offers a theoretical means to understand major properties of the simulated plasma. Plasma simulation provides valuable insights into plasma dynamics and when adequately developed can contribute significantly to design methodologies for plasma systems. Yet plasma simulation is usually challenged by considerable complexity of plasma dynamics and by limited availability of reliable reaction data.

To capture the behaviour of the simple APGD system of figure 2.1, the self-consistent continuum or fluid model, originated from the Boltzmann equation, is adopted here. The basic mathematical model developed in this project consists of the electric circuit equation, a set of convection-diffusion equations for different plasma species, coupled with Poisson's equation and boundary conditions of the plasma reactor. Its solution provides the space and time variations of the electric field and that of the number densities of plasma species including electrons, ions, excited species and neutral particles. It also gives the time variations of the gas voltage, the memory voltage and the current density. The whole approach is summarised in figure 2.2, and each component of the numerical algorithm is introduced in the following sections.
2.2.2.1 Electric circuit equation

Considering the plasma generator system of figure 2.1 in one dimension, the following circuit equation of voltage is satisfied:

\[ V_a(t) = V_{d1}(t) + V_g(t) + V_{d2}(t) = V_g(t) + V_m(t) \]  

and the equation of current:

\[ i(t) = C_{d1} \frac{dV_{d1}(t)}{dt} = C_{d2} \frac{dV_{d2}(t)}{dt} = C_g \frac{dV_g(t)}{dt} = \frac{s}{L_0} \int j(x,t) \, dx \]

where \( j(x,t) \) is the current density of the discharge induced by charged particles' movement in the gas gap.
\[ j(x,t) = e \left[ \Sigma(n_p(x,t)W_p(x,t)) - \Sigma(n_n(x,t)W_n(x,t)) - \Sigma(n_e(x,t)W_e(x,t)) \right] \]  \hspace{1cm} (2.6)

where \( n(x,t) \) is charged particles' number density and \( W(x,t) \) is their drift velocity. The subscripts \( p, n \) and \( e \) denote positively charged ions, negatively charged ions and electrons respectively. The negative sign in front of the discharge current term in eq. (2.5) is due to the fact that the discharge current flows in an opposing direction to the circuit current. From eq. (2.5), we have

\[
\frac{dV_{dd1}(t)}{dt} = \frac{C_g}{C_{dd1}} \left\{ \frac{dV_g(t)}{dt} - \frac{1}{\varepsilon_0 \varepsilon_g} \int j(x,t)dx \right\}, \hspace{1cm} (2.7)
\]

where \( \varepsilon_g \) is the relative permittivity of the background gas. Integrate eq. (2.7) over time:

\[
[V_{dd1}(t) - V_{dd1}(0)] = \frac{C_g}{C_{dd1}} \left\{ \left[ V_g(t) - V_g(0) \right] - \frac{1}{\varepsilon_0 \varepsilon_g} \int_0^t \int j(x,t)dx \right\} \] \hspace{1cm} (2.8)

\[
V_{dd1}(t) = \frac{C_g}{C_{dd1}} \left\{ V_g(t) - \frac{1}{\varepsilon_0 \varepsilon_g} \int_0^t \int j(x,t)dx \right\} - \frac{C_g}{C_{dd1}} V_g(0) + V_{dd1}(0) \hspace{1cm} (2.9)
\]

Substituting eq. (2.2) into the above equation, the memory voltage can be calculated as following:

\[
V_m(t) = V_{d1}(t) = V_{dd1}(t) + V_{dd2}(t)
\]

\[
= \frac{C_g}{C_{dd1}} \left\{ V_g(t) - \frac{1}{\varepsilon_0 \varepsilon_g} \int_0^t \int j(x,t)dx \right\} + \frac{C_g}{C_{dd2}} \left\{ V_g(t) - \frac{1}{\varepsilon_0 \varepsilon_g} \int_0^t \int j(x,t)dx \right\}
\]

\[
+ \left( \frac{C_g}{C_{dd1}} V_g(0) + V_{dd1}(0) - \frac{C_g}{C_{dd2}} V_g(0) + V_{dd2}(0) \right)
\]

\[
= \left( \frac{1}{C_{dd1}} + \frac{1}{C_{dd2}} \right) C_g \left\{ V_g(t) - \frac{1}{\varepsilon_0 \varepsilon_g} \int_0^t \int j(x,t)dx \right\}
\]

\[
- \left( \frac{1}{C_{dd1}} + \frac{1}{C_{dd2}} \right) C_g V_g(0) + V_{dd}(0)
\]

\[
= \frac{C_g}{C_{dd1}} \left\{ V_g(t) - \frac{1}{\varepsilon_0 \varepsilon_g} \int_0^t \int j(x,t)dx \right\} - \frac{C_g}{C_{dd1}} V_g(0) + V_{dd}(0)
\]

\[
= \frac{C_g}{C_{dd1}} \left\{ V_g(t) - \frac{1}{\varepsilon_0 \varepsilon_g} \int_0^t \int j(x,t)dx \right\} + \left( 1 + \frac{C_g}{C_{dd2}} \right) V_m(0)
\]  \hspace{1cm} (2.10)
Chapter 2  Mathematical APGD Model

where $V_a(0) = 0$ and $V_g(0) + V_m(0) = 0$ have also been used. As the externally applied voltage $V_a(t)$ is known, $V_g(t)$ can be obtained by solving eq. (2.4) and (2.10). As shown in Appendix 2-A, it is given as:

$$V_g(t) = \frac{C_{ds}}{C_{ds} + C_g} \left[ V_o(t) + \frac{S}{C_{ds} L} \int_0^t j(x,t)dxdt \right] - V_m(0) \quad (2.11)$$

The electric field $E$ in the plasma consists of two parts, one introduced by the externally applied field, $E_g$, and the other by space charges, $E_c$, whose value is dependent on the difference between positively charged particles and negatively charged particles (including electrons) and is governed by Poisson Equation:

$$\frac{\partial E_{nc}(x,t)}{\partial x} = \frac{|e|}{\varepsilon_0} \left[ \Sigma n_p(x,t) - \Sigma n_e(x,t) - n_e(x,t) \right] \quad (2.12)$$

So the electric field is represented as:

$$E(x,t) = E_g(t) + E_{nc}(x,t) = \frac{V_g(t)}{L} + E_{nc}(x,t) \quad (2.13)$$

The number density of different plasma species used in computing the electric field is calculated from the convection-diffusion equations derived in the next sub-section.

2.2.2.2 Convection-diffusion equation

Function $f(\vec{r}, \vec{v}, t)$ is defined as the distribution of a given plasma species in a six dimensional phase space $(\vec{r}, \vec{v})$ as shown in figure 2.3, where $\vec{r}$ is the particle's position and $\vec{v}$ is the particle's velocity. At any time $t$, some particles flow into the marked space volume while some particles flow out off the space volume. In other words, new particles appear in the space volume and some of the existing particles disappear from the space volume. This is a constant feature of the particle dynamics. The number of particles inside this six dimensional space volume $d^3r d^3v$ at time $t$ can be defined as $f(\vec{r}, \vec{v}, t)d^3r d^3v$. Here one dimension in position and velocity is
considered. Quantity $a_x = dv_x / dt$ is defined as the flow velocity in $v_x$, and $v_x = dx / dt$ as the flow in the $x$ direction. Defining the $x$ direction as from the left to the right for the horizontal axis and the $v_x$ direction as from the bottom to the top for the vertical axis, the particles flowing in or out the space volume are defined as:

**Bottom face (flowing in):**

$$f(x,v_x,t)dx dv_x = f(x,v_x,t)dx a_x(x,v_x,t)dt;$$

**Top face (flowing out):**

$$f(x,v_x + \Delta v_x,t)dx (v_x + \Delta v_x) = f(x,v_x + \Delta v_x,t)dx a_x(x,v_x + \Delta v_x,t)dt;$$

**Left face (flowing in):**

$$f(x,v_x,t)dx dv_x = f(x,v_x,t)dv_x v_x(x,t)dt;$$

**Right face (flowing out):**

$$f(x + \Delta x,v_x,t)d(x + \Delta x)dv_x = f(x + \Delta x,v_x,t)dv_x v_x(x + \Delta x,t)dt;$$

![Figure 2.3: Space volume of particle distribution.](image)

During the interim between time $t + \Delta t$ and $t$, the particles travel from $x$ to $x + \Delta x$ horizontally and $v_x$ to $v_x + \Delta v_x$ vertically, so the difference in total number of
particles inside the space volume is defined as:

\[
f(x,v_x,t + \Delta t) \, dx \, dv_x - f(x,v_x,t) \, dx \, dv_x
= \left[ f(x,v_x,t) \, dx \, a_x(x,v_x,t) \, dt - f(x,v_x + \Delta v_x,t) \, dx \, a_x(x,v_x + \Delta v_x,t) \, dt \right]
+ \left[ f(x,v_x,t) \, dv_x \, v_x(x,t) \, dt - f(x + \Delta x,v_x,t) \, dv_x \, v_x(x + \Delta x,t) \, dt \right]
= \left[ f(x,v_x,t) a_x(x,v_x,t) - f(x,v_x + \Delta v_x,t) a_x(x,v_x + \Delta v_x,t) \right] dx \, dt
+ \left[ f(x,v_x,t) v_x(x,t) - f(x + \Delta x,v_x,t) v_x(x + \Delta x,t) \right] dv_x \, dt
\]

Dividing the above equation by \( dx \, dv_x \, dt \), we have:

\[
\frac{\partial f}{\partial t} = -\frac{\partial}{\partial x} (f v_x) - \frac{\partial}{\partial v_x} (f a_x) \tag{2.14}
\]

Noting from figure 2.3, velocity \( v_x \) is independent of position \( x \). We may assume that the acceleration \( a_x = F_x / m \) of the particles does not depend on velocity \( v_x \).

Note that the force considered here is only induced by the electric field but not the magnetic field. Thus \( v_x \) and \( a_x \) in eq. (2.14) can be put outside of the bracket:

\[
\frac{\partial f}{\partial t} = -v_x \frac{\partial f}{\partial x} - a_x \frac{\partial f}{\partial v_x}
\]

\[
\frac{\partial f}{\partial t} + v_x \frac{\partial f}{\partial x} + a_x \frac{\partial f}{\partial v_x} = 0 \tag{2.15}
\]

For multi-dimensional case, eq. (2.15) can be written as:

\[
\frac{\partial f}{\partial t} + \mathbf{v} \cdot \nabla_r f + \mathbf{a} \cdot \nabla_v f = 0 \tag{2.16}
\]

with

\[
\nabla_r = \frac{\partial}{\partial x} + \frac{\partial}{\partial y} + \frac{\partial}{\partial z}
\]

and

\[
\nabla_v = \frac{\partial}{\partial v_x} + \frac{\partial}{\partial v_y} + \frac{\partial}{\partial v_z}.
\]

On the other hand, particles can 'suddenly' appear in or disappear from the volume due to inter-particle collisions. Such collisions can instantaneously change the velocity, but not the position, of a particle. Therefore

\[
\frac{\partial f}{\partial t} + \mathbf{v} \cdot \nabla_r f + \frac{\mathbf{F}}{m} \cdot \nabla_v f = \left. \frac{\partial f}{\partial t} \right|_{\text{collision}} \tag{2.17}
\]

eq. (2.17) is called Boltzmann Equation.

For any type of particles, the Boltzmann equation describes the kinetic behaviour
very well. To solve them for all particle types, it is often useful to first simplify the
equations by replacing the detailed microscopic treatment by a coarse approach for
macroscopic information$^{18,19}$. The new equations are now macroscopic equations.
They no longer permit the access to the energy distribution of the particles, however
they allow the determination of the space and temporal variation of the particle density,
their average speed, and their average energy$^{18,19}$.

Consider a specific species $k$, with a distribution function of $f_k(\vec{r},\vec{v},t)$. The
macroscopic quantities are defined as following:

Particle density:

$$n_k(\vec{r},t) = \int_{\vec{v}} f_k(\vec{r},\vec{v},t)d\vec{v}$$

Average velocity:

$$\vec{u}(\vec{r},t) = \frac{1}{n_k(\vec{r},t)} \int_{\vec{v}} \vec{v} f_k(\vec{r},\vec{v},t)d\vec{v}$$

In the same way, the average value of any unspecified quantity $z(\vec{r},\vec{v},t)$ can be
defined as:

$$\bar{Z}(\vec{r},t) = \frac{1}{n_k(\vec{r},t)} \int_{\vec{v}} \bar{z}(\vec{r},\vec{v},t) f_k(\vec{r},\vec{v},t)d\vec{v}$$

To derive the convection-diffusion equation, the information about mass,
momentum, and energy balance is required. Mass balance is defined as the integral of
the $0^{th}$ power of the velocity over the distribution function in eq. (2.17) (e.g.
$$\int_{\vec{v}} \frac{1}{m} \frac{\partial f_k}{\partial t} + \frac{1}{m} \vec{v} \cdot \nabla f_k \pm (\vec{v}) \frac{1}{m} \cdot \nabla f_k \right) d\vec{v} = \int_{\vec{v}} \frac{1}{m} \frac{\partial f_k}{\partial t} \bigg|_{\text{collision}} d\vec{v}$$
in which the minus sign is for electrons or negative charged ions and plus signs for
positive charged ions.

So the mass balance equation can be written as:

$$\frac{\partial n_k}{\partial t} + \nabla \cdot (n_k \vec{u}) = R_e - R_i = S_k(\vec{r},t) \tag{2.18}$$
where $R_c$ and $R_l$ are respectively the creation and loss of the plasma species due to the particle collisions; and $S_k$ is the source term that describes its appearance and disappearance. Because the particle collisions can produce and absorb the plasma species, both $R_c$ and $R_l$ exist in the mass balance equation of eq. (2.18). To differentiate them mathematically, we assign a plus sign for $R_c$ and a minus sign for $R_l$. The detailed format of the source term depends on the chemical reactions the species participates, and their reaction rates under relevant discharge conditions.

Momentum balance is defined as the integral of the $1^\text{st}$ power of the velocity over the distribution function in eq. (2.17) (e.g. $\int (m\vec{v}) f_k d\vec{v}$):

$$\int \left( m\vec{v} \frac{\partial f_k}{\partial t} + m\vec{v} \cdot \nabla f_k \pm m\vec{v} \cdot \nabla \cdot f_k \right) d\vec{v} = \int m\vec{v} \left( \frac{\partial f_k}{\partial t} \right)_\text{col} d\vec{v}$$

in which the negative sign is for electrons or negative charged ions and positive signs for positive charged ions. As shown in Appendix 2-B, the momentum balance can be written as:

$$\frac{\partial}{\partial t} (mn_k \vec{u}) + \nabla \cdot (mn_k \vec{u} \vec{u}) \mp n_k \vec{F} = \int \left( \frac{\partial f_k}{\partial t} \right) \vec{v} d\vec{v}$$

Several assumptions can be made to simplify the above equation:

1) the frequencies of electron creation and loss are much smaller than their momentum transfer frequency;
2) the drift velocity is smaller or at most the same order of magnitude as the thermal velocity;
3) the angular frequency is much less than the momentum transfer frequency.

These assumptions are validated for the atmospheric pressure DBD in Appendix 2-B. With the above assumption and as shown in Appendix 2-B, the momentum balance for the one dimensional case can be further simplified to:

$$n_k(x,t)u(x,t) = n_k(x,t)W_k(x,t) - \frac{\partial(n_k(x,t)D_k(x,t))}{\partial x}$$  (2.19)
where $W$ and $D$ is the drift velocity and diffusion coefficient respectively and defined as following:

$$W = \mp \mu E$$

$$\mu = \frac{e}{m v_m}$$

$$D = \frac{v_t^2}{3v_m}$$

where $\mu$ is the mobility, $m$ the mass, $v_m$ the effective momentum transfer frequency, and $v_t$ the thermal velocity component.

For APGD generated within a short gas gap (e.g. less than 1cm), the electron processes can be approximated to be locally and instantaneously in equilibrium with the electric field\(^{24}\). Under these conditions, the electron-transport coefficients can be determined solely by the magnitude of the local electric field. This assumption is called the local field approximation or the hydrodynamic approximation. Its validity for APGD has been established as reasonable\(^{24}\).

By substituting eq. (2.19) into the continuity equation of eq. (2.18), the Continuation-diffusion Equation for the one dimensional case is formed as following:

$$\frac{\partial n_k(x,t)}{\partial t} + \frac{\partial}{\partial x} \left[ n_k(x,t) W_k(x,t) - \frac{\partial (n_k(x,t) D_k(x,t))}{\partial x} \right] = S_k(x,t),$$

which can be further re-arranged to become:

$$\frac{\partial n_k(x,t)}{\partial t} = S_k(x,t) - \frac{\partial [n_k(x,t) W_k(x,t)]}{\partial x} + \frac{\partial^2 [n_k(x,t) D_k(x,t)]}{\partial x^2}. \tag{2.20}$$

Eq. (2.20) contains complete information of particle flow dynamics in the plasma, and it needs to be solved for any kinds of plasma species considered in order to describe fully the macroscopic plasma characteristics. It is worth mentioning that microscopic information, for example the velocity distribution of plasma species, is not possible with eq. (2.20).
2.2.2.3 Governing equations

Considering a one dimensional (in the axial direction of the plasma reactor) case in which only the electron, the positive charged ions and the neutral ground or metastables exist, the governing equations of a hydrodynamic plasma model can be summarized from eq. (2.4), (2.6), (2.11), (2.12), (2.13) and (2.20) as following:

\[ V_g(t) = V_g(t) + V_m(t) \]  
\[ j(x,t) = e \left[ \Sigma(n_p(x,t)W_p(x,t)) - \Sigma(n_e(x,t)W_e(x,t)) \right] \]  
\[ V_g(t) = \frac{C_d}{C_d + C_g} \left[ V_g(t) + \frac{s}{C_d} \int_0^t j(x,t) dx dt \right] - V_m(0) \]  
\[ \frac{\partial E(x,t)}{\partial x} = \frac{|e|}{\varepsilon_0} \left[ \Sigma n_p(x,t) - n_e(x,t) \right] \]  
\[ E(x,t) = E_g(t) + E_{sc}(x,t) = \frac{V_g(t)}{L} + E_{sc}(x,t) \]  
\[ \frac{\partial n_e(x,t)}{\partial t} = S_e(x,t) - \frac{\partial[n_e(x,t)W_e(x,t)]}{\partial x} + \frac{\partial^2 [n_e(x,t)D_e(x,t)]}{\partial x^2} \]  
\[ \frac{\partial n_p(x,t)}{\partial t} = S_p(x,t) - \frac{\partial[n_p(x,t)W_p(x,t)]}{\partial x} + \frac{\partial^2 [n_p(x,t)D_p(x,t)]}{\partial x^2} \]  
\[ \frac{\partial n_n(x,t)}{\partial t} = S_n(x,t) + \frac{\partial^2 [n_n(x,t)D_n(x,t)]}{\partial x^2}. \]

where subscript \( e \), \( p \) and \( n \) denotes the quantities of the electron, the positive ions and the neutral species respectively.

In the above eight equations, there are eight unknown quantities namely \( V_g \), \( V_m \), \( n_e \), \( n_p \), \( n_n \), \( j \), \( E_{sc} \) and \( E \). Other quantities, for example \( V_a \), \( W \), \( D \) and \( S \), are known to the system directly or indirectly. To solve this set of equations, we need to know the boundary and initial conditions, which are introduced in the next section.
2.2.2.4 Initial and boundary conditions

The initial densities of plasma species ($n_e$, $n_p$, and $n_n$) are assumed to be uniformly distributed over the entire plasma reactor and the plasma is assumed to be initially in a quasi-neutral state, in which $n_e(x,0) = n_p(x,0) = 10^8 \text{ cm}^{-3}$. Therefore, there is no space charge initially, $E_{ne}(x,0) = 0$ and $E(x,0) = E_g(0) = V_g(0)/L$. At the initial time instant, the sinusoidal applied voltage is zero, $V_a(0) = \sin(0) = 0$. Thus $V_g(0) = -V_a(0)$ according to eq. (2.21a). Also we assume the current density is initially zero, or $j(x,0) = 0$.

The choice of the boundary conditions in modeling plasma process has significant effects on the structure of the generated discharge. Under the effect of the electric field and diffusion, the charged particles produced in the gas gap move to the dielectric layers that are coated on the electrodes. The direction of the charge flow depends on that of the instantaneous electric field and the polarity of the charged particles. The particle flow, $\phi$ in unit of cm$^2$s$^{-1}$, towards the dielectric wall is written as:

$$
\phi = a n_k W_k + 0.25 n_k V_{thk}
$$

where $n_k$ is the density of species $k$ considered in the model; $W_k$ denotes its drift velocity; $V_{thk}$ is the velocity caused by the species' thermal agitation. Coefficient $a$ is equal to 0 for the neutral particles and for those charged particles whose velocity is away from the dielectric wall. For other cases, it is equal to 1. The term $0.25 n_k V_{thk}$ represents the flow of a thermal motion. As the thermal motion of the species is very weak in nonthermal APGD, it is acceptable to ignore the thermal term in the particle flow to simplify the numerical simulation model.

Particle flow in the gas gap results in accumulation of ions on the dielectric walls, and the arrival or bombardment of these ions at the dielectric layers releases secondary electrons from the wall. This is called secondary emission. It can be induced not
only by the ion bombardment, but also by that of the excited particles. The flow of electrons generated from secondary emission can be formulated as:

\[ \phi_e = \sum_{k=1}^{p} \gamma_k \phi_k \]  

(2.23)

where \( \phi_e \) is the electron flow emitted from either walls; \( \phi_k \) is the flow of ions or metastables \( k \); and \( \gamma_k \) is the secondary emission rate caused by bombardment of species \( k \). The secondary emission can also be represented as:

\[ n_e = \sum_{k=1}^{p} \gamma_k n_k \]  

(2.24)

This is employed in this study. The secondary emission rate depends on the material of the wall, the electric field at the wall surface and properties of the incidental ions or metastables. The choice of value of \( \gamma \) is essential because it strongly influences the electric field near the electrode and thus it will modify the plasma structure. In this study, we only consider the secondary electron emission caused by the ion bombardment. Therefore the boundary condition of electron density is:

Cathode: \( n_e(x,t) = \sum_{i=1}^{p} \gamma_i n_i(x,t) \)

Anode: \( n_e(x,t) = 0 \).

For positive ions, their flux on the boundary can be assumed to be driven by the electric field, and the diffusive flux can be set to zero on the electrode surface at any time, i.e.,

\[ \frac{\partial n_i}{\partial x} = 0 \]  

(2.25)

This condition can avoid developing the very steep layer on the boundary. Eq. (2.25) is also applicable to the neutral metastables with their diffusive flux set to zero. The values of current density \( j \) at the boundary are calculated from the boundary values of the density and drift velocity of charged particles from eq.(2.21b).

Poisson equation of eq. (2.21d) governs the electric field induced by the space
charges. At the central point between the two electrodes, there is negligibly small amount of space charge. Thus it is reasonable to assume the value of $E_{sc}$, which is the electric field caused by space charge only, at the central position between the two electrodes to be zero at any time. With this assumption, eq. (2.21d) can be calculated from the centre position to two electrodes simultaneously. This method avoids the difficulty in setting the electric field on the electrode surfaces to a fixed value. Effectively this is the boundary condition for $E_{sc}(x,t)$. As a result the boundary condition for $E(x,t)$ is $E(L/2,t) = E_g(t)$.

2.3 Numerical Algorithms

The mathematical model derived in the previous section includes a series of convection-diffusion equations for different species, Poisson equation and the electric circuit equation. These equations form a non-linear and strongly coupled mathematical system, and it is a system that generally depends on several variables, such as time and position vector. Taken into account the complexity of the phenomena present in an electrical discharge, the set of equations are very difficult, if not impossible, to be solved analytically. Thus numerical solutions are often used. Our intended physical quantities of APGD include the gap voltage, the discharge current, the particle number densities and the electric field as well as their temporal and spatial distribution. The development of appropriate computational models and numerical algorithms has been a subject of many recent work.\textsuperscript{2,12,18,22} Computer resources and accuracy are the most important issues. In this section, two numerical algorithms, TDMA and FCT, used in solving the plasma fluid model are introduced in detail.

2.3.1 Tri-diagonal matrix algorithm (TDMA)

To make the introduction of numerical algorithm easy to understand, one-dimensional case is discussed here, in which case all the unknown variables in eq.
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(2.21) are functions of time and only one spatial co-ordinate. The convection-diffusion equation of the species \( k \) can be re-arranged to the following format:

\[
\frac{\partial n_k(x,t)}{\partial t} + \frac{\partial}{\partial x} \left[ n_k(x,t) W_k(x,t) \right] = \frac{\partial^2 [D_k(x,t)n_k(x,t)]}{\partial x^2} + S_k(x,t) \quad (2.26)
\]

where \( n_k, W_k, D_k \) and \( S_k \) are respectively the number density, the drift velocity, the diffusion coefficient and the source term.

\[\begin{array}{c}
\Delta x_0 \\
i-1 \\
i \\
i+1 \\
\end{array}\]

\[\begin{array}{c}
\Delta x_0 \\
\Delta x \\
\end{array}\]

Figure 2.4: Spatial mesh grid of the 1D TDMA algorithm.

A mesh grid for the spatial domain used to find the value of function \( n_k(x,t) \) on specific grid point \( i \) and at the time point \( j \) is drawn in figure 2.4. In the spatial domain, the numerical value of each grid point can be represented by its neighbours' values, such as the use of values at the grid points \( (i-1) \) and \( (i+1) \) to represent the value at the grid point \( i \) in the 1-D grid scheme. In the time domain, there are three ways to perform the discretization: explicit, Crank-Nicolson and implicit.

\[\begin{array}{c}
\Delta t \\
n(t) \\
n(t-\Delta t) \\
\end{array}\]

\[\begin{array}{c}
f = 1 \\
Implicit \\
f = 0.5 \\
Crank-Nicolson \\
f = 0 \\
Explicit \\
\end{array}\]

Figure 2.5: Methods for discretization in time.
Figure 2.5 shows the difference among these three schemes, for which the format for integrating a variable over time can be generalised as:

$$\int_{t-\Delta t}^{t} ndt = \left[fn(t) + (1-f)n(t-\Delta t)\right] \Delta t$$

(2.27)

When \( f = 0 \), \( \int_{t-\Delta t}^{t} ndt = n(t-\Delta t)\Delta t \). This is called the explicit scheme, in which the value of variable \( n \) at the previous time instant, \( (t-\Delta t) \), is used to calculate the intermediate value (e.g., grey points in figure 2.4) between \( (t-\Delta t) \) and \( t \). Explicit scheme requires a very small \( \Delta t \) to keep the numerical computation stable when \( \Delta x \) is reduced to improve the spatial resolution. When \( f = 0.5 \),

$$\int_{t-\Delta t}^{t} ndt = (0.5n(t) + 0.5n(t-\Delta t))\Delta t.$$  

This is called Crank-Nicolson scheme, in which the value of \( n \) at the current time instant, \( t \), and at the previous time instant, \( (t-\Delta t) \), are both used to calculate the intermediate value between \( (t-\Delta t) \) and \( t \). Crank-Nicolson scheme is accurate in computation, but extra computation may be induced in solving the problem. When \( f = 1 \), \( \int_{t-\Delta t}^{t} ndt = n(t)\Delta t \). This is called the implicit scheme, in which the value of \( n \) at the current time instant, \( t \), is used to evaluate the intermediate value between \( (t-\Delta t) \) and \( t \). Implicit scheme is not as accurate as the Crank-Nicolson scheme for small \( \Delta t \), but its advantage lies in avoiding the excessive computation and restrictions in the choice of \( \Delta t \) and \( \Delta x \).2,23,24

Integrating each term in eq. (2.26) over time and space, and adopting the implicit scheme in temporal discretization, 1D convection-diffusion equation can be discretized in the following form (see details in Appendix 2-Q):

$$\frac{\Delta x}{\Delta t} \left( n_i^j - n_i^{j-1} \right) = n_i^{j-1} \left[ \frac{D_e}{\Delta x} + \|W_e,0\| \right] + n_i^{j-1} \left[ \frac{D_e}{\Delta x} + \|W_o,0\| \right]$$

$$+ n_i^j \left[ -\frac{D_e}{\Delta x} - \frac{D_e}{\Delta x} - \|W_e,0\| - \|W_o,0\| \right] + S_i/\Delta x$$

(2.28)
where subscript \( i \) denotes the variation in the space domain, superscript \( j \) denotes that in the time domain. The subscript \( k \) previously used to denote species \( k \) has been dropped for simplifying the representation of variables. Subscripts \( e \) and \( o \) here denote the intermediate spatial phase illustrated in figure 2.4; the values of \( W \) and \( D \) on these phases are defined in the format:

\[
\begin{align*}
W_e &= \frac{2W_{i-1}W_i}{W_{i-1} + W_i} \\
W_o &= \frac{2W_iW_{i+1}}{W_i + W_{i+1}} \\
D_e &= \frac{2D_{i-1}D_i}{D_{i-1} + D_i} \\
D_o &= \frac{2D_iD_{i+1}}{D_i + D_{i+1}}
\end{align*}
\tag{2.29}
\]

The operator \( \parallel \parallel \) in eq. (2.28) is a maximum operator, which is defined as:

\[
\|x - y\| = \begin{cases} 
x & x \geq y \\
y & x < y
\end{cases}
\]

Define the following coefficients:

The coefficient of upstream neighbour: 

\[
b'_i = \frac{D_o}{\Delta x} + \|W_e, 0\|;
\]

The coefficient of downstream neighbour: 

\[
c'_i = \frac{D_o}{\Delta x} + \|W_o, 0\|;
\]

The coefficient of present grid point: 

\[
a'_i = b'_i + c'_i + W_e - W_o + \frac{\Delta x}{\Delta t};
\]

The other source influenced present grid point: 

\[
d'_i = \frac{\Delta x}{\Delta t} n_{i-1} + S'_i \Delta x.
\]

So, the discretization of eq. (2.28) finally becomes (see Appendix 2-C)

\[
a'_i n'_i = b'_i n'_{i+1} + c'_i n'_{i-1} + d'_i
\]

(2.30)

For each time step, a series of discretized and linear equations are constructed and each grid point in the grid space is treated in the way introduced above. This is repeated for all plasma species considered including electrons, ions and metastables. Thus the complexity of the numerical model and the total computation time is dependent on what the size of solution grid space is and how many plasma species are considered in the model.

The coefficients of this newly formed numerical system form a tri-diagonal matrix,
which is a square matrix with nonzero elements only on the central diagonal and two
"shifted" diagonals. The format of tri-diagonal matrix is:

\[
\begin{bmatrix}
    a_i^1 & -b_i^1 & 0 & 0 & \cdots & 0 & 0 & 0 \\
    -c_i^1 & a_i^1 & -b_i^1 & 0 & 0 & \cdots & 0 & 0 \\
    0 & -c_i^1 & a_i^1 & -b_i^1 & 0 & \ddots & \ddots & \vdots \\
    0 & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & 0 \\
    \vdots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \vdots \\
    \vdots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots \\
    0 & 0 & \cdots & \cdots & \cdots & -c_{i-2}^N & a_{i-2}^N & -b_{i-2}^N \\
    0 & 0 & \cdots & \cdots & \cdots & 0 & -c_{i-1}^N & a_{i-1}^N & -b_{i-1}^N \\
    0 & 0 & \cdots & \cdots & \cdots & 0 & 0 & -c_{i}^N & a_{i}^N \\
\end{bmatrix}
\] (2.31)

Subscript $N$ denotes the total grid point along the spatial dimension. Therefore, this
method is called Tri-Diagonal Matrix Algorithm (TDMA)\textsuperscript{223}, for which detailed
derivation is given in Appendix 2-D. Through this method, the values for all grid
points along spatial dimension for a specific time instant can be worked out together
simultaneously. TDMA is easy to implement and fast to run. The emphasis of
solving the plasma fluid model using the TDMA method is how to construct a
tri-diagonal matrix. As long as this matrix is constructed, the problem can be solved.

2.3.2 Flux-corrected transport (FCT) algorithm

Flux corrected transport (FCT) algorithm is a numerical method developed by
Boris and Book\textsuperscript{225} for integrating partial differential equations using finite difference
techniques. The difference forms for indicating order of spatial accuracy are given as
following\textsuperscript{225}:

- Second order: $F_{i+1/2} = \frac{1}{2} (f_{i+1} + f_i)$
- Fourth order: $F_{i+1/2} = \frac{7}{12} (f_{i+1} + f_i) - \frac{1}{12} (f_{i+2} + f_{i-1})$
- Sixth order: $F_{i+1/2} = \frac{37}{60} (f_{i+1} + f_i) - \frac{2}{15} (f_{i+2} + f_{i-1}) + \frac{1}{60} (f_{i+3} + f_{i-2})$
- Eighth order:
  \[F_{i+1/2} = \frac{533}{840} (f_{i+1} + f_i) - \frac{139}{840} (f_{i+2} + f_{i-1}) + \frac{29}{840} (f_{i+3} + f_{i-2}) - \frac{29}{280} (f_{i+4} + f_{i-3})\]
Function $f$ represents the flux term, and its subscript denotes spatial variation. The second order relation is normally used as a low-order difference scheme, while others can be chosen to be high-order scheme. High-order difference scheme offers high accuracy but with dispersive ripples which might cause numerical instability, while the low-order scheme produces little ripples but suffer from low accuracy and difficulty in numerical convergence. The objective of FCT is to overcome the disadvantages of low- and high-order schemes, while maximising their advantages. The key operation of FCT is to construct the net transportive flux as a weighted average of a low-order flux and a high-order flux, and the weighting is done on the principle of ensuring that the high-order flux is used to the greatest extent without introducing any non-physical ripples. In the FCT algorithm, the non-linear corrective flux can be cancelled by an opposite antidiffusive flux when the diffusion is clearly not needed. The operation that determines how much of the diffusive flux is cancelled is called flux correction or flux limiting. The definition of flux limiter in FCT is very important because errors can arise if the flux limiter over-corrects the fluxes and leaves an unnecessarily large net transportive flux.

A generalized fluid equation is in the format as:

$$\frac{\partial n(x,t)}{\partial t} + \frac{\partial F}{\partial x} = 0$$

where $F = n(x,t)W(x,t) - \frac{\partial [n(x,t)D(x,t)]}{\partial x}$ is the transportive flux term. It is in the same format as eq. (2.20) without the source term. The finite difference approximation in flux form would be:

$$n_i^{t+1} = n_i^t - \frac{\Delta t}{\Delta x_i} (F_i^{t+(1/2)} - F_i^{t-(1/2)})$$

where the superscript denotes the temporal variation, and the subscript denotes the spatial variation. The general procedure of solving eq. (2.32) using the FCT algorithm is:
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(1) Compute the transportive flux by using a low-order scheme, \( F_{i+1/2}^L \).

(2) Compute the transportive flux by using a high-order scheme, \( F_{i+1/2}^H \).

(3) Define the "antidiffusive flux":
\[
A_{i+1/2} = F_{i+1/2}^H - F_{i+1/2}^L 
\]  
(2.34)

The definition of antidiffusive flux can also be in other forms\(^{229}\).

(4) Compute the updated low order solution:
\[
n_{i+1} = n_i + \frac{\Delta t}{\Delta x_i} \left( F_{i+1/2}^L - F_{i-1/2}^L \right) 
\]  
(2.35)

(5) Limit the antidiffusive flux \( A_{i+1/2} \) in a manner such that \( n_{i+1}^{\text{new}} \) as computed in the next step are free of extrema not found in \( n_i^{\text{old}} \) and \( n_i^{\text{new}} \):
\[
A_{i+1/2}^{\text{c}} = C_{i+1/2} A_{i+1/2} 
\]  
(2.36)

This step is very critical in the FCT algorithm as errors can arise if the flux limiter over-corrects the antidiffusive fluxes and leaves an unnecessarily large net flux. The ideal flux limiter would not generate new maxima or minima in the solution, nor accentuate already existing extrema. A more general flux limiter was given by Zalesak\(^{27}\). The choice of flux limiters depends on the physics of the problem, and on the numerical properties of the integration scheme.

(6) Apply the limited antidiffusive flux to eq. (2.33):
\[
n_i^{j+1} = n_i^j - \frac{\Delta t}{\Delta x_i} \left( A_{i+1/2}^{\text{c}} - A_{i-1/2}^{\text{c}} \right) 
\]  
(2.37)

Thus the solution of particle density \( n \) at the spatial grid point \( i \) and temporal grid point \( j \) can be obtained.

With the source term included, the solving procedure tends to be more complicated, and the details are summarised well by Arminjon and Smith\(^{30}\). In their study, they decompose the solution of eq. (2.20) into fractional steps\(^{231-233}\), which correspond to the source term, the convective term and the diffusive term. The anti-diffusive correction term is only applied in the calculation of the convective
Chapter 2 Mathematical APGD Model

fractional step. This is useful to correct the convection effectively without over-correcting other fractions. They claimed that the introduction of an anti-diffusion term in the convective fractional step enable them pursue the calculation of density up to 100 times higher\textsuperscript{2-30} than those in a previous study\textsuperscript{234}.

In this project, both TDMA and FCT are used to solve the fluid equations that describe atmospheric dielectric barrier discharges. Their advantages and disadvantages will be discussed in Chapter 3 and Chapter 4.

2.4 Simulation Flow Chart and Program Environment

The numerical model for plasma processes is implemented in a computer code following the flow chart shown in figure 2.6. The convection-diffusion equations of all plasma species are integrated in time and space, and different numerical methods are adopted here to solve the mathematical problem. Electrical characteristics of APGD are mainly controlled by the circuit equation and Poisson equation. The electric properties of the power source, the dielectric properties and the chemical properties of the working gas are all taken into consideration in the code. The final results provide the time and spatial variation of particles' densities and electric field, and also the time dependence of voltage and discharge current. These are major parameters in APGD as they reveal the basic characteristics of APGD.

The engineering computer language, MATLAB, is chosen to implement the DBD APGD model. All the simulation results presented in this work are computed on a 1GHz Pentium III PC with 256M RAM.
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Figure 2.6: Flow chart of numerical computation.
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2.5 Summary

This chapter introduces the physical model for atmospheric dielectric barrier discharges as well as their numerical model. The dielectric layers coated on the electrodes prevent the formation of arcing by limiting the discharge current. This is both desirable and essential for the generation of stable glow discharges at atmospheric pressure. With a local field approximation, the mathematical model for atmospheric pressure dielectric barrier discharges is derived from Boltzmann equation. The final form of the governing equations is a set of convection-diffusion equations for all plasma species, coupled with the Poisson equation and the circuit equation. Secondary electron emission is taken into account via the external circuit equation. The use of the local field approximation enables the numerical simulation of APGD to be easily implemented without significant compromise of accuracy. To solve this hydrodynamic plasma model, two numerical algorithms, TDMA and FCT, are considered. Their principles and numerical procedures are discussed.
Reference


Chapter 3

Glow Discharges in Atmospheric Helium

3.1 Introduction

Glow discharges have been generated in many gases at atmospheric pressure. These nonthermal discharge plasmas offer a vacuumless means for a wide range of material processing applications\textsuperscript{31,32}, and as such are advantageous over the widely used low-pressure plasmas generated in a vacuum chamber. Recently, much attention has been paid to this subject and a great deal of research work has been undertaken on various aspects of APGD. Both experimental and computational investigations help understand the fundamental processes of APGD and broaden the applications of such discharge plasmas in many industrial sectors.

Helium is one of the most commonly used gases for generating glow discharges at atmospheric pressure. Much of the research work on APGD is done with helium as the background gas, and helium APGD are also extensively used in a wide range of applications, for example etching and deposition of thin films\textsuperscript{33}, surface modification\textsuperscript{34} and sterilization\textsuperscript{35}. Some special characteristics of helium make it a popular choice as
the working gas. Compared to other gases, helium is characterised by the high potential energy of its metastables and its low breakdown voltage\textsuperscript{36,37}. Helium metastables have a relatively long lifespan. For example the lifespan of He(2'S) species is 130\textmu{}s and that of He(2'S) species is 8\textmu{}s\textsuperscript{36,38}. These characteristics of helium make it particularly suitable for the generation of stable glow discharges at atmospheric pressure. Chemical property of helium makes it the simplest of all gases. Electron impact on helium atoms can produce only two kinds of ions, He\textsuperscript{+} and He\textsuperscript{2+}. Through a charge transfer reaction, He\textsuperscript{+} attaches rapidly helium atoms on the ground state to form He\textsuperscript{2+}. It is also known that excited states of He\textsuperscript{+} ions are unlikely to survive more than a few gas kinetic collisions\textsuperscript{39}. Thus, in pure helium gas, the ionic chemistry is expected to be very simple\textsuperscript{39}. Furthermore helium is an inert and non-toxic gas, and this is particularly useful for environment control and personnel protection.

Helium discharge plasmas are ideal for theoretical and numerical study. In addition to its simple chemical properties, its transport parameter is known to good accuracy\textsuperscript{3,10} and this is important for the creditability of simulation results. If a more complex molecular gas or gas mixture is studied instead, it is necessary to include more chemical reactions with more chemical species thus demanding a much longer computational time to solve relevant governing equations\textsuperscript{3,10}. Therefore it is appropriate to study helium plasmas as the first example of APGD.

In this Chapter, we develop a numerical model to study stable discharges generated in atmospheric pure helium. Our model includes five species, namely electrons, e; helium atomic ions, He\textsuperscript{+}; helium molecular ions, He\textsuperscript{2+}; excited helium atoms, He(2'S); and background helium atoms, He(1'S). The chemical processes considered in the model include direct ionization, excitation, stepwise ionization, recombination and charge transfer. This study focuses on the basic characteristics of stable helium APGD, their stability and effects of key system parameters on their dynamic behaviours. The numerical methods used here are detailed in Chapter 2.
3.2 Validation Benchmark

As highlighted in Chapter 1, numerical studies of atmospheric glow discharges are comparatively few. Most reported computational work is based on hydrodynamical models in which electrons are assumed to be in equilibrium with the local electrical field. For nonthermal dielectric barrier discharges in atmospheric gases, there has been no theoretical work so far that removes the hydrodynamic assumption with a more accurate physical model. In other words, it is not possible at this point of development of the field to validate our numerical predictions with results of a more sophisticated theoretical model. As a result, we use typical experimental data of helium APGD as a benchmark to validate our numerical results.

![Figure 3.1: Temporal variation of current and voltage measured in a helium APGD experiment](image)

Experimental studies of atmospheric glow discharges have been performed by many research groups. A typical oscillogram of the discharge voltage and discharge current during a single cycle of the excitation voltage is shown in figure 3.1. The discharge current is characterized by one sharp spike every half cycle with the
current spike typically at some tens of milliampere. The rise time of the current spike is normally several μs, a small fraction of one half-period. Its tail first undergoes a rapid drop and then follows a much more gradual reduction profile. The main features of the discharge current remain exactly the same from cycle to cycle, and it has the same periodicity as the external voltage. The current peak usually occurs at an early point of the rising phase of the excitation voltage. This differs from the normal behaviour of silent discharges\textsuperscript{315}, whose current and voltage peaks occur near the maximum of the applied voltage.

Experimental results show that the positive current peaks may differ from the negative ones in amplitude, but the behaviours of all positive peaks are similar when the discharge reaches its steady state. This is also true for negative current peaks\textsuperscript{311}. The voltage across the gas gap is $V_g$, and the total voltage across the dielectric barriers, $V_{ds}$, is often known as the memory voltage, $V_m$. More specifically $V_g = V_a - V_{ds}$, whereas $V_a$ is the applied voltage and the memory voltage is initially set to a negative value so that $-V_{ds} > 0$. As $V_a$ increases, the gap voltage increases. Once the gap voltage reaches the breakdown voltage of the gas gap, a discharge plasma is ignited and charged particles (e.g. electrons and ions) are produced. Under the influence of the electric field in the gas gap, electrons are driven towards the instantaneous anode and ions towards the instantaneous cathode. Some of these charged particles reach the electrodes and start to accumulate on their dielectric surfaces. As a result, the initial negative memory voltage becomes less negative with reducing amplitude and eventually reverses its initial polarity. This leads to a rapid reduction in the gas voltage via $V_g = V_a - V_{ds}$, until it is below the gas breakdown voltage and the current becomes too small to sustain the discharge. At this point, the discharge plasma extinguishes. In the next half cycle, the applied voltage reverses its polarity and as such adds to the memory voltage that has already reversed its own polarity. As the applied voltage increases, the gap voltage increases again through $V_g = V_a - V_{ds}$ till it reaches the gas
breakdown voltage. Then a new discharge is initiated. Again the charged particles produced from the discharge are driven onto the dielectric surfaces of the electrodes and this reduces the memory voltage thus the gap voltage. Similar to the previous half cycle, the reducing gap voltage leads to the quenching of the discharge. This process then becomes cyclic. The features of current and voltage are the main characteristics of APGD, and will be used to validate our numerical data.

The dissipated power in the discharge in figure 3.1 is 300mW/cm³, and it increases with frequency and voltage. Plasma power found in similar helium APGD experiments varies from 4 to 600mW/cm³ in Roth's work.

Anode

![Anode Diagram]

Cathode

Figure 3.2: Photograph of the gap taken when the discharge current is the maximum. The gap length is 0.5cm and the cathode is located at the bottom.

Apart from the time variation, the spatial distribution of light intensity in the gap offers additional insight into the characteristic of glow discharges. Figure 3.2 is a photograph of the gap taken in an APGD experiment when the discharge current is the maximum, corresponding to the positive peak in figure 3.1. In this photograph, three obvious luminous domains can be distinguished: (1) a narrow region of high light intensity near the cathode at the bottom; (2) an adjacent dark region of about the same thickness as the previous one and (3) a slightly luminous zone in the remaining gap space. These are similar to the features observed in low-pressure glow discharge, and correspond to respectively the cathode and negative glow (they are very close at high pressure), the Faraday dark space and the positive column.
3.3 Model Description

Our simulation considers a dielectric coupled discharge reactor whose structure is detailed in Chapter 2. A dielectric layer with the thickness of 0.06 cm is coated on each of the two electrodes, and normally we assume its relative permittivity to be 8.5. The gap distance between the two coated electrodes is 0.8 cm, and the radius of electrodes is 2 cm. Pure helium gas is assumed to fill the gap between the electrodes at atmospheric pressure of 760 Torr. The effects of small amount of impurity gases will be considered in Chapter 4. An impedance-matched voltage generator works as a power supplier in the system, and the amplitude of its sinusoidal voltage is 1.6 kV. In addition to the geometry of plasma reactor, relevant plasma species of the background gas are the most important factor in our computational model because they influence directly the chemical reactions and the transport parameters of relevant particles.

Our one-dimensional model is based on a simultaneous solution of the convection-diffusion equations for different plasma species, Poisson's equation and the circuit equation. Similar to most studies of high-pressure discharges, electrons and ions are assumed to be in equilibrium with the local electric field. So their transport parameters can be calculated as a function of the local electric field. Our model provides information of the space and time variations of the electric field as well as the electron and ion densities. In addition, the current-voltage characteristics can be computed as a function of time. Charge accumulation on the dielectric layer during the discharge process is taken into account by considering the equivalent circuit of three equivalent capacitors of the gas gap and two dielectrics connected in series. Secondary emission of electrons caused by ion bombardment to the dielectric wall is also considered in the model.

3.3.1 Key helium species and their reactions

We now consider the chemical properties of helium. Figure 3.3 is a simplified energy level diagram for pure helium. This diagram shows the energy levels for
helium atom transferring from the ground state to different excited states. This is an intermediate state in which atoms or molecules are excited by electron impact before the ionization occurs. The atom at excited state is called metastable. There are two metastable categories for helium atom, one is called singlet and the other triplet. The atoms with all electron spins paired are in singlet state, and those with one set of electron spins unpaired are in triplet state.

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>Ionization Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>24.04 eV</td>
<td>24.05 eV</td>
</tr>
<tr>
<td>24.01 eV</td>
<td>24.05 eV</td>
</tr>
<tr>
<td>24.04 eV</td>
<td>24.05 eV</td>
</tr>
<tr>
<td>23.74 eV</td>
<td>23.75 eV</td>
</tr>
<tr>
<td>23.67 eV</td>
<td>23.75 eV</td>
</tr>
<tr>
<td>23.07 eV</td>
<td>23.09 eV</td>
</tr>
<tr>
<td>22.92 eV</td>
<td>23.01 eV</td>
</tr>
<tr>
<td>22.72 eV</td>
<td>23.59 eV</td>
</tr>
<tr>
<td>22.07 eV</td>
<td>23.01 eV</td>
</tr>
<tr>
<td>21.21 eV</td>
<td>20.61 eV</td>
</tr>
<tr>
<td>20.96 eV</td>
<td>19.82 eV</td>
</tr>
<tr>
<td>19.82 eV</td>
<td></td>
</tr>
<tr>
<td>1.1 eV</td>
<td></td>
</tr>
</tbody>
</table>

Figure 3.3: Energy level diagram for helium.

From table 3.1, it is seen that the lifespan of a species is shorter if its excitation energy threshold is higher. The characteristics of metastable triplets He(2'S) make them very stable in the discharge, thus they play an important role in plasma dynamics. For this reason, we consider triplets He(2'S) as the only excited product species in this pure helium plasma model.
Table 3.1: The excitation energy and lifespans of major excited species in pure helium discharges.

<table>
<thead>
<tr>
<th>Product Species</th>
<th>Excitation Energy (eV)</th>
<th>Lifespan (μs)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>He(21S)</td>
<td>20.61</td>
<td>8</td>
<td>Ref. 3.19,3.20</td>
</tr>
<tr>
<td>He(23S)</td>
<td>19.82</td>
<td>130</td>
<td>Ref. 3.19,3.20</td>
</tr>
<tr>
<td>He(21P)</td>
<td>21.21</td>
<td>4.3x10^4</td>
<td>Ref. 3.6</td>
</tr>
<tr>
<td>He(23P)</td>
<td>20.96</td>
<td>9.8x10^2</td>
<td>Ref. 3.6</td>
</tr>
</tbody>
</table>

When electrons colliding onto neutral gas particles are of sufficient energy, atomic ions and electrons will be produced as a result, and this is called ionization reaction. When the free electrons produced by pre-ionization in the gas volume impact on the neutral particles, the potential inside each of these neutral particles increases and drives them to an excited state without generating electrons. This process is called excitation. Neutral particles at excited states, or metastables as previously referred to, can further interact with the helium gas atoms on the ground state, electrons and other species, and the corresponding reactions are known as excitation, de-excitation and stepwise ionization respectively. Atomic ions reacting with the ground state atoms can have molecular ions as product particles, and this works as a charge transfer process in the helium plasma system. Both atomic and molecular ions can recombine with electrons in the gas bulk, and these processes can generate the neutral atoms, molecules and atomic or molecular metastables. Table 3.2 gives a full reaction list, as well as the reaction rate for each reaction.
Table 3.2: Reactions considered in pure He discharge and their coefficients.

<table>
<thead>
<tr>
<th>No</th>
<th>Reaction</th>
<th>Reaction rate</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$\text{He}(1S) + e \rightarrow \text{He}^+ + e + e$</td>
<td>$\alpha_1$</td>
<td>Ref. 3.11,3.21,3.22</td>
</tr>
<tr>
<td>2</td>
<td>$\text{He}(1S) + e \rightarrow \text{He}(2S) + e$</td>
<td>$\beta_1$</td>
<td>Ref. 3.6</td>
</tr>
<tr>
<td>3</td>
<td>$\text{He}(2S) + 2\text{He}(1S) \rightarrow \text{He}_2^+ + \text{He}(1S)$</td>
<td>$1.9 \times 10^{-3} \text{cm}^3/\text{s}$</td>
<td>Ref. 3.23</td>
</tr>
<tr>
<td>4</td>
<td>$\text{He}(2S) + e \rightarrow \text{He}(1S) + e$</td>
<td>$4.2 \times 10^{-9} \text{cm}^3/\text{s}$</td>
<td>Ref. 3.19</td>
</tr>
<tr>
<td>5</td>
<td>$\text{He}(2S) + \text{He}(1S) \rightarrow \text{He}(1S) + \text{He}^+ + e$</td>
<td>$2.9 \times 10^{-9} \text{cm}^3/\text{s}$</td>
<td>Ref. 3.24</td>
</tr>
<tr>
<td>6</td>
<td>$\text{He}^+ + 2\text{He}(1S) \rightarrow \text{He}_2^+ + \text{He}(1S)$</td>
<td>$6.3 \times 10^{-3} \text{cm}^3/\text{s}$</td>
<td>Ref. 3.25,3.6</td>
</tr>
<tr>
<td>7</td>
<td>$\text{He}^+ + e \rightarrow \text{He}(1S)$</td>
<td>$2.0 \times 10^{-11} \text{cm}^3/\text{s}$</td>
<td>Ref. 3.26</td>
</tr>
<tr>
<td>8</td>
<td>$\text{He}_2^+ + e \rightarrow \text{He}_2^+$</td>
<td>$5.0 \times 10^{-10} \text{cm}^3/\text{s}$</td>
<td>Ref. 3.27</td>
</tr>
<tr>
<td>9</td>
<td>$\text{He}^+ + e + \text{He}(1S) \rightarrow \text{He}(1S) + \text{He}(2S)$</td>
<td>$1.0 \times 10^{-27} \text{cm}^3/\text{s}$</td>
<td>Ref. 3.26</td>
</tr>
<tr>
<td>10</td>
<td>$\text{He}^+ + 2e \rightarrow \text{He}(1S) + e$</td>
<td>$7.1 \times 10^{-20} \text{cm}^3/\text{s}$</td>
<td>Ref. 3.25,3.6</td>
</tr>
<tr>
<td>11</td>
<td>$\text{He}_2^+ + e \rightarrow \text{He}(2S) + \text{He}(1S)$</td>
<td>$5.0 \times 10^{-9} \text{cm}^3/\text{s}$</td>
<td>Ref. 3.23</td>
</tr>
<tr>
<td>12</td>
<td>$\text{He}_2^+ + e + \text{He} \rightarrow \text{He}_2^+ + \text{He}(1S)$</td>
<td>$5.0 \times 10^{-17} \text{cm}^3/\text{s}$</td>
<td>Ref. 3.27</td>
</tr>
<tr>
<td>13</td>
<td>$\text{He}_2^+ + 2e \rightarrow 2\text{He}(1S) + e$</td>
<td>$2.0 \times 10^{-20} \text{cm}^3/\text{s}$</td>
<td>Ref. 3.26</td>
</tr>
</tbody>
</table>

As it is shown in table 3.2, we consider five species namely the electrons, the atomic helium ions, the molecular helium ions, the atomic metastables (triplet) and the ground state helium atoms. The molecular helium metastable is not considered in this study although they exist on the right hand side of some reactions listed in above table. The reason for this choice is that both experimental work \cite{11,12} and theoretical work \cite{31,32} of other groups have established those five species we considered as the major species in helium APGD. Heavy species such as He$_2^+$ ions are important in atmospheric pressure glow plasmas \cite{29}. This is different from low-pressure glow discharges in which direct ionization dominates and He$^+$ ions are the only ion species \cite{29}.

For this study, we have also experimented a simpler model than that highlighted in table 3.2 for helium discharges, in which only direct ionization and recombination occur.
reaction are considered. Numerical examples based on this simplified model show that the stable plasma can only be generated and sustained when the recombination reaction rate is increased several magnitudes artificially. The possible reason for this is that when the direct ionization is the only production mechanism and the recombination the only loss mechanism, the original low recombination rate is not able to sustain the dynamic balance among the plasma species. Thus, it is essential to consider all other reactions listed in table 3.2, particularly reactions that produce molecular helium ions.

3.3.2 Transport parameters

As established in Chapter 2, gas species can be treated as a fluid and mathematically they can be represented by the convective-diffusion equation:

$$\frac{\partial n_e(\vec{r},t)}{\partial t} = S_e(\vec{r},t) - \frac{\partial [n_e(\vec{r},t)W_e(\vec{r},t)]}{\partial \vec{r}} + \frac{\partial^2 [n_e(\vec{r},t)D_e(\vec{r},t)]}{\partial \vec{r}^2}. \quad (3.1)$$

To solve this equation, the transport parameters, which include the drift velocity $W$ and the diffusion coefficient $D$, need to be defined well before the simulation. The drift velocity is the speed at which charged particles travel between the two electrodes because of the electric field imposed on them. As the particle's movement is treated as a fluid, the drift velocity is the instantaneous speed of the flow of electrons or ions. Its value can be positive and negative, depending on the flow direction at a specific time.

A number of authors have measured the drift velocity of charged particles in a gas with a homogeneous electric field applied to it, and established that the drift velocity is a function of $E^{318}$:

$$W = f(E) = \mu E \quad (3.2)$$

where $\mu$ is the mobility that describes the mobile property of flow. The mobility of electrons in the unit of cm$^2$V$^{-1}$s$^{-1}$ is given by$^{318}$:

$$\mu_e = \frac{e}{mV_m} \quad (3.3)$$
where $e$ is the elementary charge, $m$ the electron mass and $\nu_m$ the effective collision frequency for momentum transfer. In literature, the electron mobility is sometimes claimed to be constant if the gas pressure, $p$, is fixed. In helium, the electron mobility is given as $0.86 \times 10^6/p \text{cm}^2\text{V}^{-1}\text{s}^{-1}$ in ref. 3.18, $1 \times 10^6/p \text{cm}^2\text{V}^{-1}\text{s}^{-1}$ in ref. 3.21 and $1.33 \times 10^6/p \text{cm}^2\text{V}^{-1}\text{s}^{-1}$ in ref. 3.25. In this study, the gas pressure is 760Torr, thus the electron mobility we used is $1315.8\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ ($=1 \times 10^6/760$). The value of electron mobility is different in different gases because their collision frequencies are different. For example under same conditions, the electron mobility is $0.42 \times 10^6/p \text{cm}^2\text{V}^{-1}\text{s}^{-1}$ for nitrogen and $0.45 \times 10^6/p \text{cm}^2\text{V}^{-1}\text{s}^{-1}$ for air.

For helium ions, their velocity can be calculated by the mobility constant times electric field, or using a formula defined as following:

$$W = \mu_+(E/p)(1 - C_+(E/p)) \quad (E/p) \leq x$$

$$W = K_+(E/p)^{1/2}[1 - D_+(E/p)^{3/2}] \quad (E/p) > x$$

where $E$ is the electric field. The coefficients $\mu_+$, $K_+$, $C_+$, $D_+$ and $x$ are gas-specific constants, and their values in pure helium are:

$$\begin{align*}
\mu_+ &= 8.0 \times 10^6 \text{cm}^2\text{Torr}^{-1}\text{s}^{-1} \\
K_+ &= 4.1 \times 10^4 \text{cm}^{3/2}\text{Torr}^{1/2}\text{V}^{-1/2}\text{s}^{-1} \\
C_+ &= 8.0 \times 10^2 \text{cm}\text{Torr}^{-1} \\
D_+ &= 27.44 \text{cm}^{-3/2}\text{Torr}^{-3/2}\text{V}^{3/2} \\
x &= 25 \text{cm}^{-1}\text{Torr}^{-1}\text{V}
\end{align*}$$

The constant mobilities of helium ions are $\mu_{He^+} = 10.4 \text{cm}^2\text{V}^{-1}\text{s}^{-1}$ and $\mu_{He^2+} = 16.7 \text{cm}^2\text{V}^{-1}\text{s}^{-1}$, as given in literatures, and these are the ion mobility value used for this study. The mobility of ions is much lower than that of electrons, because they are much heavier than electrons.

Diffusion describes the process in which plasma species that are unevenly distributed in a field-free gas move from regions of high concentration to those of low concentration. Diffusion coefficient is used to quantify this process. The value of
Chapter 3  Glow Discharges in Atmospheric Helium

diffusion coefficients is inversely proportional to the pressure and directly proportional to the temperature\textsuperscript{3,17}. For the electrons and ions in pure helium, the diffusion coefficient values can be found in several papers\textsuperscript{3,6,18,3,19,25}. The diffusion coefficient of electrons used in this study is 1737 cm\textsuperscript{-1}s\textsuperscript{-1} (=1.33×10\textsuperscript{6}/760)\textsuperscript{3,25}. Like the mobility, the diffusion coefficient of ions is much lower than that of electrons. In this study, we chose the values for three plasma species to be: \(D_{\text{He}^+} = 410/(p \times 273 / 293) \text{ cm}^\text{s}^{-1}\), \(D_{\text{He}^+} = 640/(p \times 273 / 293) \text{ cm}^\text{s}^{-1}\), \(D_{\text{He}^{(2+)}} = 420/(p \times 273 / 293) \text{ cm}^\text{s}^{-1}\), with \(p\) is 760 Torr.

Alternatively, the diffusion coefficients for electrons and ions when the electric field is not too strong can also be derived from the values of mobility via the Einstein relation\textsuperscript{3,18}:

\[
\frac{D}{\mu} = \frac{kT_m}{|q|}
\]  

(3.5)

where \(k\) is Boltzmann's constant, \(T_m\) is the particle's temperature, and \(q\) is electrical charge of the considered particles. The studies show that the performance of discharge is not altered much by using the constant diffusion coefficients or the values derived via eq. (3.5).

3.3.3 Ionization coefficient and breakdown voltage

Gas breakdown occurs when the following condition\textsuperscript{3,31} is satisfied:

\[
\gamma(e^{\alpha L} - 1) = 1
\]  

(3.6)

where \(\alpha\) and \(\gamma\) are respectively Townsend's first and second ionization coefficients, and \(L\) is the gap distance between the anode and the cathode. In the hydrodynamic model considered here, Townsend's first ionization coefficient is a function of the local field only\textsuperscript{3,11,3,32}, and can be formulated as\textsuperscript{3,21}:

\[
\alpha = Ap \exp\left( - B \sqrt{p/E} \right)
\]  

(3.7)
where $p$ is the gas pressure, $E$ is the electric field, and $A$ and $B$ are two gas-specified constants. Therefore the Townsend value is an exponential function of the local electric field $E$. When the electric field is between $10\text{V/cm}$ to $10^5\text{V/cm}$, $\alpha$ varies very significantly from $10^{-40}\text{cm}^{-1}$ to $10^3\text{cm}^{-1}$.

Townsend's second ionization coefficient, $\gamma$, is also called secondary electron emission rate, defined as the ratio of the total number of electrons leaving a wall to the number of particles that re-enter in contact with the wall\textsuperscript{16}. The value of $\gamma$ depends on the property of the electrode material, or the material of dielectric layer if it is coated, the electric field on the wall surface, the types of incidental ions and their energy. The choice of $\gamma$ value is significant since it strongly influences the value of the electric field at the cathode and can modify the structure of the discharge\textsuperscript{16}. Its value is between $0.01\text{3.15,3.33}$ to $0.21\text{3.18}$ for helium atomic and molecular ions. In this study, the adopted value for $\gamma$ is $0.1\text{3.34}$.

In the region where the gap voltage is small, the direct ionization coefficient is very low so that the direct ionization is not effective compared to other chemical processes in the discharge. When the direct ionization coefficient increases exponentially with the electric field to a certain level, the direct ionization starts to dominate. At this point the avalanche occurs, and there is a very large amount of charged particles produced during this process. The detailed processes involved in the avalanche have been discussed in Chapter 2. When the gas breakdown is reached, the voltage at this point is called the breakdown voltage. In other words, the breakdown voltage is the minimum threshold voltage required for the occurrence of electron avalanche. Rearranging eq. (3.6) and (3.7), the breakdown condition in terms of the electric field can be written as:

$$B_{\sqrt{p/E_b}} = \ln(A/\ln(1+1/\gamma)) + \ln(pL) = C_1 + \ln(pL)$$ \hspace{1cm} (3.8)

Therefore the breakdown voltage across the gas gap is:
A = 4.4 cm$^1$ Torr$^1$ and $B = 14 V^{1/2} cm^{1/2} Torr^{1/2}$. At $L = 0.5 cm$, the breakdown voltage calculated from eq. (3.9) is 1.738 kV. This is higher than the suggested breakdown voltage of 1.55 kV for a helium APGD experiment and 1.1 kV used in its numerical simulation. This difference is strongly dependent on the value of the secondary emission rate. For example, if $\gamma = 0.2$ is used in eq. (3.9), the breakdown voltage is found to be 1.593 kV. Although $\gamma = 0.1$ is suggested by several papers and adopted for the present work, it is conceivable that the effective secondary emission can be enhanced by cathode bombardment by metastable species and by potentially favourable surface conditions of the dielectric-coated electrode in practice. As a compromise, we choose the breakdown voltage to be a constant of 1.3 kV for the electrode gap between 0.3 cm and 1 cm. Numerical examples suggest that while the choice of the secondary emission rate and indeed the breakdown voltage does affect the precise value of the discharge current and voltage, the characteristics of plasma dynamics remain largely unchanged. Given that our simulation aims at a generic description of APGD dynamics rather than detailed data analysis for a specific APGD experiment, the choice of a constant breakdown voltage at 1.3 kV is reasonable.

3.4 Numerical Results

3.4.1 V-I characteristics and their validation

We consider an atmospheric barrier discharge in a helium gap of 0.8 cm and with a voltage excitation at 10 kHz. The breakdown voltage of the helium gap is assumed to be 1.3 kV. Figure 3.4 shows the temporal profile of the discharge voltage and current computed from our code. At the beginning of the simulation, there are transients. These transient components are then suppressed over several cycles of the voltage excitation by the strong and repeatable discharge events. At this point, the discharge
plasma reaches its steady state with its discharge voltage and current repeating themselves cycle after cycle. This repetition pattern is an important indication of stable atmospheric glow discharges. The applied voltage has a sinusoidal waveform with a magnitude of 1.6kV, and is 0V at the beginning of the simulation. The initial gap voltage is 950V and the initial memory voltage $V_m$ is -950V. For a breakdown voltage is 1.3kV, a 350V increase of $V_a$ is sufficient to turn on the discharge. It is noticeable that $V_g$ is about 650V at the beginning of the applied voltage cycle after the discharges reaches the steady state. A 650V increase of $V_a$ is then required for the ignition of the discharge. As soon as the gap voltage reaches the breakdown voltage, the discharge is turned on. An avalanche occurs at the same time, during which a large amount of electrons and ions is generated in the gas gap, supporting a number of processes including ionization and secondary emission. The sharp current spikes indicate this avalanche process in figure 3.4. This increase lasts only 3μs, similar to experimental observation in figure 3.1. After the current reaches its maximum value of 22.1mA, it begins to decrease. The decrease of the discharge current is over about a period of 28μs, much longer than the risetime of 3μs. The 28μs period consists of a quick decrease about 3μs followed by a slower decrease for about 25μs. The current peak is about 1μs later than the peak of the gas voltage. During the discharge period of approximately 31μs (=3μs +28μs), the gap voltage drops about 600V. The current maintains at a very low level before and after the applied voltage changes its polarity.
Figure 3.4: Temporal variation of voltage and current computed using our code for an APGD in pure helium.

Simulation predications in figure 3.4 show close resemblance to the experimental results in figure 3.1. There is also a close agreement for all voltage and current waveforms, the duration of the current spike, and the current risetime and tail time. The peak value of the simulated discharge current is 22.1mA, and this is much smaller than the experimental figure of 80mA in figure 3.1. One possible reason is that our simulation is for pure helium APGD and so does not include the Penning reaction that have been shown to be a major source of ionization by spectroscopic studies. We will discuss this in Chapter 4.
Table 3.3: Comparison of work on pure helium atmospheric pressure glow discharge.

<table>
<thead>
<tr>
<th></th>
<th>Massines at Wang at el¹¹,¹²,³²</th>
<th>Mangolini at el¹³,³⁶</th>
<th>This work</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pressure (Torr)</strong></td>
<td>760</td>
<td>760</td>
<td>760</td>
</tr>
<tr>
<td><strong>Frequency (kHz)</strong></td>
<td>10</td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td><strong>Gap Distance (cm)</strong></td>
<td>0.5</td>
<td>1</td>
<td>0.25</td>
</tr>
<tr>
<td><strong>Radius (cm)</strong></td>
<td>2</td>
<td>Not specified</td>
<td>Not specified</td>
</tr>
<tr>
<td><strong>Dielectric Material</strong></td>
<td>Alumina</td>
<td>Not specified</td>
<td>Alumina</td>
</tr>
<tr>
<td><strong>Dielectric Permittivity</strong></td>
<td>Not specified</td>
<td>7.5</td>
<td>9</td>
</tr>
<tr>
<td><strong>Applied Voltage (kV)</strong></td>
<td>1.5</td>
<td>2.8</td>
<td>Not specified</td>
</tr>
<tr>
<td><strong>Breakdown Voltage (kV)</strong></td>
<td>1.1</td>
<td>Not specified</td>
<td>Not specified</td>
</tr>
<tr>
<td><strong>Secondary Emission Rate</strong></td>
<td>0.02</td>
<td>Not specified</td>
<td>Not specified</td>
</tr>
<tr>
<td><strong>Maximum Current (mA)</strong></td>
<td>80</td>
<td>Not specified</td>
<td>22.1</td>
</tr>
<tr>
<td><strong>Maximum Current Density</strong> (mA/cm²)</td>
<td>6.4</td>
<td>1.4</td>
<td>1.3</td>
</tr>
<tr>
<td><strong>Maximum Electron Density</strong> (cm⁻³)</td>
<td>10¹¹</td>
<td>2x10¹⁰</td>
<td>Not specified</td>
</tr>
<tr>
<td><strong>Maximum Ion Density</strong> (cm⁻³)</td>
<td>10¹¹</td>
<td>8.3x10¹⁰</td>
<td>Not specified</td>
</tr>
</tbody>
</table>

On the other hand, plasma power density can be calculated from the voltage and current data and in the case of figure 3.4, this is found to be 237mW/cm². This compares favourably with the experimental data of 300mW/cm².¹¹ The greatest discrepancy between figure 3.1 and figure 3.4 is the peak value of the discharge current. The maximum current density from our simulation is 22.1mA/(πx2²)=1.8mA/cm², where the maximum current density in figure 3.1 is 80mA/(πx2²)=6.4mA/cm². To explore this feature, we consider results from two other groups. Wang's simulation of a similar pure helium APGD found the maximum current density is 1.4mA/cm², whereas Mangolini's experimental measurements gave 1.3mA/cm². Therefore our results are consistent with these two studies. Table 3.3 gives the comparison of the major parameters of these numerical or experimental studies of helium discharges.
3.4.2 Electric field and particle densities

Spatial profiles of the electric field and particle densities are important indicators of the structure of the generated plasmas. For low-pressure glow discharges, these quantities are usually measured using Langmuir probe and spectroscopic techniques. Under atmospheric conditions however, both ionizations and particle collisions are very significant. As a result, much of the theoretical foundation of the standard probe and spectroscopic techniques need to be reassessed and their interpretation of atmospheric plasmas data readjusted. There is very little, if any, in literature that reports a quantitative measurement of the electric field and the particle densities for dielectric-barrier discharges at atmospheric pressure. Nevertheless qualitatively optical emission data suggest four distinct regions of the generated atmospheric plasma in the inter-electrode space, namely (a) a cathode fall region; (b) a negative glow region; (c) a Faraday region and (d) a positive column. We first compare our simulation results with these qualitative experimental observations.

Figure 3.5 shows the spatial variation of the electric field, ion and electron densities along the axial direction of the plasma reactor at the instant when the discharge current reaches its positive and negative maxima. The four specific regions observed in APGD experiments are also apparent in our simulation results. In the region close to the instantaneous cathode (the left side in figure 3.5a and the right side in figure 3.5b), there is a very rapid drop of electric field of some 2kV/cm. This is the cathode fall region. A negative glow region exists next to the cathode fall, within which the electron density peaks. At high pressure, the cathode glow region and the negative glow region are very close to each other, thus they are very difficult to be clearly distinguished. We would say the glow region in this case extended from 0cm to 0.15cm in figure 3.5a. The following region with a rising of electric field is known as a Faraday region, and in figure 3.5a this is between 0.15cm and 0.4cm. In the region from the gap centre to the instantaneous anode (the right side in figure 3.5a and the left side in figure 3.5b), the electric field remains roughly constant and the electron and ion
densities are very similar. This quasi-neutral region is known as the positive column. Therefore the spatial profile of the electric field and particle densities agree favourably with the experimental observations\textsuperscript{140}.

It is also possible to obtain a quantitative comparison with numerical computations by other groups. In particular we consider a computational study of dielectric barrier discharges in atmospheric helium-nitrogen mixture for which electric field and particle density profiles are shown in figure 3.6. The presence of nitrogen, however small, enables a strong Penning reaction through helium metastables and this contributes significantly to the overall level of gas ionization. Therefore we expect the ionization level of figure 3.6 to be stronger than that in figure 3.5. Indeed the peak electric field in figure 3.6 is 18kV/cm whereas that in figure 3.5 is 3.2kV/cm. This difference is at least partly responsible for the difference between the observed discharge current in figure 3.1 and the computed discharge current in figure 3.4. We will re-visit this issue in Chapter 4 when simulation results of helium-nitrogen APGD are presented.
Figure 3.5: Spatial variation of the electric field, ion and electron density at the time when the discharge current is maximum: (a) $I_d$ reaches its positive maximum; (b) $I_d$ reaches its negative maximum.
3.4.3 Effects of the dielectric layer

The coating of a dielectric layer to one or both electrodes of the plasma reactor is suggested as an important factor to achieve and stabilize the glow discharge at atmospheric pressure\textsuperscript{311}. As the dielectric layers provide a negative feedback thus controlling the electric field during the breakdown process, the rapid discharge process is then slowed down and contained. This mechanism enables the generation of nonthermal uniform glow discharges at atmospheric pressure. Variations of the dielectric layers change the degree of this negative feedback, and as such it is important to study how it affects the discharge dynamics and discharge structure.

Figure 3.7 shows the variation of the discharge current when the dielectric constant of the dielectric layers changes. The thickness of dielectric layers is 0.06cm in all cases, and the radius is 2cm. Relative permittivity is 2, 4 and 8 for the three cases, corresponding to a capacitance of the dielectric layers at 18.54pF, 37.09pF and 74.18pF.
respectively. The result shows that the greater the capacitance of the dielectric layers, the higher the discharge current obtained. The discharge current is 6mA, 17mA and 21.8mA for the corresponding cases. This is can be explained by the following equation:

\[ i(t) = C_{\varepsilon} \frac{dV_{\varepsilon}}{dt} = \frac{dQ}{dt} \quad (3.10) \]

Under an excitation voltage at the same frequency, the charges reaching the dielectric layer increases as the capacitance of the dielectric layer increases. This leads to an increase in the discharge current. For the same reason, reduction in the thickness of the dielectric layers increases the capacitance of the dielectric layer \((C = \varepsilon_{\varepsilon} \varepsilon_{s} / d)\) and as such results in an increase in the discharge current.

![Discharge current waveforms for dielectric coatings of different relative permittivity.](image)

**Figure 3.7:** Discharge current waveforms for dielectric coatings of different relative permittivity.
3.4.4 Effects of other parameters

Apart from the parameters that have been discussed in previous sections, other parameters might affect the characteristics of the generated discharge such as secondary emission rate, initial conditions, the electrode area and the excitation frequency. Variation of the secondary emission rate in the suggested region from $0.01^{13,33}$ to $0.21^{18}$ does not change the simulation results very much. In particular it has no effect on the voltage-current waveform. The initial number density of different plasma species does affect the discharge dynamics at the initial stage of significant transients, but makes little difference when the discharge reaches its steady state. As to the surface area of the electrode, it can only change the peak value of the discharge current largely through a capacitance effect similar to the dielectric layer thickness, but not its pattern. The frequency issue will be discussed in Chapter 6.

The recombination reaction of helium atomic ions with electrons (reaction 8 in table 3.2) need to be mentioned specifically here. The reaction rate is suggested to be the order of $10^{-12}\text{cm}^3\text{s}^{-1}^{13,42}$. The stable plasma can be generated by choosing the rate of this order when the numerical model include helium molecular ions ($\text{He}_2^+$) and helium metastables ($\text{He}(2^3\text{S})$) as well as the reactions that involve $\text{He}_2^+$ and $\text{He}(2^3\text{S})$. The current and voltage characteristics are shown in figure 3.4. By contrast if we simplify our model further and consider only direct ionization (reaction 1) and recombination (reaction 8) through atomic helium ions and electrons, a stable discharge cannot be produced with the same recombination rate of $10^{-12}\text{cm}^3/\text{s}$. In this case, the absence of the typical pattern of one current peak per half cycle confirms that no glow discharge is generated. A large and artificial increase of this rate to the order of $10^6$ is required for the generation of a stable discharge in such a simple model, and a similarly enhanced recombination reaction rate is also used by Ben Gadri for achieving stable APGD with a similar simplistic model$^{14}$,6. This indicates the importance of helium molecular ions and helium metastables in the pure helium discharge model.
3.5 Multi-peak Phenomena of Discharge Current

The typical waveform of the discharge current for an APGD is one peak every half cycle of the applied voltage. But variation in some parameters, for example the magnitude of the applied voltage and the gas gap, can alter this pattern. Figure 3.8 shows the voltage-current waveforms with the magnitudes of the applied voltage set to 1.6kV, 2kV and 2.3kV. All other system parameters are kept the same as those used in figure 3.4. To achieve the gas breakdown and consequently a sharp current spike, the rise of the applied voltage needs to be great enough to enable the gap voltage reaching the breakdown voltage. With the same initial memory voltage, and so the same initial gap voltage, the absolute rise of the applied voltage needed for gas breakdown to be triggered remains the same. However at different applied voltage amplitude (e.g. 1.6kV, 2kV and 2.3kV), this absolute voltage rise represents different proportion of the peak applied voltage. The greater the applied voltage magnitude is, the smaller the proportion is. Therefore, when the magnitude of the applied voltage is great enough, further increase of the applied voltage in the same half-cycle may still be sufficient to cause further gas breakdowns after the initial gas breakdown has already been achieved. This is despite of the fact that the magnitude of the memory voltage has been reduced due to the previous breakdown event. As a result, multiple current spikes appear every half cycle of the voltage excitation, as shown in figure 3.8b and figure 3.8c. Noted that subsequent current spikes have a smaller maximum value, this is a result of the memory voltage being progressively reduced through charge particles accumulating on the dielectric surfaces of the electrodes. It is also noticed from figure 3.8c that there are two current spikes during any positive half cycle but three current spikes during any negative half cycle. This difference between positive and negative cycles are also sometimes observed in experiments and may be due to a mismatch of accumulated charges on the electrodes in positive and negative cycles.
Figure 3.8: Temporal voltage-current waveform at different applied voltages:

(a) \( V_a = 1.6 \text{kV} \); (b) \( V_a = 2 \text{kV} \) and (c) \( V_a = 2.3 \text{kV} \).
With the same applied voltage of 2.3kV but an increased gas gap, the multi-peak phenomenon disappears as shown in figure 3.9. When the gap distance changes from 0.8cm in figure 3.9a to 1.2cm in figure 3.9b, the multi-peak waveform of the discharge current is replaced by a single-peak waveform. The low value of the maximum current density and the flatten current peak are both due to a smaller electric field applied to the plasma reactor compared to the case of figure 3.9a. The maximum electric field applied to the discharge system in case of figure 3.9a is 2kV/cm, while the maximum field in case of figure 3.9b is 1.5kV/cm.

It is found from our study that the distance of the gas gap and the magnitude of the applied voltage are the two most important parameters which can alter the usual discharge characteristic of one current peak every half cycle to a pattern of multiple current peaks every half cycle. The multi-peak phenomenon observed here agrees well with those studied numerically by Wang et al.\textsuperscript{15} and experimentally by Golubovskii et al.\textsuperscript{27}.
Figure 3.9: Temporal voltage-current waveform for different gap distance:
(a) $L = 0.8$ cm; (b) $L = 1.2$ cm.
3.6 Summary

This Chapter concentrates on numerical simulation of atmospheric pressure glow discharges in pure helium. The plasma reactor simulated here is a dielectric-barrier discharge reactor with two parallel and dielectrically coated electrodes. Several important species are considered, including electrons, atomic and molecular ions, metastables and ground state atoms. In our numerical code, reactions considered include ionization, excitation, recombination and charge transfer. Numerical predictions agree with relevant experiment data and computational results by other research groups. Our simulated voltage-current characteristic has the typical plasma dynamic feature of one current peak per half cycle, and the spatial distribution of the electric field and particle densities is also in good agreement with spectroscopic measurements of helium APGD. A parametric study using our numerical model shows that the applied voltage, the gap distance and properties of the dielectric layer can alter the dynamic behaviour of APGD in a very significant way.
Reference


Chapter 4

Atmospheric Glow Discharges in Helium-Nitrogen Mixture

4.1 Introduction

Helium is one of the most common gases used for atmospheric plasma generation because of its outstanding capability to stabilise high-pressure gas discharges. This has been established comprehensively by many research groups through both computational and experimental studies\textsuperscript{41-44}. In Chapter 3, we have discussed stable glow discharges produced in pure atmospheric helium and our numerical predication of their temporal and spatial characteristics agrees well with those obtained experimentally. However in reality, gas purity is difficult to achieve and 100\% pure gas is impossible. Thus the impurity in the background helium gas is inevitable in any experiment. Significantly, impurity gases play a very important role in plasma chemistry of atmospheric helium discharges as suggested in many studies\textsuperscript{45-47}. The presence of a small amount of impurity can increase markedly the discharge current density as well as densities of electrons, ions and energised metastables. This is due to the fact that the addition of impurity gases introduces many more chemical reactions with large reaction
coefficients, thus providing more pathways for generation of relevant plasma species. Among these additional chemical reactions, Penning ionization, charge transfer and three-body reaction are the most significant and they will be detailed in this Chapter.

The issue of impurity gases has drawn a lot of attention in the research of atmospheric discharge plasmas. So far studies have been undertaken for APGD in helium-nitrogen mixture\(^4\), argon-nitrogen mixture\(^4\), and neon-nitrogen mixture\(^4\). It has been proven that nitrogen impurity is important in all cases. Similarly it has been shown that plasma dynamics change significantly when other reactive gases (such as oxygen) are introduced\(^4\). In this case, the presence of a small amount of oxygen is advantageous because it allows for the production of highly oxidising agents such as atomic oxygen and ozone that are central to many applications including sterilization and decontamination. Consequently oxygen is often intentionally added into the background gas of helium. Although plasma dynamics of atmospheric He-O\(_2\) discharges are outside the scope of this thesis, it is clear that APGD in gas mixtures rather than pure gas are both inevitable in practices and useful for their applications.

In this Chapter, we focus on the significant effect of nitrogen impurity in APGD generated in He-N\(_2\) mixture. In section 4.2, major issues of their physical models and numerical implementations are discussed. We present discussion and selection of the transport parameters of the plasma system, the ionization coefficient, the breakdown voltage, the key plasma species and chemical reactions. Considerations of these issues form the basis of the physical model of atmospheric He-N\(_2\) discharges in a dielectric-barrier configuration. Furthermore we discuss key issues of the numerical implementation of our physical model. The importance of the Penning reaction is discussed specifically in section 4.3. Section 4.4 concentrates on the simulation results in comparison with those for pure helium APGD so as to contrast out the effect of nitrogen impurity. Finally, findings of this Chapter will be summarised in section 4.5.
4.2 Physical Models and Numerical Implementations

In this section, we describe both the physical model for atmospheric glow discharges in helium-nitrogen mixture and its associated numerical model. Similar to our physical model of APGD in pure helium, the key assumption here is the hydrodynamic approximation whereby electrons are assumed to be in equilibrium with the local electric field and as such the ionization coefficient and other reaction coefficients are treated as a function of the local electric field. The geometric configuration of the plasma reactor under consideration is the same as that considered for the pure helium case of Chapter 3. This allows for a direct comparison between these two different APGD systems. The addition of nitrogen introduces more chemical reactions and more plasma species. These need to be considered in our physical model and its numerical implementation.

4.2.1 Transport parameters

Similar to our treatment of pure helium discharges, the spatial-temporal distribution of plasma species is calculated by solving their individual convective-diffusion equations. For electrons and ions, both drift and diffusion influence their spatial-temporal distribution. For neutral species including metastables, only diffusion is important because the electric field between the electrodes affects the drift of charged particles but not the motion of neutral particles.

In our simulation, the drift velocities of any charged species are function of the local electric field, and the relationship is represented as the following formula:

\[ W = f(E) = \mu E. \] (4.1)

where \( \mu \) is the mobility. A simple relation, known as the Einstein equation\textsuperscript{44,11}, relates the mobility of a plasma species to its diffusion coefficient:

\[ \frac{D}{\mu} = \frac{kT_{\text{en}}}{|q|} \] (4.2)
where \( k \) is Boltzmann's constant, \( T_{en} \) is the temperature, and \( q \) is electrical charge of the considered particles.

The considerations of transport parameters in the gas mixture are different from that in the pure gases, because their values vary with gas composition, although the mobility and diffusion coefficient are both found to vary inversely with the number density of the pure gases\textsuperscript{4,12}. The Blanc's law\textsuperscript{4,12} can be used to calculate the mobilities and diffusion coefficients for all plasma species:

\[
\frac{1}{X_{\text{mix}}} = \frac{x_1}{X_1} + \frac{x_2}{X_2} + \cdots + \frac{x_n}{X_n}.
\]

The capital \( X \) in the denominator is used to represent either the mobility, \( \mu \), or the diffusion coefficient, \( D \), and the lowercase \( x \) in the numerator represents mole fraction of each constituent gas in the gas mixture. The subscript represents different gases that make up the gas mixture. In this way, the mobility and diffusion coefficient of a specific plasma species in a gas mixture is represented as a function of their values in individual pure gases of the gas mixture and their percentage concentrations.

The individual values of the mobility and diffusion coefficient of electrons and heavy particles in pure helium and pure nitrogen can be found in many literatures\textsuperscript{4,12-4,17} at different pressures and temperatures. Table 4.1 summarises the values used in this work.
Table 4.1: Transport parameters in helium and nitrogen at atmospheric pressure and room temperature.\textsuperscript{4,12,17}

<table>
<thead>
<tr>
<th>Mobility (cm(^2)V(^{-1})s(^{-1}))</th>
<th>Background Gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electron (e)</td>
<td>1132 Helium</td>
</tr>
<tr>
<td></td>
<td>553 Nitrogen</td>
</tr>
<tr>
<td>Helium atomic ion (He(^+))</td>
<td>14.82 Helium</td>
</tr>
<tr>
<td></td>
<td>1.36 Nitrogen</td>
</tr>
<tr>
<td>Helium molecular ion (He(_2^+))</td>
<td>24.03 Helium</td>
</tr>
<tr>
<td></td>
<td>2.20 Nitrogen</td>
</tr>
<tr>
<td>Helium triplet metastable (He(_2^3)S))</td>
<td>0 Helium</td>
</tr>
<tr>
<td></td>
<td>0 Nitrogen</td>
</tr>
<tr>
<td>Nitrogen molecular ion (N(_2^+))</td>
<td>29.93 Helium</td>
</tr>
<tr>
<td></td>
<td>2.74 Nitrogen</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Diffusion coefficient (cm(^2)s(^{-1}))</th>
<th>Background Gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electron (e)</td>
<td>1737 Helium</td>
</tr>
<tr>
<td></td>
<td>381.5 Nitrogen</td>
</tr>
<tr>
<td>Helium atomic ion (He(^+))</td>
<td>0.383 Helium</td>
</tr>
<tr>
<td></td>
<td>0.035 Nitrogen</td>
</tr>
<tr>
<td>Helium molecular ion (He(_2^+))</td>
<td>0.621 Helium</td>
</tr>
<tr>
<td></td>
<td>0.057 Nitrogen</td>
</tr>
<tr>
<td>Helium triplet metastable (He(_2^3)S))</td>
<td>4.116 Helium</td>
</tr>
<tr>
<td></td>
<td>0.378 Nitrogen</td>
</tr>
<tr>
<td>Nitrogen molecular ion (N(_2^+))</td>
<td>0.773 Helium</td>
</tr>
<tr>
<td></td>
<td>0.071 Nitrogen</td>
</tr>
</tbody>
</table>
4.2.2 Ionization coefficient and breakdown voltage

With the hydrodynamic model, the local electric field approximation is used in the calculation of both transport parameters and ionization coefficients. The ionization coefficients for helium and nitrogen are defined differently as following:\[18\]:

\[
\alpha = \begin{cases} 
Ap \exp\left(-Bp/E\right) & \text{Helium} \\
Ap \exp\left(-Bp/E\right) & \text{Nitrogen}
\end{cases}
\]

The unit of \(\alpha\) is \(\text{cm}^{-1}\). For helium, constant \(A\) is \(4.4 \text{cm}^{-1}\text{Torr}^{-1}\) and \(B\) is \(14\sqrt{1/2} \text{cm}^{1/2}\text{Torr}^{1/2}\). For nitrogen, the values of \(A\) and \(B\) are 4.11:

\[
\begin{cases} 
A = 12.0, & B = 342 & E / p > 100 \\
A = 8.8, & B = 155 & E / p < 100
\end{cases}
\]

In this case, the unit for \(A\) is \(\text{cm}^{-1}\text{Torr}^{-1}\), and the unit for \(B\) is \(\text{Vcm}^{-1}\text{Torr}^{-1}\) respectively.

![Figure 4.1: Townsend ionization coefficients of helium atoms in pure atmospheric helium (solid line) and nitrogen molecules in pure atmospheric nitrogen (dotted line).](image_url)
Ionization coefficients of eq.(4.4) describe direct gas ionization by electron impact on both neutral helium and nitrogen species in the ground state. The effective ionization coefficient for a gas mixture can be defined as follows:

\[ \alpha = \alpha_{\text{helium}} \times (1 - \eta) + \alpha_{\text{nitrogen}} \times \eta, \]  

where \( \eta \) is the percentage nitrogen content in the background gas. Townsend ionization coefficients for pure helium and pure nitrogen calculated from eq. (4.4) are shown figure 4.1. For our simulation study, the breakdown voltage is chosen to be 1.3kV based on the previous discussion on pure helium discharges in Chapter 3. Given that the peak gap voltage needs to be greater than the breakdown voltage and that the space charges increase the gap voltage even further, we assume, somewhat arbitrarily, the peak gap voltage to be 20% more than the breakdown voltage. We further assume the discharge gap to be between 0.3cm - 1cm as this range of the electrode gap would realistically lead to stable APGD. This suggests a gap electric field within 0 - 5.2kV/cm. Because the breakdown voltage chosen for this study is 1.3kV, the minimum electric field is 1.3kV/cm at the gap distance of 1cm. So the effective ionization region is in 1.3kV/cm - 5.2kV/cm (marked as the shadow region in figure 4.1). It is noticed that in this region the ionization coefficient for nitrogen is at least seven orders of magnitudes below that of helium. Thus, the addition of nitrogen impurity does not affect the direct ionization in any significant way.

4.2.3 Key chemical reactions and species

Table 4.2 lists all chemical reactions and their corresponding reaction rates considered in this study. With the addition of a small amount of nitrogen into the background helium gas, seven nitrogen species are likely to be produced. They are (1) nitrogen molecules, \( \text{N}_2 \); (2) nitrogen atoms, \( \text{N} \); (3) nitrogen molecular excited species, \( \text{N}_2^* \); (4) nitrogen molecular ions, \( \text{N}_2^+ \); (5) nitrogen atomic ions, \( \text{N}^+ \), and (6) other nitrogen ions, \( \text{eg}, \text{N}_3^+ \) and \( \text{N}_4^+ \). Ion species \( \text{N}^+ \) and \( \text{N}_2^+ \) can be produced directly from the ionization of nitrogen molecules on ground state, and their ionization energy levels are presented in table 4.3.
Table 4.2: Reactions considered for a He-N₂ discharge and their rate coefficients

<table>
<thead>
<tr>
<th>No</th>
<th>Reaction</th>
<th>Reaction rate</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Direct ionization</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.</td>
<td>He(1S) + e → He⁺ + e + e</td>
<td>( a_1 )</td>
<td>Ref. 4.6, 4.18</td>
</tr>
<tr>
<td>2.</td>
<td>N₂ + e → N₂⁺ + e + e</td>
<td>( a_2 )</td>
<td>Ref. 4.6, 4.19</td>
</tr>
<tr>
<td><strong>Excitation</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>He(1S) + e → He(2S) + e</td>
<td>( \beta_1 )</td>
<td>Ref. 4.16</td>
</tr>
<tr>
<td>4.</td>
<td>He(2S) + 2He(1S) → He₂⁺ + He(1S)</td>
<td>( 1.90 \times 10^{-34} \text{ cm}^6 \text{ s}^{-1} )</td>
<td>Ref. 4.20</td>
</tr>
<tr>
<td><strong>De-excitation</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.</td>
<td>He(2S) + e → He(1S) + e</td>
<td>( 4.20 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1} )</td>
<td>Ref. 4.21</td>
</tr>
<tr>
<td><strong>Penning reaction</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.</td>
<td>He(2S) + N₂ → He(1S) + N₂⁺ + e</td>
<td>( 8.00 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1} )</td>
<td>Ref. 4.16</td>
</tr>
<tr>
<td><strong>Stepwise ionization</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.</td>
<td>He(2S) + He(2S) → He(1S) + He⁺ + e</td>
<td>( 2.90 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1} )</td>
<td>Ref. 4.22</td>
</tr>
<tr>
<td><strong>Charge transfer</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.</td>
<td>He⁺ + 2He(1S) → He₂⁺ + He(1S)</td>
<td>( 3.00 \times 10^{-32} \text{ cm}^6 \text{ s}^{-1} )</td>
<td>Ref. 4.1, 4.16</td>
</tr>
<tr>
<td><strong>Recombination</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9.</td>
<td>He⁺ + e → He(1S)</td>
<td>( 2.00 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1} )</td>
<td>Ref. 4.23</td>
</tr>
<tr>
<td>10.</td>
<td>He₂⁺ + e → He₂⁺</td>
<td>( 5.00 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} )</td>
<td>Ref. 4.24</td>
</tr>
<tr>
<td>11.</td>
<td>He⁺ + 2e → He(1S) + e</td>
<td>( 7.10 \times 10^{-20} \text{ cm}^6 \text{ s}^{-1} )</td>
<td>Ref. 4.1, 4.16</td>
</tr>
<tr>
<td>12.</td>
<td>He₂⁺ + e → He(2S) + He</td>
<td>( 5.00 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1} )</td>
<td>Ref. 4.20</td>
</tr>
<tr>
<td>13.</td>
<td>He₂⁺ + 2e → 2He⁺ + e</td>
<td>( 2.00 \times 10^{-20} \text{ cm}^6 \text{ s}^{-1} )</td>
<td>Ref. 4.16</td>
</tr>
<tr>
<td>14.</td>
<td>N₂⁺ + e → N + N</td>
<td>( 4.80 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1} )</td>
<td>Ref. 4.15</td>
</tr>
<tr>
<td>15.</td>
<td>N₂⁺ + 2e → N₂ + e</td>
<td>( 1.40 \times 10^{-26} \text{ cm}^6 \text{ s}^{-1} )</td>
<td>Ref. 4.15</td>
</tr>
<tr>
<td><strong>Three body reaction</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16.</td>
<td>He⁺ + e + He → He(1S) + He(2S)</td>
<td>( 1.00 \times 10^{-27} \text{ cm}^6 \text{ s}^{-1} )</td>
<td>Ref. 4.23</td>
</tr>
<tr>
<td>17.</td>
<td>He₂⁺ + e + He → He₂⁺ + He</td>
<td>( 5.00 \times 10^{-27} \text{ cm}^6 \text{ s}^{-1} )</td>
<td>Ref. 4.24</td>
</tr>
<tr>
<td>18.</td>
<td>N₂⁺ + e + N₂ → 2 N₂</td>
<td>( 3.12 \times 10^{-29} \text{ cm}^6 \text{ s}^{-1} )</td>
<td>Ref. 4.15</td>
</tr>
</tbody>
</table>
Table 4.3: Ionization energy of nitrogen ion species.

<table>
<thead>
<tr>
<th>Product Species</th>
<th>Ionization Energy (eV)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>N⁺</td>
<td>21.60</td>
<td>Ref. 4.9</td>
</tr>
<tr>
<td>N₂⁺</td>
<td>18.70</td>
<td>Ref. 4.9</td>
</tr>
</tbody>
</table>

Since N⁺ ions have a higher ionization energy than N₂⁺, their production is less significant than N₂⁺ and so N₂⁺ ions are expected to be more abundant. The ion species N₃⁺ and N₄⁺ cannot be produced through such mechanism, and they can only be generated through the further reaction between the nitrogen molecules, on either the ground or excited states, and the ion species N₂⁺. This suggests that the ion species, N₃⁺ and N₄⁺, have higher ionization energy level than N₂⁺. Again N₂⁺ is expected to dominate and this suggests that it may well be adequate to include N₂⁺ as the only nitrogen ions in our simulation. This is further supported by three considerations: (1) the leading reaction in He-N₂ discharges, Penning reaction, produces predominantly the nitrogen molecular ion, N₂⁺; (2) N₂⁺ has lower energy level than other ion species; and (3) optical emission spectroscopy studies of He-N₂ atmospheric glow discharges suggest that the nitrogen molecular ion, N₂⁺, is the dominant impurity species. So in our simulation study, except for those species we considered for pure helium plasmas and the nitrogen molecules N₂, only the nitrogen molecular ion, N₂⁺, is taken into account. The nitrogen atom, N, is not included in the simulation because (1) its density is normally two to three orders of magnitude lower than the density of the nitrogen molecules; and (2) it can easily react with the nitrogen atomic ions, N⁺, and helium atoms to form the nitrogen molecular ions, N₂⁺. The two nitrogen species considered in our model, N₂ and N₂⁺, lead to a total of five additional reactions compared to the case of pure helium APGD (e.g. reaction 2, 6, 14, 15, and 18 in table 4.2). These are discussed below.

Similar to the direct ionization of helium atoms (reaction 1), electron
bombardment on nitrogen molecules causes their direct ionization. This is governed by reaction 2, the direct ionization of nitrogen:

\[ \text{N}_2 + e \rightarrow \text{N}_2^+ + e + e. \]

From figure 4.1, we know the direct ionization of nitrogen is much weaker than that of helium. The direct ionization of nitrogen does not contribute much to the production of electron and nitrogen ions, which is the reason why some research groups do not consider it in their numerical simulation\textsuperscript{416}.

Reaction 6 is the Penning reaction,

\[ \text{He} (2^3S) + \text{N}_2 \rightarrow \text{He} (1^1S) + \text{N}_2^+ + e, \]

and it provides an important and significant route for electron production. Reaction 14 and 15 are recombination processes between nitrogen molecular ions and electrons,

\[ \text{N}_2^+ + e \rightarrow \text{N} + \text{N} \]
\[ \text{N}_2^+ + 2e \rightarrow \text{N}_2 + e. \]

In other words they are both pathways for consuming nitrogen molecular ions. Reaction 18 is a three-body reaction that involves nitrogen molecular ions, electrons and nitrogen molecules:

\[ \text{N}_2^+ + e + \text{N}_2 \rightarrow 2 \text{N}_2. \]

This also provides a pathway for nitrogen molecular ions and electrons to be consumed in the plasma process.

Table 4.4: The range of species density in atmospheric He-N\(_2\) discharges.

<table>
<thead>
<tr>
<th>Product Species</th>
<th>Minimum Density (cm(^{-3}))</th>
<th>Maximum Density (cm(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>e</td>
<td>(1.8 \times 10^6)</td>
<td>(1.5 \times 10^{10})</td>
</tr>
<tr>
<td>He(^+)</td>
<td>(1.6 \times 10^4)</td>
<td>(1.7 \times 10^{10})</td>
</tr>
<tr>
<td>He(_2^+)</td>
<td>(4.7 \times 10^4)</td>
<td>(2.0 \times 10^{10})</td>
</tr>
<tr>
<td>He (2(^3)S)</td>
<td>(4.5 \times 10^4)</td>
<td>(7.0 \times 10^{10})</td>
</tr>
<tr>
<td>N(_2^+)</td>
<td>(2.0 \times 10^8)</td>
<td>(5.0 \times 10^9)</td>
</tr>
</tbody>
</table>
Because each chemical reaction contributes to the production of relevant species at different levels, it is important to understand their relative contributions. Table 4.4 lists the maximum and minimum particle density of all the species considered in this study. These extreme values are compiled from the numerical simulations performed by ourselves and by other research groups. From these particle densities and the relevant reaction coefficients, the parametric range of densities of any product species can be estimated for each chemical reaction and these listed in table 4.5. For reaction 1 and 2, the ionization coefficient at the breakdown electric field at a gap size of 0.8 cm is used. As it is clearly seen, electron production by reaction 6, the Penning reaction, is much higher than that by direct ionization and indeed by any other electron production reaction (Reaction 2 and 7). This highlights the importance of the Penning ionization in atmospheric He-N₂ plasmas.

Helium atomic ions are mainly produced by direct ionization and stepwise ionization, and consumed by the charge transfer process (reaction 8). Reaction 8 is the major reaction for the production of helium molecular ion He₂⁺ and reaction 17 is the major reaction that consumes He₂⁺. For nitrogen species, reaction 6 is the dominant reaction that produces nitrogen molecular ions N₂⁺, and consumes the helium triplet metastable He(2³S). N₂⁺ particles recombine with electrons through reaction 14, 15 and 18. The dominant reaction that produces helium triplet metastable He(2³S) is reaction 16.

From the chemical reactions considered in the model, we notice that the balance between the production and loss mechanisms of any species is very important for the generation and sustainment of stable plasma. We have discussed this partly in Chapter 3. Production and consumption of any plasma species, especially charged particles in our cases, must be dynamically balanced, and anything breaking this balance can finally result in the collapse of stable discharge either through arcing or through extinction.
Table 4.5: Production (+) and consumption (−) of plasma species in He-N₂ discharges.

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction Rate</th>
<th>Minimum Source</th>
<th>Maximum Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrons:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.</td>
<td>2.32 x 10⁻¹ cm⁻¹</td>
<td>4.73 x 10⁸ cm⁻³s⁻¹</td>
<td>3.94 x 10¹² cm⁻³s⁻¹</td>
</tr>
<tr>
<td>2.</td>
<td>2.20 x 10⁻²⁸ cm⁻¹</td>
<td>4.48 x 10⁻¹⁹ cm⁻³s⁻¹</td>
<td>3.74 x 10⁻¹⁵ cm⁻³s⁻¹</td>
</tr>
<tr>
<td>6.</td>
<td>8.00 x 10⁻¹¹ cm³ s⁻¹</td>
<td>1.00 x 10¹⁴ cm⁻³s⁻¹</td>
<td>1.00 x 10¹⁶ cm⁻³s⁻¹</td>
</tr>
<tr>
<td>7.</td>
<td>2.90 x 10⁻⁹ cm⁻³ s⁻¹</td>
<td>2.90 x 10⁹ cm⁻³s⁻¹</td>
<td>2.90 x 10¹⁴ cm⁻³s⁻¹</td>
</tr>
<tr>
<td>9.</td>
<td>2.00 x 10⁻¹² cm³ s⁻¹</td>
<td>-2.00 x 10⁶ cm⁻³s⁻¹</td>
<td>-2.00 x 10⁹ cm⁻³s⁻¹</td>
</tr>
<tr>
<td>10.</td>
<td>5.00 x 10⁻¹⁰ cm³ s⁻¹</td>
<td>-5.00 x 10⁸ cm⁻³s⁻¹</td>
<td>-5.00 x 10¹⁰ cm⁻³s⁻¹</td>
</tr>
<tr>
<td>11.</td>
<td>7.10 x 10⁻²⁰ cm³ s⁻¹</td>
<td>-7.10 x 10⁷ cm⁻³s⁻¹</td>
<td>-7.10 x 10¹⁵ cm⁻³s⁻¹</td>
</tr>
<tr>
<td>12.</td>
<td>5.00 x 10⁻⁹ cm³ s⁻¹</td>
<td>-5.00 x 10⁶ cm⁻³s⁻¹</td>
<td>-5.00 x 10¹⁴ cm⁻³s⁻¹</td>
</tr>
<tr>
<td>13.</td>
<td>2.00 x 10⁻²³ cm³ s⁻¹</td>
<td>-2.00 x 10⁶ cm⁻³s⁻¹</td>
<td>-2.00 x 10⁹ cm⁻³s⁻¹</td>
</tr>
<tr>
<td>14.</td>
<td>4.80 x 10⁻⁸ cm⁻³ s⁻¹</td>
<td>-4.80 x 10¹⁰ cm⁻³s⁻¹</td>
<td>-4.80 x 10¹³ cm⁻³s⁻¹</td>
</tr>
<tr>
<td>15.</td>
<td>1.40 x 10⁻²⁶ cm³ s⁻³</td>
<td>-1.40 x 10⁹ cm⁻³s⁻¹</td>
<td>-1.40 x 10¹⁴ cm⁻³s⁻¹</td>
</tr>
<tr>
<td>16.</td>
<td>1.00 x 10⁻²⁷ cm³ s⁻³</td>
<td>-2.50 x 10¹⁰ cm⁻³s⁻¹</td>
<td>-2.50 x 10⁻²⁷ cm⁻³s⁻¹</td>
</tr>
<tr>
<td>17.</td>
<td>5.00 x 10⁻²⁷ cm³ s⁻³</td>
<td>-1.25 x 10¹¹ cm⁻³s⁻¹</td>
<td>-1.25 x 10³ cm⁻³s⁻¹</td>
</tr>
<tr>
<td>18.</td>
<td>3.12 x 10⁻²⁹ cm³ s⁻³</td>
<td>-3.90 x 10⁶ cm⁻³s⁻¹</td>
<td>-3.90 x 10⁻⁶ cm⁻³s⁻¹</td>
</tr>
<tr>
<td>Helium atomic ion: He⁺</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.</td>
<td>1.90 x 10⁻³⁴ cm³ s⁻¹</td>
<td>1.56 x 10¹⁴ cm⁻³s⁻¹</td>
<td>1.56 x 10¹⁵ cm⁻³s⁻¹</td>
</tr>
<tr>
<td>8.</td>
<td>3.00 x 10⁻³² cm³ s⁻¹</td>
<td>1.88 x 10¹⁶ cm⁻³s⁻¹</td>
<td>1.88 x 10¹⁷ cm⁻³s⁻¹</td>
</tr>
<tr>
<td>10.</td>
<td>5.00 x 10⁻¹⁰ cm³ s⁻¹</td>
<td>-5.00 x 10⁸ cm⁻³s⁻¹</td>
<td>-5.00 x 10¹⁰ cm⁻³s⁻¹</td>
</tr>
<tr>
<td>12.</td>
<td>5.00 x 10⁻⁹ cm³ s⁻¹</td>
<td>-5.00 x 10⁸ cm⁻³s⁻¹</td>
<td>-5.00 x 10¹⁰ cm⁻³s⁻¹</td>
</tr>
<tr>
<td>13.</td>
<td>2.00 x 10⁻²⁰ cm³ s⁻¹</td>
<td>-2.00 x 10⁷ cm⁻³s⁻¹</td>
<td>-2.00 x 10⁹ cm⁻³s⁻¹</td>
</tr>
<tr>
<td>17.</td>
<td>5.00 x 10⁻²⁷ cm³ s⁻¹</td>
<td>-1.25 x 10¹¹ cm⁻³s⁻¹</td>
<td>-1.25 x 10¹³ cm⁻³s⁻¹</td>
</tr>
<tr>
<td>Nitrogen molecular ion: N₂⁺</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>2.20 x 10⁻²⁸ cm⁻¹</td>
<td>4.48 x 10⁻¹⁹ cm⁻³s⁻¹</td>
<td>3.74 x 10⁻¹⁵ cm⁻³s⁻¹</td>
</tr>
<tr>
<td>6.</td>
<td>8.00 x 10⁻¹¹ cm³ s⁻¹</td>
<td>1.00 x 10¹⁴ cm⁻³s⁻¹</td>
<td>1.00 x 10¹⁵ cm⁻³s⁻¹</td>
</tr>
<tr>
<td>14.</td>
<td>4.80 x 10⁻⁸ cm⁻³ s⁻¹</td>
<td>-4.80 x 10¹⁰ cm⁻³s⁻¹</td>
<td>-4.80 x 10¹³ cm⁻³s⁻¹</td>
</tr>
<tr>
<td>15.</td>
<td>1.40 x 10⁻²⁶ cm³ s⁻³</td>
<td>-1.40 x 10⁹ cm⁻³s⁻¹</td>
<td>-1.40 x 10¹⁴ cm⁻³s⁻¹</td>
</tr>
<tr>
<td>18.</td>
<td>3.12 x 10⁻²⁹ cm³ s⁻³</td>
<td>-3.90 x 10⁶ cm⁻³s⁻¹</td>
<td>-3.90 x 10⁻⁶ cm⁻³s⁻¹</td>
</tr>
<tr>
<td>Helium metastable: He(2pS)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>2.32 x 10⁻¹⁴ cm⁻¹</td>
<td>4.73 x 10⁸ cm⁻³s⁻¹</td>
<td>3.94 x 10¹² cm⁻³s⁻¹</td>
</tr>
<tr>
<td>4.</td>
<td>1.90 x 10⁻³⁴ cm³ s⁻¹</td>
<td>-1.56 x 10¹⁴ cm⁻³s⁻¹</td>
<td>-1.56 x 10¹⁵ cm⁻³s⁻¹</td>
</tr>
<tr>
<td>5.</td>
<td>4.20 x 10⁻⁹ cm³ s⁻¹</td>
<td>-2.90 x 10⁹ cm⁻³s⁻¹</td>
<td>-2.90 x 10¹⁰ cm⁻³s⁻¹</td>
</tr>
<tr>
<td>6.</td>
<td>8.00 x 10⁻¹¹ cm³ s⁻¹</td>
<td>-1.00 x 10¹⁴ cm⁻³s⁻¹</td>
<td>-1.00 x 10¹⁵ cm⁻³s⁻¹</td>
</tr>
<tr>
<td>7.</td>
<td>2.90 x 10⁻⁹ cm³ s⁻¹</td>
<td>-2.90 x 10⁹ cm⁻³s⁻¹</td>
<td>-2.90 x 10¹⁰ cm⁻³s⁻¹</td>
</tr>
<tr>
<td>12.</td>
<td>5.00 x 10⁻⁹ cm³ s⁻¹</td>
<td>5.00 x 10⁹ cm⁻³s⁻¹</td>
<td>5.00 x 10¹⁰ cm⁻³s⁻¹</td>
</tr>
<tr>
<td>16.</td>
<td>1.00 x 10⁻²⁷ cm³ s⁻¹</td>
<td>2.50 x 10¹⁰ cm⁻³s⁻¹</td>
<td>2.50 x 10¹² cm⁻³s⁻¹</td>
</tr>
</tbody>
</table>
4.2.4 Secondary emission rates

In this study, the secondary emission of electron from electrode is caused by three positive ions, and they are \( \text{He}_2^+ \), \( \text{He}^+ \) and \( \text{N}_2^+ \). Because the discharge rig configuration is the same as the pure helium one, in which the alumina dielectric layers are assumed to be coated on the two parallel electrodes, we choose the secondary emission rates to be \( 0.1^{+26} \), \( 0.1^{+26} \) and \( 0.02^{+27} \) for \( \text{He}_2^+ \), \( \text{He}^+ \) and \( \text{N}_2^+ \) respectively.

4.2.5 Numerical implementation

In Chapter 2, the two numerical algorithms considered in this project have been described in details. The first algorithm, IDMA, requires relatively small computational resources. This is because IDMA treats the entire set of the original convection-diffusion equations (eq. (2.20)) as a whole, and calculates the unknown particle density at all different spatial positions simultaneously. As a result, IDMA avoids the massive iteration loop that is usually necessary for calculating particle densities at successive spatial points, and hence saves a lot of computation time. IDMA is also easy to implement. As long as the convection-diffusion equations for each species is discretized into the format of eq. (2.30), the spatial-temporal distribution of particle densities can be obtained by IDMA, and the specific range of transport parameters does not require any modification on the computer code of IDMA. This allows for a good IDMA code to be used for simulation of different plasma systems without any change to the algorithm structure.

By contrast, FCT is centred around a combined utilization of low- and high-order discretization schemes so as to avoid, as much as possible, the local maxima and minima. By minimising calculation around local maxima and minima, the FCT algorithm is intrinsically more stable and capable of treating less-stable gas discharge systems accurately. It is also likely to be more accurate than IDMA, particularly for high-current plasma systems which tend to have large local maxima and minima. Under certain conditions, proper implementation of the FCT algorithm can increase the calculated particle density by up to two orders of magnitude compared to results of
other numerical simulation of the same gas discharge\textsuperscript{4,28}. Therefore for atmospheric plasmas of large current density, the FCT algorithm should in principle be used. However this is at the expense of implementation simplicity and computation time. The reasons lie in the additional calculation of the flux corrective limiter, the associated additional time and spatial computation loops, and the restricted small time step that is necessary for the stability of the simulation. Typically for the same APGD case, the FCT algorithm takes approximately 20 times as much as the TDMA algorithm.

In the case of pure helium discharges discussed in Chapter 3, the two methods produce similar results in terms of the voltage-current waveform and the magnitude of key physical quantities including the discharge current density and the electron density. In the case of helium-nitrogen discharges, both methods produce similar current-voltage characteristics at low nitrogen contents ($\leq 0.01\%$), yet the magnitude of discharge current and electron density produced by FCT implementation is in general lower than that of TDMA one. This is understandable because the FCT algorithm avoids the calculation in maxima/minima region to some extent. However the FCT algorithm is more stable and capable of simulating atmospheric He-N\textsubscript{2} discharges with high nitrogen content (up to 50%), whereas the TDMA algorithm is numerically stable only at low nitrogen content ($\leq 0.01\%$). Therefore for He-N\textsubscript{2} APGD at large nitrogen content ($>0.01\%$) and hence large discharge current density (typically $>3\text{mA/cm}^2$), FCT must be used largely because of its capability of dealing with less stable plasmas.

As an illustration of FCT's capability of modelling He-N\textsubscript{2} APGD at large nitrogen content, an FCT code is used to calculate the electron density and the discharge current density for the percentage nitrogen content up to 50%. The code employs eq. (4.3) for electron mobility and for electron diffusion, and is numerically stable for all cases studied. The results are shown in figure 4.2. There is a peak value in both the discharge current and electron density when the nitrogen concentration increases. When the nitrogen concentration reaches 1%, the further increase does not change the discharge characteristics too much, and the discharge current and electron density remain approximately constant. On the other hand, the TDMA algorithm leads to
significant numerical instability with overflow of the discharge current and rapid oscillation of the gap voltage when the nitrogen content is above 100ppm. A comparison of the two algorithms is given in table 4.6 to summarize their computational efficiency, accuracy and numerical stability. It should be mentioned that the CPU time is obtained on a 1GHz Pentium III PC with 256M RAM. It should also be noted that the limit of 0.01% nitrogen for stable TDMA implementation is dependent on the plasma configuration, for example the excitation frequency and the breakdown voltage. We will find this limit increases (up to 5%) when the excitation frequency and the breakdown voltage increase in later Chapter 6.

Figure 4.2: Effects of nitrogen concentration on the maximum discharge current and the maximum electron density.
Table 4.6: A comparison between the TDMA and FCT algorithms

<table>
<thead>
<tr>
<th></th>
<th>TDMA</th>
<th>FCT</th>
</tr>
</thead>
<tbody>
<tr>
<td>CPU time</td>
<td>185 second/cycle</td>
<td>3548 second/cycle</td>
</tr>
<tr>
<td>Accuracy</td>
<td>Similar when (\eta \leq 0.01%)</td>
<td></td>
</tr>
<tr>
<td>Stability</td>
<td>Stable when (\eta \leq 0.01%)</td>
<td>Stable at any (\eta).</td>
</tr>
</tbody>
</table>

Given that trace nitrogen in industrial helium used in APGD experiments is likely to be less than 100 ppm and that TDMA is numerically stable for \(\eta \leq 0.01\%\), the TDMA algorithm is preferred for its computational efficiency over the FCT algorithm in this Chapter.

4.3 Results and Discussion

The plasma reactor simulated here is of a dielectric barrier discharge configuration identical to that used in Chapter 3 for pure helium APGD. A dielectric layer of 0.06 cm thickness is coated on each of the two plane electrodes. The gap distance is 0.8 cm between the two electrodes of radius of 2 cm. The gas pressure in the plasma reactor is assumed to be atmospheric pressure at 760 Torr. A small amount of nitrogen, 100 ppm, is mixed with helium to form the background gas in the plasma reactor. This choice is based on the fact that the purity of industrial helium supplied. For example, purity of helium supplied by the BOC GASES varies from 99.9% and 99.9999% for gas grade 3 to grade 6. In other words the impurity content is 1 ~ 1000 ppm. An impedance-matched voltage source is assumed to provide a sinusoidal voltage of 1600 V peak. In Chapter 3, we have already discussed the influences to the production of discharge plasmas and their characteristics by the reactor geometry and the properties of the voltage source. With a small amount of nitrogen impurity, our simulation finds that those characteristics and their variation established for pure helium.
discharges are still valid for He-N₂ discharges. The only difference is that the addition of nitrogen impurity increases the plasma instability and the discharge is now more sensitive to the variation of the reactor's geometrical parameters and that of the voltage source. As we have already discussed these parametric effects in Chapter 3, we will not discuss this issues further in this chapter while keep our focus on the effects of gas impurity induced.

4.3.1 Voltage-current characteristics

Figure 4.3 illustrates the electrical characteristics of an APGD generated (a) in the pure helium gas; (b) in the helium-nitrogen gas mixture. Similar to the case of the pure helium APGD, the discharge current in the He-N₂ APGD is characterised by a one-peak-per-half-cycle pattern, in which there is a sharp current pulse at each half cycle of the applied voltage. The magnitude and pulse width of the discharge current are two parameters that we use to evaluate the degree of avalanche. It is noticed that the discharge current has a greater magnitude at 30mA in the helium-nitrogen discharge than 22.1mA in the case of the pure helium discharge. To compare the width of the discharge current pulse in both cases, we take the pulse width at \( I_{dc} = 5\)mA as an indicative value. The pulse width is \( 5.2\mu s \) for the He-N₂ discharge and \( 4.9\mu s \) for the pure helium discharge. Both the greater current amplitude and the wider pulse width in the He-N₂ discharge suggest that its avalanche is more significant than that in the pure helium case. In both cases, the discharge current peaks appear in the first quarter of each half cycle, right after the gap voltage reaches its peak and well before the peak of the applied voltage. These peaks exist periodically after the steady state is reached. The positions of the maximum discharge current are strongly dependent on the level of pre-ionization at the beginning of each driving cycle. In both the He-N₂ discharge and the pure helium discharge, the discharge current peaks at about \( 11\mu s \) after the beginning of each half cycle. This suggests that the pre-ionization processes are very similar in both cases.
Figure 4.3: Temporal variation of voltage and current in (a) pure helium discharge; (b) He-N₂ discharge.
In general, the sharp rising and slow tailing behaviour of the He-N$_2$ discharge is very similar to that of the pure helium plasma and to experimental observation$^{416}$. The current and voltage waveforms remain identical from cycle to cycle in the steady state. The major difference between these two discharges is the peak value of the discharge current. The maximum discharge current is 30mA for the He-N$_2$ discharge, which corresponding to a maximum discharge current density of 2.39mA/cm$^2$ (=30mA/$\pi 2^2$cm$^2$). This is about 36% higher than 22.1mA, the peak current value in pure helium discharge. Because the only difference between the pure helium plasma model and the He-N$_2$ plasma model is the composition of background gas, we can conclude that the increase in the discharge current is purely due to the nitrogen content. This conclusion is supported by electron production to be discussed in section 4.3.2.

The voltage-current curve follows the common pattern of typical characteristics of glow discharges, and the magnitude of our simulation discharge current is comparable to the values reported by other groups. The University of Tennessee group reports a peak current density around 1mA/cm$^2$ measured from a series of very comparable experiments$^{429}$. The Okazaki Group at Sophia University in Japan measured a peak current density of around 0.4mA/cm$^2$ (=11.25mA/$\pi 3^2$cm$^2$) with 3kHz excitation$^{430}$. Another Japanese group obtained 1.8mA/cm$^2$ for a 100kHz APGD experiment$^{431}$. More recently, a helium APGD experiment performed at the University of Minnesota recorded a peak current density at 0.5mA/cm$^2$ with a 15kHz driving voltage$^{432}$. Our computed current density falls into the region of these experimental measurements, indicating a good current prediction capability of our model. However both our numerical prediction and measurements obtained by the all aforementioned four groups are markedly smaller than that reported by a French group at University of Toulouse III - Paul Sabatier. They reported a peak current density of 6.4mA/cm$^2$ (=80mA/$\pi 2^2$ cm$^2$)$^{416}$. While it is unclear what may have resulted in such a large peak current density, it appears to be an abnormally large figure for discharge current in He-N$_2$ APGD.
4.3.2 Production of electrons

As established from the last section, the current has a higher magnitude in the He-N₂ discharge than in the pure helium discharge. The discharge current is strongly dependent on how many electrons are produced during the discharge process. This is because electrons are much lighter than ions, excited metastables, and neutral atoms and molecules, and so are much more mobile than other species. To provide more insights, we develop further discussion on electron production in this section.

There are only 4 reactions that contribute to the production of electrons. These are direct ionization (reaction 1 and 2), Penning ionization (reaction 6) and stepwise ionization (reaction 7). The electron production by these reactions can be represented respectively as follows:

\[
\begin{align*}
S_1 &= \alpha_{\text{He}} n_e W_e; \\
S_2 &= \alpha_{\text{N}_2} n_e W_e; \\
S_6 &= K_6 n_{\text{He}(2^3S)} n_{\text{N}_2}; \\
S_7 &= K_7 n_{\text{He}(2^3S)} n_{\text{He}(2^3S)};
\end{align*}
\]

(4.7)

where \( \alpha \) is the direct ionization coefficient; \( K_6 \) and \( K_7 \) are respectively the rates for reaction 6 and 7; \( n \) and \( W \) denote the particle density and drift velocity. Both reaction 6 and 7 involve helium metastables, and this highlights the importance of metastable species in the discharge model.

In figure 4.4, electron production rates by each reaction are shown at two specific time steps, one at the peak discharge current and the other when the magnitude of discharge current is the smallest.
Figure 4.4: Electron production by individual chemical reactions when (a) the discharge current reaches the maximum, and (b) its magnitude is the smallest.
In figure 4.4a, the electron production rate by each of the four reactions is plotted as a function of distance at the instant when the discharge current is highest and the left electrode is the cathode. It is clear that electron production is more efficient in the small region close to the cathode. This is the sheath region, and the large electron production in sheath is similar to the case in low- and medium-pressure glow discharges. It is also clear that the most significant electron production mechanism is the Penning ionization, followed by the direct ionization of helium atoms and stepwise ionization. The latter two have comparable ionization rates. Nitrogen direct ionization is the least significant. This indicates the enhanced discharge induced by nitrogen impurity is not due to the direct ionization process but due to the Penning ionization.

In figure 4.4b for the case when the magnitude of the discharge current is the smallest, the electric field between the gas gap is very low, which means the electric field is not high enough to activate the direct ionization. The Penning ionization is again the most significant with its electron production rate being four and seven orders of magnitude above that of helium direct ionization and stepwise ionization respectively. Again, the nitrogen direct ionization is the most insignificant reaction.

From the above discussion, we can clearly see the importance of the nitrogen impurity and the helium metastables, and that of the Penning reaction in the helium-nitrogen discharge.
Figure 4.5: Spatial distribution of the electric field and charged particle densities when the discharge current reaches (a) the positive maximum; (b) the negative maximum.
4.3.3 Spatial profile of electric field and particle densities

Figure 4.5a presents the spatial profiles of electric field and charged particle densities at the time instant of the positive current maximum and the cathode being on the left. Under the effect of electric field between two electrodes, the positive ions move towards the instantaneous cathode, and bombard the cathode surface. As a result secondary electrons are emitted from the cathode (see figure 4.6). These secondary electrons drift towards the anode and in their movement produce more ions. As ions are not as mobile as electrons, they form a sheath near the cathode and this sheath of ions results in an additional electric field, $E_{sh}$.

![Diagram of motion of charged particles]

**Figure 4.6:** Schematic diagram of the motion of charged particles closed to the instantaneous cathode.

This additional electric field leads to a large voltage fall from the cathode surface to the plasma bulk, extending over a region of about 0.1cm in this case, and this region is also known as the cathode fall. In this region, the electric field decreases nearly linearly from the cathode surface to the bulk region, and so is the ion density. The
maximum electric field of 3.89 kV/cm and the maximum ion density of 3.8 x 10^6 cm^-3 both occur in this region. The secondary electrons are accelerated by the large electric field in the sheath region, and thus enhance the direct ionization. From the anode side of the ion-sheath to the anode, there is a wide region in which the electric field is relative constant. The electrons and ions are of roughly the same density in this region, and the space charges are insignificantly. This quasi-neutral region is called the positive column. The electric field in this region is mainly dependent on the external field. Between the cathode fall and positive column regions, a narrow negative glow region and a Faraday dark space can be observed experimentally from optical emission of the discharge, which is approximately the region of 0.15 cm - 0.3 cm from the cathode in figure 4.5a. The spatial distributions of particle density and electric field in figure 4.5b are very similar to the above discussion, but now with the cathode on the right.

The spatial profiles of the electric field and charged particles density of figure 4.5 are similar to that of glow discharge at low- and medium-pressures\(^{41}\). They are also similar to that of the DC APGD\(^{43}\) and RF APGD\(^{44}\) presented in figure 4.7. It should be noted that the ion density of RF APGD does not peak near the cathode surface. This is resulted from the rapid oscillation of ions at the very high frequency of the driving RF power in RF APGD. It is also worth mentioning that the electric field and particle density in our study are not of the same magnitude as that of the DC and RF APGD, but this is consistent with relevant experimental observations\(^{42,45}\).

It is seen in figure 4.5 that maximum electric field is 3.89 kV/cm. This is within the range of the electric field used in estimating the direct ionization coefficient \(\alpha_1\) and \(\alpha_2\) in section 4.2.2 and figure 4.1. Therefore our estimation for the effective direct ionization coefficient is valid.
Figure 4.7: Spatial profiles of the electric field and charged particles of (a) DC APGD\textsuperscript{433} and (b) RF APGD\textsuperscript{434}.
Figure 4.8: Spatial profile of the electric field, the electron density and the helium metastable density when (a) the discharge current reaches the maximum, and (b) its magnitude is the smallest.
Figure 4.8 shows the spatial distribution of helium metastable and that of the electric field and the electron density at two specific instants. Figure 4.8a shows the spatial profiles corresponding to the time instant when the discharge current reaches its positive peak. At this time, the direct ionization as well as the direct excitation of helium atom is effective, so the production of helium metastable is mainly through the direct excitation. The profile of helium metastable has the similar trend to that of the electric field, and the density of helium metastable in the cathode fall region is much larger than that in plasma bulk region. At the time instant when the magnitude of discharge current is the smallest, the electric field in the plasma region is too weak to activate the direct ionization and excitation (see figure 4.8b), and the direct excitation of helium atom is no longer the dominant mechanism of the production of helium metastable. Other reactions, for example reaction 12 and 16 in table 4.5, are now more important. Thus, the spatial profile of helium metastable does not follow the trend of the electric field. Comparing the electron production (figure 4.4) and the profile of helium metastable (figure 4.8) at both time instants, we can clearly see the close relationship between them, and again this proves the importance of Penning ionization in He-N₂ atmospheric pressure glow discharge.

4.4 Summary

Because the inevitability of gas impurity in real APGD systems, we study the atmospheric pressure glow discharges generated in a helium-nitrogen gas mixture in this Chapter. The relevant issues that gas impurity brings into the discharge system are studied through numerical simulation. Two numerical methods, IDMA and FCT, are used to implement our plasma model. The former is advantageous in terms of computer resource and computation time, and the latter is superior in terms of computational stability. With the addition of 100ppm nitrogen, the discharge system produces more electrons as well as increases the discharge current and the electric field. Comparing this study to the pure helium discharge, the discharge current is increased by
about 36%, and both the electric field and particle densities are increased by about 15%.
For He-N$_2$ APGD, the Penning reaction is shown to be the most significant reaction, and its important role is clearly illustrated by comparing electron production of four ionization processes and by the spatial profile of helium metastable. In general, the spatial profiles of the electric field and particle density are very similar to those of low- and medium-pressure glow discharge, and also consistent to experimental observations of such plasmas. The qualitative and quantitative comparisons between our results and those reported by other groups result in favourable agreement and as such validate our numerical code for the further studies of dielectric barrier APGD.
Reference


4.15. P. Segur and F. Massines, “The role of numerical modeling to understand the behaviour and to predict the existence of an atmospheric pressure glow discharge controlled by a dielectric barrier”, *International Conference on Gas Discharge and Their Applications, Glasgow, UK*, pp. II.3, 2000.


4.24. P. C. Hill and P. R. Herman, "Reaction processes in a $\text{He}_2^+ (\text{C}_2 \Pi_u \rightarrow \text{A}^2 \Sigma_g^+)$ flash lamp", *Physical Review A*, vol. 47, no. 6, pp. 4837-4844, 1993.


4.34. J. J. Shi, private communication, Loughborough University, UK.

Chapter 5

APGD with Pulsed Excitation

5.1 Introduction

So far, we have studied numerically atmospheric pressure glow discharges generated in both pure helium gas and helium-nitrogen gas mixture. Their physical, electrical and chemical characteristics have been discussed in Chapter 3 and Chapter 4. Computationally predicted properties of these APGD are very similar to those obtained experimentally. While these characteristics of APGD have allowed for their widespread applications, it is always advantageous to be able to influence and control them so as to enhance their current applications and facilitate new applications. For example surface modification usually requires high electron density to provide sizeable fluxes of active plasma species (e.g. O and O₂), but also favours low electron energy to mitigate damage to the surface material\textsuperscript{51}. A capability of tailoring these specific plasma properties is therefore both desirable and essential. In the case of atmospheric pressure glow discharges, this is pursued mainly through plasma reactor designs and plasma reactants, and to a lesser extent through an appropriate choice of the excitation frequency\textsuperscript{52}.

For streamer-dominated atmospheric gas discharges, pulsed-plasma generation has
been known to facilitate better energy efficiency and greater control of the glow-to-arc transition. If similar improvement can be achieved for diffuse atmospheric glow discharges through pulsed excitation, it will offer a considerable scope to improve many applications including surface modification. In this Chapter, we consider pulsed excitation voltage as a way to control and optimise the properties of atmospheric pressure glow discharges. This Chapter aims to study the electrical properties of atmospheric pressure glow discharges under pulsed excitation. Two specific questions will be answered: 1) whether pulsed excitation can lead to a saving in electrical power needed to sustain a given APGD and 2) if so, how the voltage waveform of the pulsed excitation may be adjusted to enhance the energy efficiency. We consider APGD generated in a helium-nitrogen gas mixture and between two dielectrically insulated parallel plate electrodes. Our study is based on the one-dimensional computer code developed in Chapter 2.

An atmospheric He-N₂ glow discharge under the usual sinusoidal excitation, as described in Chapter 4, is used as a standard case for comparison, and its main features are summarised in section 5.2 for future reference. Effects of pulsed excitation are discussed in section 5.3 with consideration of three different pulsed waveforms, namely: 1) peak-levelled sinusoidal; 2) peak-levelled and tail-trimmed sinusoidal; and 3) Gaussian-tailed sinusoidal.

5.2 Key APGD Features under Sinusoidal Excitation

Sinusoidal is the most common and pervasive waveform of the excitation voltage for plasma generation. For a plasma reactor with a gap distance of 0.8cm and a radius of 2cm, we have considered in Chapter 4 a sinusoidal source voltage at 10kHz with a peak voltage of 1.6kV. The background gas is made of 99.99% helium and 0.01% nitrogen, and its breakdown voltage is assumed to be 1.3kV. Figure 5.1 shows the applied voltage, the gas voltage, and the discharge current as a function of time, reproduced from our results of Chapter 4. We have compared this $V$-$J$ characteristics
to those obtained in a comparable experiment and its numerical simulation\textsuperscript{5,5,6}, and found they are very similar in both waveform pattern and magnitude. The simulated discharge has the typical pattern of atmospheric glow discharges, which has one discharge event every half cycle of the applied voltage and whose current peaks occur far ahead of the nearest peaks of the applied voltage. The peak discharge current is found to be 30mA, and its corresponding current density is 2.39mA/cm\textsuperscript{2}. This discharge has an average dissipation power density of 260.7mW/cm\textsuperscript{3} and a maximum electron density of 1.17x10\textsuperscript{10}cm\textsuperscript{3}. These properties all fall into the region of relevant experimental data reported by the majority of other APGD research groups\textsuperscript{5,1,5,5,9}. The temporal and spatial distribution of electrons is shown in figure 5.2, and this is also in a similar trend to those discovered through numerical and experimental studies\textsuperscript{5,5}.

![Graph showing V-I characteristics under the sinusoidal excitation.](image)

Figure 5.1: \textit{V-I} characteristics under the sinusoidal excitation.

In general, numerical data of the \textit{V-I} characteristics and that of the temporal and spatial distribution of plasma species compare favourably with available experimental data of similar APGD. Therefore, our plasma model is capable of capturing the main plasma features accurately and can be used reliably to study the benefits of APGD with the pulsed excitation.
5.3 Effects of Pulsed Excitation

The potential benefits of pulsed excitation can be best understood from the $V-I$ characteristics in figure 5.1. It is noticed that the peaks of the discharge current occur in the rising part of the excitation voltage in each half cycle when the applied voltage has relatively low magnitude, and the duration of the discharge current is very short, about several microseconds. After this short period of current surge, the discharge current decreases in magnitude while the applied voltage keeps increasing till its maximum value. This suggests that from the tailing-off of the current surge to the polarity reversal point of the applied voltage in the same half cycle, the applied voltage does not contribute to the plasma generation but encourage large power dissipation in the plasma. This additional power dissipation during the "plasma-off" phase leads to unnecessary heating of electrons. Through their collisions with heavy neutral particles,
electrons transfer their kinetic energy to the heavy particles and this results in an increase in gas temperature. Therefore, by reducing the excitation voltage over this inactive period of electron production, the gas temperature can be lowered and the electrical power dissipation in the plasma can be reduced as well. To this end, we consider shaping the waveform of the excitation voltage.

5.3.1 Peak-levelled sinusoidal waveform

First of all, we consider a very simple pulsed voltage as shown in figure 5.3. This waveform is essentially derived from a sinusoidal wave with its peak (both positive and negative) levelled to a flat top. This waveform is a realistic option for pulsed excitation because it can be easily achieved electronically. The magnitude of the original sinusoidal voltage, \( V_s \), is fixed at 1.6kV, whereas that of the peak-levelled voltage, \( V_p \), varies within a certain range. Clearly, the more voltage magnitude levelled down, the more input power is likely to be saved. However a too aggressive levelling can lead to premature extinction of the generated APGD, and so \( V_p \) needs to be within a suitable range. The repetition frequency of the excitation voltage remains at 10kHz as that in the sinusoidal excited plasma of figure 5.1. The peak-levelled sinusoidal waveform can be described by the following formula in order to be implemented in the numerical algorithm:

\[
V_p(t) = \begin{cases} 
V_s \sin\left(\frac{\pi}{2} - x_i\right) & \left(\frac{\pi}{2} - x_i\right) < \text{rem}(2\pi ft, 2\pi) < \left(\frac{\pi}{2} + x_i\right) \\
V_s \sin\left(\frac{3\pi}{2} - x_i\right) & \left(\frac{3\pi}{2} - x_i\right) < \text{rem}(2\pi ft, 2\pi) < \left(\frac{3\pi}{2} + x_i\right) \\
V_s \sin(2\pi ft) & \text{else} 
\end{cases}
\]  

(5.1)

where \( 0 \leq x_i \leq \frac{\pi}{2} \), \( \text{rem}(2\pi ft, 2\pi) \) gives the remainder after the division. The value of \( x_i \) determines how much the sinusoidal peak is levelled off, and is an initial parameter pre-set in the computer code. For all numerical examples considered in this subsection, \( V_s = 1.6 \text{kV} \).
Figure 5.3: A peak-levelled sinusoidal excitation voltage.

Figure 5.4 shows the voltage and current characteristics of an atmospheric pressure glow discharge generated with the pulsed excitation voltage of figure 5.3 having its peak value, \( V_p \), at 1.28kV and \( V_p/V_s = 0.8 \). It is found that the discharge current remains repetitive and stable throughout many tens of cycles of the applied voltage. Therefore under the conditions considered here, replacing the sinusoidal plasma-generating voltage with a peak-levelled sinusoidal voltage does not appear to significantly affect the establishment of the atmospheric pressure glow discharge. More specifically the waveform of the discharge current remains relatively unchanged from that under the sinusoidal excitation, and the peak discharge current, around 28mA, is very similar to the sinusoidal case in figure 5.1.
Figure 5.4: $V-I$ characteristics under the peak-levelled sinusoidal excitation.

By levelling the sinusoidal peak down, the basic $V-I$ characteristics remain relatively unchanged until $V_p$ decreases below 1.18kV at which point the generated plasma becomes unsustainable and eventually extinguishes. This variation is illustrated in figure 5.5, where the normalized maximum electron density and the normalized averaged plasma power are plotted against the normalized magnitude of the applied voltage, $V_p/V_s$. All normalisation is against values obtained with the sinusoidal excitation. It is clearly shown that when $V_p/V_s \geq 0.8$, pulsed excitation does not significantly affect the electron density while the plasma power is reduced by up to 20%. Our simulation results also show that ion densities are almost unaffected by decreasing $V_p$ as long as $V_p/V_s \geq 0.8$. Given that the electron and ion densities remain approximately the same and that the waveforms of the discharge current and the gas voltage undergo relatively small changes, the basic plasma characteristics should remain relatively unchanged. In other words, the peak-levelled sinusoidal excitation of figure
5.3 affects little those applications that rely on the production of electrons or/and ions, yet achieves in an obvious power saving.

![Normalized particles density and normalized plasma power density as a function of the normalized magnitude of the applied voltage.](image)

**Figure 5.5:** Normalized particles density and normalized plasma power density as a function of the normalized magnitude of the applied voltage in a He-N\textsubscript{2} APGD ([N\textsubscript{2}]=100ppm).

It is of interest to understand how reaction chemistry may influence the level of achievable power saving. In the case of pure helium APGD shown in figure 5.6, the amount of power saved by the pulsed excitation is similar to that in the helium-nitrogen APGD of figure 5.5. It is therefore conceivable that similar power saving can also be achieved in pulsed APGD in other atmospheric gas mixtures, and the proposed power saving technique is generic.

As an additional indication of the similarity between the sinusoidal case of figure 5.1 and the peak-levelled sinusoidal case of figure 5.4, temporal and axially spatial variation of the electron density for figure 5.4 is plotted in figure 5.7 and these is similar to that in figure 5.2. This again indicates the little affected plasma characteristics. As a reference for comparison, the peak electron density in this case is 1.16x10\textsuperscript{10}cm\textsuperscript{-3}.
Figure 5.6: Normalized particles density and normalized plasma power density as a function of the normalized magnitude of the applied voltage in a pure helium APGD.

Figure 5.7: Electron density distribution under the peak-levelled sinusoidal excitation.
5.3.2 Peak-levelled and tail-trimmed sinusoidal excitation

This is a pulsed excitation for which a peak-levelled sinusoidal is trimmed further to enhance plasma production efficiency. The waveform of the tail-trimmed voltage is shown in figure 5.8.

![Figure 5.8: A peak-levelled and tail-trimmed sinusoidal excitation voltage.](image)

The excitation source can be implemented with the following formula:

\[
V_s(t) = \begin{cases} 
V_s \sin \left( \frac{\pi}{2} - x_1 \right) & \text{if } \left( \frac{\pi}{2} - x_1 \right) < \text{rem}(2\pi f t, 2\pi) \leq \left( \frac{\pi}{2} + x_1 - x_2 \right) \\
V_s \sin \left( \frac{\pi}{2} - x_1 \right) \sin(2\pi f t + \theta) & \text{if } \left( \frac{\pi}{2} + x_1 - x_2 \right) < \text{rem}(2\pi f t, 2\pi) < \pi \\
V_s \sin \left( \frac{3\pi}{2} - x_1 \right) & \text{if } \left( \frac{3\pi}{2} - x_1 \right) < \text{rem}(2\pi f t, 2\pi) \leq \left( \frac{3\pi}{2} + x_1 - x_2 \right) \\
V_s \sin \left( \frac{\pi}{2} - x_1 \right) \sin(2\pi f t + \theta) & \text{if } \left( \frac{3\pi}{2} + x_1 - x_2 \right) < \text{rem}(2\pi f t, 2\pi) < 2\pi \\
V_s \sin(2\pi f t) & \text{else}
\end{cases}
\]
$$0 \leq x_1 \leq \frac{\pi}{2} \quad 0 \leq x_2 \leq 2x_1$$

$$T' = 2\left(\frac{1}{2} - \frac{x_1}{\pi} + \frac{x_2}{\pi}\right)T$$

$$f' = \frac{1}{T'}$$

$$\theta = \pi(1 - f'/f)\text{ceil}(2, f)$$

Function $\text{ceil}(2, f)$ gives the nearest integer to $(2, f)$ towards infinite. $x_1$ and $x_2$ are two pre-set parameters used to control the shape of the voltage tailing-off.

Our simulation results suggest that within a certain range of trimming it is possible to achieve modest power saving without affecting the production and properties of the atmospheric glow discharge. More specifically, the key parameters of the atmospheric pressure glow discharge, such as the discharge current, the gas voltage and the particle density, are affected little by trimming the voltage tail. This is shown in figure 5.9.

![Figure 5.9: V-I characteristics of a He-N₂ APGD ([N₂]=100ppm) under the peak-levelled and tail-trimmed sinusoidal excitation.](image)

For a specific peak-levelled applied voltage, for example in the case of figure 5.4, the variation of $x_2$ in eq. (5.2) allows for further decrease of the plasma power as
shown in figure 5.10. When the voltage tail is not trimmed, \( x_2 = 0 \) and so 
\[
\frac{(2x_1 - x_2)}{2x_1} = 1.
\]
This corresponds to the peak-levelled sinusoidal case with 
\[
\frac{V_p}{V_s} = \sin\left(\frac{\pi}{2} - x_1\right).
\]
Quantities in figure 5.10 are normalized to values of the peak-levelled sinusoidal case with \( \frac{V_p}{V_s} = 0.8 \). In this case, the plasma power can be further reduced by more than 8%. Therefore the peak-levelled and tail-trimmed sinusoidal excitation can save as much as 1-81.6\%\times(1-8\%)=25\% in electrical power consumption over the case with sinusoidal excitation of figure 5.1. It should be noted also that the electron density is reduced by 11\% from that in figure 5.1 when the power saving of 25\% is achieved. When \( \frac{(2x_1 - x_2)}{2x_1} < 0.7 \), the plasma can hardly be generated because the power delivered into the system is insufficient to initiate and sustain a discharge.

![Figure 5.10: Normalized particles density and normalized plasma power density as a function of the normalized tail-trimmed degree in a helium APGD.](image-url)
Figure 5.11: Electron density distribution under the peak-levelled and tail-trimmed sinusoidal excitation.

Figure 5.11 is the temporal and axially spatial variation of the electron density. The distribution is very similar to that of the sinusoidal and peak-levelled cases, especially the latter one. The maximum electron density of figure 5.11 is $1.04 \times 10^{10} \text{ cm}^{-3}$, which is about 10% lower than $1.16 \times 10^{10} \text{ cm}^{-3}$ in the case of the peak-levelled sinusoidal of figure 5.4.

### 5.3.3 Gaussian-tailed sinusoidal excitation

In section 5.3.1 and 5.3.2, two simple pulsed excitations are studied for helium APGDs. The results indicate significant power saving achieved by decreasing the voltage magnitude without affecting the basic plasma behaviour. Now, we consider how pulsedwidth may affect plasma generation. As an example, a particular type of the pulsed voltage signal is constructed from a sinusoidal signal for the voltage rise phase and a Gaussian decay for the voltage tail phase. The reason for constructing such a particular pulsed source is that the rising part of excitation source contributes mainly to discharge production, while the tailing part contributes to sustaining rather than
generating APGD. Thus, power saving occurred in the rising part may affect plasma in a more sensitive way than that in the tailing part.

Mathematically, in each cycle, the Gaussian-tailed sinusoidal excitation may be expressed in the following format:

\[
V_\theta(t) = \begin{cases} 
V_s \sin \omega t & \text{if } 2N\pi \leq t < t_0 + 2N\pi \\
V_1 \exp \left[-\left(t - t_0 - 2N\pi\right)^2 / \tau^2\right] & \text{if } t_0 + 2N\pi \leq t < 2N\pi + \pi \\
V_s \sin \omega t & \text{if } 2N\pi + \pi \leq t < t_0 + 2N\pi + \pi \\
-V_1 \exp \left[-\left(t - t_0 - 2N\pi - \pi\right)^2 / \tau^2\right] & \text{if } t_0 + 2N\pi + \pi \leq t < 2N\pi + 2\pi 
\end{cases}
\]

(5.3)

where \(V_s\) is the peak value of the sinusoidal signal, \(V_1\) is the peak value of the Gaussian decay signal, \(\tau\) is the pulse width of the Gaussian signal, \(\omega = 2\pi / T\) is the angular frequency of the sinusoidal applied voltage with \(T\) being its period, and \(t_0\) the instant at which the sinusoidal and the Gaussian signals joint. \(T_0\) and \(t_0\) are defined as follows

\[
T_0 = \frac{T}{2\pi} \arcsin \left[\frac{V_1}{V_s}\right],
\]

\[
t_0 = T_0 + kT/2,
\]

\(k = \text{mod}(t, T/2)\)

Function \(\text{mod}(t, T/2)\) gives the signed remainder after division of \(t\) over \(T/2\).

To compare to the sinusoidal case in figure 5.1, \(V_s\) is set to 1.6kV, \(V_1\) is set to 1.46kV. In order to form a smooth Gaussian-tailed sinusoidal excitation, the variation range of \(\tau\) is \(T/7\) to \(T/30\). The waveform of the Gaussian-tailed sinusoidal excitation is shown in figure 5.12. \(x_3\) is an intermediate variable used for normalization, and defined as \(x_3 = \left[\arcsin \left(\frac{V_1}{V_s}\right) - \arcsin(\exp(-1))\right]/(2\pi / T)\).
The voltage and current waveforms of the generated atmospheric plasma are shown in figure 5.13, with $V_{\text{i}} = 1.46\text{V}$ and $\tau = T/19$. It is evident that the pattern of one discharge every half cycle of the applied voltage remains and again this is repetitive for many tens of cycles. Thus, the generated discharge excited by the Gaussian-tailed sinusoidal excitation is a stable discharge, similar to what is generated under the sinusoidal excitation. On the other hand, it is noticed that the gas voltage is markedly different in figure 5.13 from that in the sinusoidal case of figure 5.1. Particularly, there is a large hump of the gas voltage preceding the main peak that causes the discharge event in each half cycle. These humps are caused by the Gaussian tailing waveform.

The magnitude of the discharge current in figure 5.13 is about 24.7mA, lower than 25.3mA of the sinusoidal case with 1.46kV voltage peak. The pulsewidth of the discharge current in this case is similar to that in the sinusoidal case, the peak-levelled sinusoidal case and the peak-levelled and tail-trimmed sinusoidal case (see figure 5.1, figure 5.4 and figure 5.9 respectively).
As indicated in eq. (5.3) and figure 5.12, the values of $V_1$ and $\tau$ determine the shape of the applied voltage. The smaller these two values are, the less power is delivered to the plasma system. For a clear comparison, we normalize the Gaussian-tailed sinusoidal cases with different $\tau$ values to a sinusoidal case with a voltage peak of $V_1$. Figure 5.14 shows plasma power and electron density with excitation of figure 5.12 and normalized to the values obtained with a sinusoidal excitation voltage of 1.46kV peak. As the width of Gaussian tail decreases from $T/7$ to $T/30$, the value of $\tau/x_1$ decreases from 0.75 to 0.17. The decrease of plasma power is faster than that of the electron density. We can see from figure 5.14 that the electron density varies little from the sinusoidal case when $\tau/x_1$ decreases from 1 to 0.26, while the plasma power decreases by about 35%. It should be noted that this power reduction is with reference to the case with a sinusoidal voltage excitation of 1.46kV peak and that the sinusoidal case in section 5.2 employs a voltage excitation of
1.6 kV peak. The further decreasing in plasma power extinguishes the plasma with much smaller amount of electrons produced. It is interesting to noticed that, in the region of $\tau/x_3 = 0.75 - 0.5$, the electron density in the pulsed excitation case is higher than the comparable sinusoidal case, but with 20% power saving. This is useful for those applications which require high electron density as well as low plasma power.

![Normalized particles density and normalized plasma power density as a function of the normalized Gaussian pulse width in a helium APGD.](image)

Figure 5.14: Normalized particles density and normalized plasma power density as a function of the normalized Gaussian pulse width in a helium APGD.

Figure 5.15 shows the temporal and axial distribution of the electrons. In this case, electrons are generated over a shorter time period than those excited by other voltage sources because the Gaussian-tailed sinusoidal excitation voltage has a narrower half-power width than all other excitation voltages. The electron density in this case is $0.972 \times 10^{10} \text{cm}^{-3}$, and this is similar to the comparable sinusoidal case with a peak voltage of 1460 V whose electron density is $0.981 \times 10^{10} \text{cm}^{-3}$. 
Chapter 5

APGD with Pulsed Excitation

5.3.4 Comprehensive comparison

In the previous sections, we have discussed individually APGD with the standard sinusoidal source and that with three pulsed excitation sources used in our study, including their waveform and their numerical implementations, the voltage-current characteristics of the discharge generated by them, their electron distribution and their plasma power ($P_p$). Here, we give a direct comparison of all these four waveforms. The data in table 5.1 are based on the sample cases of each waveform, corresponding respectively to the cases shown in figure 5.1, figure 5.4, figure 5.9 and figure 5.13. It is clearly seen that all three pulsed excitations can save certain amount of power without reducing the electron density too much.

Comparing these three pulsed excitations, the peaked-levelled sinusoidal excitations is the easiest to be realized and has a reasonable good capability (about 20%) in saving power. Within this level of power saving, stable APGD can be generated without
reducing the electron density. This capability is very important to those applications in which both the high electron density is desirable and the low power is preferable. As what we have mentioned before, the peak-levelled and tail-trimmed sinusoidal excitation is a fine tuning step to the peak-levelled sinusoidal excitation. Although it can save more power than the peak-levelled excitation of the same voltage magnitude, similar reduction in the electron density is induced at the same time. Considering the fact that the tail-trimmed waveform cannot be easily realized, this pulsed excitation is most appropriate for those applications in which low power consumption is critical. The Gaussian-tailed sinusoidal excitation is easier to realize than the peak-levelled and tail-trimmed sinusoidal excitation. The theoretical analysis shows that a proper choice of the magnitude and the width of the Gaussian tail can save up to 42% of plasma power with a 17% reduction of the electron density. This suggests that the Gaussian-tailed sinusoidal excitation is suitable for those applications with a critical requirement for low power saving and a relaxed need for high electron density. Therefore, the proper choice of the pulsed excitations can be used to cater the requirements of different plasma applications. It should be mentioned that there are pulsed excitations with other waveforms. Those pulsed excitations are out of the scope of this study.

**Table 5.1: Comparisons among different excitation sources.**

<table>
<thead>
<tr>
<th>$V_0$ (V)</th>
<th>Max $I_{ds}$ (mA)</th>
<th>Max $n_e$ ($\text{cm}^{-3}$)</th>
<th>Mean $P_p$ Density (mWcm$^{-3}$)</th>
<th>Power Saving Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sinusoidal ($V_0=1600\text{V}$)</td>
<td>29.3</td>
<td>$1.17 \times 10^{10}$</td>
<td>260.7</td>
<td>0%</td>
</tr>
<tr>
<td>Peak-levelled</td>
<td>28.0</td>
<td>$1.16 \times 10^{10}$</td>
<td>212.8</td>
<td>18.4%</td>
</tr>
<tr>
<td>Tail-trimmed</td>
<td>27.4</td>
<td>$1.04 \times 10^{10}$</td>
<td>201.2</td>
<td>22.8%</td>
</tr>
<tr>
<td>Gaussian-tailed</td>
<td>24.7</td>
<td>$0.97 \times 10^{10}$</td>
<td>151.8</td>
<td>41.8%</td>
</tr>
</tbody>
</table>
5.4 Effects of Impurity

The addition of impurity introduces some additional chemical reactions into the plasma system, and typically this adds to plasma instability. Impurity gases also change the total effective ionization coefficients. This change depends on the amount of impurity and the ionization coefficients of the constituent gases of the gas mixture. The effect to the amount of power saving caused by the addition of impurity has already been discussed before in this chapter. In our early work\textsuperscript{5,9}, the ionization coefficient for pure nitrogen in all simulation cases is extrapolated from that of pure helium by using a source term technique. In this chapter, the following formula and constants\textsuperscript{5,10} are used to calculate the ionization coefficient of nitrogen.

\[
\alpha(cm^{-1}) = \begin{cases} 
12 \exp(-342p/E) & E/p > 100(V/cm\cdot Torr^{-1}) \\
8.8 \exp(-155p/E) & E/p > 100(V/cm\cdot Torr^{-1})
\end{cases}
\]  

(5-4)

where \( p \) and \( E \) are the gas pressure and the electric field respectively. The use of eq. (5.4) is more accurate and also allows for effects of the ionization coefficients to be established.

\[\text{Figure 5.16: Comparison of the effective Townsend ionization coefficient.}\]
The difference between these two methods can be seen in figure 5.16. The breakdown voltage for this study is assumed to be 1.3kV, which gives $E/p = 2.14(V/cm^{-1} \text{Torr}^{-1})$. It is noticeable that the Townsend ionization coefficient adopted in this study is lower than that used in our previous study in the APGD operation region ($E/p \geq 2.14(V/cm^{-1} \text{Torr}^{-1})$).

Here we summarize in table 5.2 the helium-nitrogen cases discussed in this work and in our early work. Our simulation results indicate that the different calculations in the ionization coefficient in both studies affect the basic characteristics of plasmas, but not the capability of pulsed excitation in saving the plasma power. This suggests that the power saving achieved by using the pulsed excitation is generic.

<table>
<thead>
<tr>
<th>Excitation Source</th>
<th>Previous work</th>
<th>This work</th>
</tr>
</thead>
<tbody>
<tr>
<td>Max $I_d$ (mA)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sinusoidal</td>
<td>31.43</td>
<td>29.3</td>
</tr>
<tr>
<td>Peak-Levelled</td>
<td>29.83</td>
<td>28.0</td>
</tr>
<tr>
<td>Tail-trimmed</td>
<td>27.69</td>
<td>27.4</td>
</tr>
<tr>
<td>Gaussian-tailed</td>
<td>25.81</td>
<td>24.7</td>
</tr>
<tr>
<td>Max $n_e$ (cm$^{-3}$)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sinusoidal</td>
<td>$1.36 \times 10^{10}$</td>
<td>$1.17 \times 10^{10}$</td>
</tr>
<tr>
<td>Peak-Levelled</td>
<td>$1.18 \times 10^{10}$</td>
<td>$1.16 \times 10^{10}$</td>
</tr>
<tr>
<td>Tail-trimmed</td>
<td>$1.10 \times 10^{10}$</td>
<td>$1.04 \times 10^{10}$</td>
</tr>
<tr>
<td>Gaussian-tailed</td>
<td>$0.93 \times 10^{10}$</td>
<td>$0.972 \times 10^{10}$</td>
</tr>
<tr>
<td>Mean Plasma Power Density (mWcm$^{-3}$)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sinusoidal</td>
<td>249.8</td>
<td>260.7</td>
</tr>
<tr>
<td>Peak-Levelled</td>
<td>206.2</td>
<td>212.8</td>
</tr>
<tr>
<td>Tail-trimmed</td>
<td>200.0</td>
<td>201.2</td>
</tr>
<tr>
<td>Gaussian-tailed</td>
<td>162.3</td>
<td>151.8</td>
</tr>
<tr>
<td>Power Saving Percentage</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sinusoidal</td>
<td>0%</td>
<td>0%</td>
</tr>
<tr>
<td>Peak-Levelled</td>
<td>17.5%</td>
<td>18.4%</td>
</tr>
<tr>
<td>Tail-trimmed</td>
<td>19.9%</td>
<td>22.8%</td>
</tr>
<tr>
<td>Gaussian-tailed</td>
<td>35.0%</td>
<td>41.8%</td>
</tr>
</tbody>
</table>
5.5 Summary

Pulsed excitations are used to generate and sustain helium atmospheric pressure glow discharges. It is found that pulsed the plasma excitation voltage can significantly reduce the electric power needed to sustain atmospheric pressure glow plasmas. Significantly, this can be achieved without considerably affecting the particle densities. We consider three examples of pulsed excitation: peak-levelled sinusoidal excitation, peak-levelled and tail-trimmed sinusoidal excitation and Gaussian-tailed sinusoidal excitation. Adjusting the pulse shape, for example the magnitude of peak-levelled sinusoidal, can achieve reduction in power consumption whilst maintaining electron density. Adjusting the pulsewidth of the Gaussian-tailed sinusoidal excitation in certain range can improve the production of electrons and metastables whilst achieving modest reduction in plasma power. It can also, in certain cases, achieve significant power saving with modest reduction in electron density. Plasma power can be reduced by more than 40% by choosing appropriate pulse shape and pulsewidth. Therefore the effects of waveform-shaping and pulsewidth-reducing are different and so can be used to cater for different applications. In general, waveform-shaping, for example through peak-levelled sinusoidal excitation and certain Gaussian-tailed sinusoidal excitation, would be useful for applications in which both high electron density and low power are desirable. On the other hand, reduction in pulsewidth, for example by means of Gaussian-tailed sinusoidal excitation, is more appropriate for applications where low power operation is the most important requirement.
Chapter 5

APGD with Pulsed Excitation

Reference


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6.1 Introduction

We have already known from previous chapters that atmospheric pressure glow discharges can be generated between dielectrically insulated electrodes. Experimental and numerical studies of DBD have so far established their current-voltage characteristics, plasma dynamics, and density range of charged particles. Some aspects of plasma chemistry have also been examined by investigating, for example, the effect of a small nitrogen content in predominantly helium plasmas. These studies are particularly important in advancing the current knowledge of atmospheric dielectric-barrier discharges. Yet an in-depth understanding of the fundamental plasma processes in the generation and operation of stable atmospheric DBD is still far from complete.

One of the missing pieces in a full understanding of atmospheric DBD is the dependence of their stable production upon temporal characteristics of the applied voltage such as excitation frequency and waveform. A sound understanding of
such correlation will offer valuable insight into the fundamental mechanisms of stable DBD generation. It will also establish the frequency range in which atmospheric DBDs are most stable and hence most appropriate for wide-ranging applications. Although stable atmospheric DBD has been generated experimentally at different and discrete frequencies of sinusoidal excitation\textsuperscript{6,3,6,4}, a generic frequency dependence of stable DBD generation can enable a practical capability of significant implications. For example it will allow for informed choice of power sources from commercial products for DBD production and facilitate design considerations for optimised and future power sources. Ultimately this generic dependence will contribute to system optimization of atmospheric dielectric-barrier discharge equipment with tailored characteristics for DBD dynamics and for power source matching.

An experimental study of the frequency range of stable DBD requires either many fixed-frequency power sources or several unoptimized variable-frequency sources to cover a frequency range as wide as possible. This is an expensive approach, particularly because the targeted frequency range is unknown at the outset of such study and so multiple power sources have to be sourced. In this chapter, we use the computer code developed in Chapter 3 and 4 to establish numerically the frequency range for the generation of stable DBD and to explore the likely mechanisms for disruption of DBD stability. It will be shown that at a too low excitation frequency the accumulating electrons on the dielectric coatings set up too quickly the opposing memory voltage and as such overly suppress the growth of the applied voltage. This results in a premature quenching of atmospheric DBD. When the excitation frequency is too high on the other hand, electrons generated in the plasma bulk become trapped within the inter-electrode space and as such are unable to reach the electrodes to form the necessary opposing memory voltage. Similarly this also disrupts the stability of the DBD and leads to plasma quenching. The above issues are investigated for two different atmospheric dielectric-barrier discharges, namely impure helium DBD (helium mixed with nitrogen) and pure nitrogen DBD. The comparison of these two DBDs will establish whether our results are generic with different plasma chemistry.
6.2 Numerical Simulations of Helium and Nitrogen DBD

Atmospheric dielectric-barrier discharges are generated between two dielectrically coated parallel-plate electrodes and usually with an ac sinusoidal excitation voltage. We have developed in Chapter 2 a useful numerical model based on a hydrodynamic technique. For the DBD generated in different background gases, they are different in terms of their specific parameters, for example the breakdown voltage and the transport parameters of plasma species. The temporal and spatial distribution of major plasma quantities have similar trends, although they might have different magnitudes in different background gases.

![Figure 6.1: Current and voltage characteristics of a helium-nitrogen DBD with a 40kHz sinusoidal excitation. Gas voltage is in solid curve, the discharge current in thick dashed curve, and the applied voltage in dot curve.](image)

For atmospheric DBD in helium mixed with a small amount of nitrogen (say 0.5%), Penning ionization is important\(^6\,^{16,5}\) and this has been discussed specifically in Chapter 4. The plasma reactor in this work has a radius of 2cm and a gap distance of 0.5cm. The alumina layer coated on the electrodes is of 0.06cm thick, and its relative permittivity is
chosen to be 9. The nitrogen content is 0.5% of the background gas mixture. An external sinusoidal driving source of 2kV and 40kHz is applied to the plasma reactor, and the current and voltage characteristics of its resulting helium-nitrogen discharge are shown in figure 6.1. This is similar to that obtained in a comparable experiment\(^6\) and our fluid simulation in Chapter 4. The typical atmospheric DBD characteristics of one current peak every half cycle of the voltage excitation are clearly shown in this figure. The discharge current density is about 13.43mA/cm\(^2\) in this case.

For the atmospheric DBD in pure nitrogen, the similar numerical considerations are taken. Again, we consider ionization, excitation, stepwise ionization, charge transfer, ionic conversions and recombination. The nitrogen discharge model includes 11 species namely electrons, atomic nitrogen ions (e.g. N\(^+\)), molecular nitrogen ions (e.g. N\(_2\)\(^+\), N\(_3\)\(^+\), and N\(_4\)\(^+\)), molecular nitrogen metastables (e.g. N\(_2\)(a\(^1\Sigma_u^+\)), N\(_2\)(a\(^3\Sigma_u^-\)), N\(_2\)(B\(^3\Pi_g\)), N\(_2\)(C\(^3\Pi_u\)), and two ground state neutral species N atoms and N\(_2\) molecules. The detailed chemical reactions and rates are all listed in table 6.1. The rate \(\gamma\) of secondary electron emission caused by nitrogen ions is chosen to be 0.01\(^6\). The radius of the parallel-plate electrodes is 2cm and the electrode separation distance is 0.2cm. The alumina coating on both electrodes is 0.015cm thick with its relative permittivity chosen to be 9. These geometrical parameters are necessarily different from those for helium DBD to better match the breakdown characteristics of nitrogen.

The transport parameters are identical to those used in the work of Segur and Massines\(^6\)\(^7\). Figure 6.2 shows the current and voltage traces of stable nitrogen discharge with a 3kHz applied voltage source of 9kV. The current peaks of pure nitrogen discharge have a much wider width than that of helium discharge. The discharge current density is 2.84mA/cm\(^2\). Now we investigate how current-voltage characteristics deviate from that in figures 6.1 and 6.2 when the excitation frequency is either too high or too low.
Table 6.1: Reactions considered for a pure N₂ discharge and their rate coefficients

<table>
<thead>
<tr>
<th>No</th>
<th>Reaction</th>
<th>Reaction rate</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Direct ionization</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>( \text{N}_2 + e \rightarrow \text{N}_2^+ + e + e )</td>
<td>( \alpha_1 )</td>
<td>Ref. 6.6</td>
</tr>
<tr>
<td>2</td>
<td>( \text{N}_2 + e \rightarrow \text{N}^+ + \text{N} + 2e )</td>
<td>( \alpha_2 )</td>
<td>Ref. 6.6</td>
</tr>
<tr>
<td></td>
<td>Excitation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>( \text{N}_2 + e \rightarrow \text{N}_2(\Lambda^2\Sigma_u^+) + e )</td>
<td>( \beta_1 )</td>
<td>Ref. 6.6</td>
</tr>
<tr>
<td>4</td>
<td>( \text{N}_2 + e \rightarrow \text{N}_2(a^1\Sigma_u^+) + e )</td>
<td>( \beta_2 )</td>
<td>Ref. 6.6</td>
</tr>
<tr>
<td></td>
<td>Recombination</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>( \text{N}_2^+ + e \rightarrow 2 \text{N}_2 )</td>
<td>( 2.0 \times 10^5 \left( \frac{T_e}{T_d} \right)^{0.5} \text{ cm}^3/\text{s} )</td>
<td>Ref. 6.7</td>
</tr>
<tr>
<td>6</td>
<td>( \text{N}_2^+ + e \rightarrow 2 \text{N} )</td>
<td>( 2.8 \times 10^7 \left( \frac{T_e}{T_d} \right)^{0.5} \text{ cm}^3/\text{s} )</td>
<td>Ref. 6.7</td>
</tr>
<tr>
<td>7</td>
<td>( \text{N}_2^+ + e \rightarrow \text{N} + \text{N} )</td>
<td>( 2.0 \times 10^7 \left( \frac{T_e}{T_d} \right)^{0.5} \text{ cm}^3/\text{s} )</td>
<td>Ref. 6.7</td>
</tr>
<tr>
<td>8</td>
<td>( \text{N}_2^+ + 2e \rightarrow 2 \text{N} + e )</td>
<td>( 1.0 \times 10^{-3} \left( \frac{T_e}{T_d} \right)^{-4.5} \text{ cm}^3/\text{s} )</td>
<td>Ref. 6.7</td>
</tr>
<tr>
<td>9</td>
<td>( \text{N}_2^+ + \text{N}_2 + e \rightarrow 2 \text{N}_2 )</td>
<td>( 6.0 \times 10^{-37} \left( \frac{T_e}{T_d} \right)^{1.5} \text{ cm}^3/\text{s} )</td>
<td>Ref. 6.7</td>
</tr>
<tr>
<td>10</td>
<td>( \text{N}_2^+ + e \rightarrow \text{N}_2 + \text{N} )</td>
<td>( 2.0 \times 10^{-17} \left( \frac{T_e}{T_d} \right)^{0.5} \text{ cm}^3/\text{s} )</td>
<td>Ref. 6.7</td>
</tr>
<tr>
<td></td>
<td>Ion-molecule collisions: ionic conversions and recombination</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>( \text{N}_2^+ + 2 \text{N}_2 \rightarrow \text{N}_2^+ + \text{N}_2 )</td>
<td>( 5.0 \times 10^{-32} \text{ cm}^3/\text{s} )</td>
<td>Ref. 6.7</td>
</tr>
<tr>
<td>12</td>
<td>( \text{N}_2^+ + \text{N}_2 + \text{N} \rightarrow \text{N}_2^+ + \text{N}_2 )</td>
<td>( 3.4 \times 10^{-29} \text{ cm}^3/\text{s} )</td>
<td>Ref. 6.7</td>
</tr>
<tr>
<td>13</td>
<td>( \text{N}_2^+ + \text{N}_2(\Lambda^2\Sigma_u^+) \rightarrow \text{N}_2^+ + \text{N} )</td>
<td>( 3.0 \times 10^{-10} \text{ cm}^3/\text{s} )</td>
<td>Ref. 6.7</td>
</tr>
<tr>
<td>14</td>
<td>( \text{N}_2^+ + \text{N} \rightarrow \text{N}^+ + \text{N}_2 )</td>
<td>( 7.0 \times 10^{-13} \text{ cm}^3/\text{s} )</td>
<td>Ref. 6.7</td>
</tr>
<tr>
<td>15</td>
<td>( \text{N}_2^+ + \text{N} \rightarrow \text{N}_2^+ + \text{N} )</td>
<td>( 6.6 \times 10^{-14} \text{ cm}^3/\text{s} )</td>
<td>Ref. 6.7</td>
</tr>
<tr>
<td>16</td>
<td>( \text{N}_2^+ + \text{N}_2 \rightarrow \text{N}_2^+ + 2 \text{N}_2 )</td>
<td>( 2.4 \times 10^{-15} \text{ cm}^3/\text{s} )</td>
<td>Ref. 6.7</td>
</tr>
<tr>
<td>17</td>
<td>( \text{N}_2^+ + \text{N} \rightarrow \text{N}^+ + 2 \text{N}_2 )</td>
<td>( 1.0 \times 10^{-11} \text{ cm}^3/\text{s} )</td>
<td>Ref. 6.7</td>
</tr>
<tr>
<td></td>
<td>Reactions involving metastables states</td>
<td></td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>( \text{N}^+ + \text{N}_2 + \text{N} \rightarrow \text{N}_2^+ + \text{N}_2 )</td>
<td>( 1.0 \times 10^{-29} \text{ cm}^3/\text{s} )</td>
<td>Ref. 6.7</td>
</tr>
<tr>
<td>19</td>
<td>( \text{N} + \text{N}_2(\Lambda^2\Sigma_u^+) \rightarrow \text{N}_2 + \text{N} )</td>
<td>( 4.0 \times 10^{-11} \text{ cm}^3/\text{s} )</td>
<td>Ref. 6.7</td>
</tr>
<tr>
<td>20</td>
<td>( \text{N}_2(\Lambda^2\Sigma_u^+) + \text{N}_2(a^1\Sigma_u^+) \rightarrow \text{N}_2^+ + \text{N}_2 )</td>
<td>( 5.0 \times 10^{-11} \text{ cm}^3/\text{s} )</td>
<td>Ref. 6.7</td>
</tr>
<tr>
<td>21</td>
<td>( \text{N}_2(a^1\Sigma_u^+) + \text{N}_2(a^1\Sigma_u^+) \rightarrow \text{N}_2^+ + \text{e} )</td>
<td>( 7.7 \times 10^{-11} \text{ cm}^3/\text{s} )</td>
<td>Ref. 6.7</td>
</tr>
<tr>
<td>22</td>
<td>( 2\text{N}_2(\Lambda^2\Sigma_u^+) \rightarrow \text{N}_2 + \text{N}_2(2\Pi_1^0) + \text{e} )</td>
<td>( 7.7 \times 10^{-11} \text{ cm}^3/\text{s} )</td>
<td>Ref. 6.7</td>
</tr>
<tr>
<td>23</td>
<td>( 2\text{N}_2(\Lambda^2\Sigma_u^+) \rightarrow \text{N}_2 + \text{N}_2(2\Pi_2^0) + \text{e} )</td>
<td>( 1.5 \times 10^{-10} \text{ cm}^3/\text{s} )</td>
<td>Ref. 6.7</td>
</tr>
<tr>
<td>24</td>
<td>( \text{N}_2(\Lambda^2\Sigma_u^+) + \text{e} \rightarrow \text{N}_2^+ + 2 \text{e} )</td>
<td>( 1.9 \times 10^{-9} \text{ cm}^3/\text{s} )</td>
<td>Ref. 6.7</td>
</tr>
</tbody>
</table>
6.3 Frequency Range of Stable Plasma Generation

We have already known from Chapter 3 and Chapter 4 that the typical voltage-current characteristics for atmospheric DBD are that: 1) the discharge current has a sharp peak every cycle of the applied voltage; 2) the current peaks well before peaks of the applied voltage. When the conditions of plasma generation vary, such as with changing excitation frequency, these typical characteristics may undergo some distortion suggesting that the properties of the generated discharge have changed. Now we investigate how current-voltage characteristics deviate from that in figures 6.1 and 6.2 when the excitation frequency is either too high or too low.

6.3.1 Controlling processes for plasma stability

To a large extent the stable state of a glow discharge depends on fundamental
processes that control electron production, removal and spatial transfer. In a stable APGD, the production and loss processes of electrons work together to achieve a dynamic balance in which the discharge has an obvious periodic characteristic. For DBD, this dynamic balance of electron density is critically related to the balance between the applied voltage, $V_a$, and the memory voltage, $V_m$, across the two dielectric layers. This is because they determine collectively the gas voltage

$$V_g = V_a - V_m$$  \hspace{1cm} (6.1)$$

that controls directly electron production and plasma quenching. Before a discharge event, the rise of $V_a$ increases $V_g$ until the latter reaches the gas breakdown voltage resulting in electron production. After the breakdown and under the influence of $V_g$, the produced electrons are driven towards the momentary anode, thus contributing to the reversal of the polarity of the initial memory voltage and eventually increasing the magnitude of $V_m$ in the direction that opposes to that of $V_a$. This provides a negative feedback route to counteract the growth of the applied voltage and as such keeps $V_g$ relatively unchanged above the breakdown voltage for a sustained period of time. For dielectric-barrier discharges, the dynamic balance between the applied voltage and the memory voltage is particularly important.

When our numerical model is used to study current-voltage characteristics of the helium DBD with decreasing excitation frequency, the usual pattern of one discharge current peak every half-cycle in figure 6.1 gradually evolves to a pattern in which a group of many small and narrow discharge current pulses occurs in every half cycle. This change is illustrated with a 5.2kHz helium DBD in figure 6.3 where the peak value of the discharge current pulses is small at 25mA compared to 168mA in figure 6.1 and its pulse duration is about 0.35μs reduced from 2μs in figure 6.1. The observed current spikes with small magnitude in figure 6.3 suggest the absence of significant electron production during the discharge procedure. It is therefore evident that electron production is much weakened at 5.2kHz and may not be able to balance
electron losses in the helium DBD. Indeed when the excitation frequency is further reduced to below 5.2kHz, stable helium DBD with a temporally repetitive discharge current cannot be produced and the initial plasma is quenched within the first few cycles of excitation.

![Graph](image)

**Figure 6.3:** Current and voltage characteristics of a helium-nitrogen DBD under 5.1kHz sinusoidal excitation with gas voltage in solid curve, the discharge current in thick dashed curve, and the applied voltage in dot curve.

On the other hand if the excitation frequency is increased, the discharge current pulses become wider and their magnitudes increase. This is illustrated for a 112kHz helium DBD in figure 6.4. The maximum discharge current of 267mA in the 112kHz case is higher than that of 168mA in the 40kHz case. For the helium DBD considered, the maximum excitation frequency for stable plasma production is 112kHz. Therefore the frequency range for the stable helium DBD is between 5.2kHz and 112kHz. It should be noted that this frequency range is specific to the geometrical parameters of the plasma rig and the nitrogen content considered and as such should not be
generalized. However with different geometrical parameters and nitrogen contents, dynamic features of the discharge current and the gap voltage at the two ends of the frequency range are very similar to that in figure 6.3 and 6.4.

![Figure 6.4](image-url)

**Figure 6.4:** Current and voltage characteristics of a helium-nitrogen DBD under 112kHz sinusoidal excitation with gas voltage in solid curve, the discharge current in thick dashed curve, and the applied voltage in dot curve.

6.3.2 Stability disruption mechanism at low frequencies

To unravel the reason why the helium DBD becomes unstable at frequencies below 5.2kHz, it is useful to examine the time scale of electron charging of the dielectric layers and that of the rise of the excitation voltage. These two timescales have to be comparable such that the memory voltage and the applied voltage are dynamically balanced to keep the gas voltage above the breakdown voltage. Electrons produced in the plasma bulk are driven to the momentary anode at the drift velocity. In helium the electron mobility is $\mu = 10^6 / p \text{ cm}^2 \text{s}^{-1} \text{V}^{-1}$ with $p$ being the gas pressure$^{66}$ and the maximum gas voltage in the 5.2kHz case is approximately 1.75kV (see figure 6.3).
Therefore the rms electric field over the 0.5 cm helium gap is \( E_{\text{rms}} = 3.50 \text{kV/cm} \) giving the drift velocity \( v_d = \mu E_{\text{rms}} = 4.61 \times 10^6 \text{ cm/s} \). So it will take \( \Delta t_d = 108 \text{ ns} \) for an electron to travel from the cathode to the anode. Essentially this is the timescale required for free electrons produced in the plasma bulk to sufficiently charge the dielectric coating of the electrodes in every half cycle of the excitation voltage. In turn this timescale is essential for establishing a substantial opposing memory voltage to control the rise of the applied voltage in the subsequent half cycle. It is desirable that the applied voltage rises at roughly the same speed as that of electron charging of the electrodes, since a simultaneous rise of \( V_m \) and \( V_a \) is particularly useful in keeping the gas voltage constant and above the breakdown voltage according to eq. (6.1). If we use 0.25\( T \) as a measure of the rise-time of the applied voltage with \( T \) being its repetition period, this rise-time is about 48\( \mu \text{s} \) at 5.2 kHz. In other words, the rise of the applied voltage is more than 444 times slower than the establishment of the memory voltage. As a result and according to eq. (6.1), the gas voltage is above the breakdown voltage only briefly after which the much faster establishment of the memory voltage reduces the gas voltage rapidly to below the breakdown voltage. To confirm this, the applied voltage and the memory voltage are plotted in figure 6.5 over a short time-span around one discharge event. It is clear that the applied voltage rises much slower than the memory voltage thus leading to a rapid reduction of the gas voltage. The timescale mismatch of more than 444 times between the applied voltage and the memory voltage is very significant and it leads to a premature and permanent quenching of the helium DBD. The resulted reduction in electron production in turn disrupts the balance between electron production and loss for subsequent cycles of the excitation voltage. Below 5.2 kHz, this unbalancing becomes irreversible and makes it impossible to generate a stable DBD.
Figure 6.5: The applied voltage, the memory voltage and the gas voltage as a function of time normalized to the electron drift time at 5.2kHz.

6.3.3 Stability disruption mechanism at high frequencies

When the excitation frequency is too high, it is possible that electrons produced in the plasma bulk become trapped between the two electrodes by the fast oscillating electric field of the applied voltage. Under such circumstances, most electrons cannot reach the electrodes and as such are unable to alter the memory voltage adequately. So the memory voltage remains relatively unchanged and is unable to maintain a dynamic balance with the applied voltage (see eq. (6.1)).

To evaluate this hypothesis, we consider electron oscillation under a sinusoidal electric field. If the excursion of most electrons from the midpoint between the two electrodes is less than half of the interelectrode distance, they will be unable to adequately charge the dielectrically coated electrodes and so the memory voltage cannot maintain a dynamic balance with the applied voltage for repetitive and stable generation.
of DBD. To this end, we estimate the oscillation amplitude of a charged particle in discharge plasma as:

$$x_m = \frac{eE_a / m}{\sqrt{\left(\omega^2 - \omega_p^2(2x_m / L)^2\right) + \omega^2v^2}}$$  \hspace{1cm} (6.2)

where \(e\) is the electron charge, \(m\) mass of the charged particle, \(E_a\) the peak electric field across the helium gap, \(\omega\) the radian frequency of the applied voltage, \(L\) the separation distance between the two electrodes, and \(v = q/m\mu\) the collision frequency. \(\omega_p\) is the plasma frequency given by:

$$\omega_p = \sqrt{\frac{e^2n_e/\varepsilon_0m}{\varepsilon_0}} = 5.65 \times 10^4 \sqrt{n_e (cm^{-3})} \text{ s}^{-1}$$  \hspace{1cm} (6.3)

Here \(n_e\) is the electron density spatially averaged across the interelectrode gap. Electron mobility in helium is \(\mu_e = 10^6 / p \text{ cm}^2\text{Torr}/(Vs)\) and the gas pressure \(p = 760 \text{ Torr}\). So the collision frequency of electrons is \(\nu_e = q/m_e\mu_e = 1.34 \times 10^{12} \text{ s}^{-1}\).

Although eq. (6.2) is derived for sinusoidal voltage and the gas voltage of figure 6.1 is not strictly sinusoidal, we use it as an approximation to estimate the amount of electron excursion normalized to 0.5L. At 112kHz, the peak gas voltage is approximately 1.75kV and so the peak electric field \(E_a = 1.75\text{kV}/0.5\text{cm} = 3.5\text{kV/cm}\). With this, eq. (6.2) is solved for \(2x_m / L\) and the results are shown in figure 6.6. For an electron located initially at the midpoint of the interelectrode space, figure 6.6 suggests that its excursion distance decreases with increasing excitation frequency. At 112kHz, \(2x_m / L\) is less than 0.5 suggesting that the electron travels at most a quarter of the interelectrode distance during one half cycle. In other words it is unlikely to reach the dielectrically coated electrodes. This supports strongly the hypothesis that the stability of atmospheric DBD is disrupted by electron trapping.
It is interesting to note that eq. (6.2) is similar to the rms displacement of charged particles formulated\(^9\):

\[
x_{\text{rms}} = \frac{2 eE_o}{\pi m \omega v}
\]  

(6.4)

if \(\omega^2 - \omega_p^2 (2x_m/L) \ll \omega v\). We have performed a number of numerical simulations for the helium DBD and found that \(\omega^2 - \omega_p^2 (2x_m/L) \ll \omega v\) is not true for electrons at atmospheric pressure. For example if we assume \(n_e = 10^{10}\text{cm}^3\) and \(2x_m/L \approx 1\), \(\omega_p = 5.65 \times 10^8\text{s}^{-1}\). At 112kHz, \(\omega^2 - \omega_p^2 (2x_m/L) \approx \omega_p^2 > \omega v\). Therefore eq. (6.2) should be used instead of eq. (6.4).

For the effect of electron trapping on the discharge's stability, we can achieve a better understanding by comparing the electron's spatial distribution at different driving frequencies as shown in figure 6.7. Figure 6.7a shows the electron distribution in the discharge driven by 5.2kHz source at different time instants: 0.137T when the discharge...
current reaches positive peak, 0.405T when the discharge current is about 0mA and 0.623T when the discharge current reaches its negative peak (see temporal variation of V-I in figure 6.3). The distribution shows that the electrons vary from low to high over the interelectrode space from the momentary cathode to the momentary anode, and their density is as low as $10^7 \text{cm}^3$. This is because the oscillation period of the applied voltage source is so long that electrons are kept near to the momentary anode for a relatively long time without new electrons created in the gas gap. Figure 6.7b shows the electron distribution in the discharge excited at 40kHz at different time instants: 0.113T when the discharge current reaches the positive peak, 0.387T when the current is close to 0 and 0.59T when the negative current peak is reached (see V-I characteristics in figure 6.1). When a breakdown event occurs, a large number of electrons are generated in the gas gap and the electron density is about $2\times10^{10} \text{cm}^3$. The electrons are not evenly distributed even when the discharge current is very small, and their distribution leans towards the momentary anode. The electron distribution in the discharge driven by a 112kHz source is shown in figure 6.7c. The time instants considered are: 0.135T when a positive current peak is reached, 0.335T when the discharge current is close to zero and 0.555T when the discharge current reaches the negative peak (see figure 6.4 for V-I variation). It is noted that the large amount of electrons are trapped in the middle region of the interelectrode space. This is because the oscillation period of the applied voltage is too short to drive electrons to the momentary anode. In other words, electrons are trapped between the two electrodes. This trapping mechanism pushes the electron density to a higher level, up to $10^{11} \text{cm}^3$, than that of the 40kHz discharge.
Figure 6.7: Spatial distribution of electron density in a helium-nitrogen discharge excited at (a) 5.2kHz, (b) 40kHz and (c) 112kHz.
Chapter 6 Frequency Effects in Atmospheric DBD

It is useful to compare the stability disruption mechanisms at both the low and the high frequency ends. At the low frequency end (e.g. 5.2kHz), the plasma stability is disrupted because the applied voltage increases too slowly with respect to the electron charging time of the dielectrically coated electrodes. This mismatched timescale causes the gas voltage to be reduced too quickly leading to a premature plasma quenching. At the high frequency end (e.g. 112kHz) on the other hand, most electrons produced in the plasma bulk are trapped and cannot reach the electrodes. As a result, the memory voltage is not increased sufficiently to counteract the rise of the applied voltage and to control the growth of the gas voltage (see eq. (6.1)). Although the specific reasons differ, both situations are associated with disruption of the dynamic balance between the applied voltage and memory voltage. These plasma stability disruption mechanisms are specific for dielectric-barrier discharges, and may not be applicable to other nonthermal atmospheric discharges that do not rely on dielectrically coated electrodes such as RF and microwave atmospheric plasmas6,10,11.

6.3.4 Plasma stability disruption in nitrogen DBD

We perform similar numerical simulations for a pure nitrogen dielectric-barrier discharge described in section 6.2. The frequency range of plasma stability for this pure nitrogen DBD is found to be between 0.6kHz and 200kHz. Plasma stability disruption mechanisms are found to be of the same nature as that for the helium DBD. One of the reasons why the nitrogen DBD has a higher upper frequency bound is because of the much larger gas voltage and hence a greater electric field across the nitrogen gap. As shown in figure 6.2, the peak gas voltage is around 7.6kV and so the maximum electric field is 38kV/cm over the 0.2cm nitrogen gap. In the case of the helium DBD, the peak gas voltage is 1.75kV and the maximum electric field is 3.5kV/cm across the 0.5cm helium gap. Therefore the electric field in the nitrogen DBD is almost 10 times that in the helium DBD. This larger electric field helps to drive electrons onto the electrodes at high excitation frequencies and is largely responsible for the higher upper frequency bound in the nitrogen DBD.
6.3.5 Effects of geometrical parameters and plasma chemistry

There are at least three key geometrical parameters that can affect discharge dynamics significantly, and they are (a) the electrode diameter, (b) the thickness of the dielectric barrier and (c) the permittivity of the dielectric barrier. Since our numerical code used in this study is one-dimensional, it is unable to address the effect of the electrode diameter. Numerical examples suggest that both the thickness and permittivity of the dielectric barrier affect the lower and upper frequency bounds. Interestingly their effects are well represented by that of the barrier capacitance on the lower and upper frequencies as shown in figure 6.8. As the barrier capacitance increases, either through increase in permittivity or through reduction in barrier thickness, the upper frequency decreases whilst the lower frequency changes little.

![Figure 6.8: Lower and upper frequency bounds at different barrier capacitance.](image)

We have already established that the upper frequency bound is due to electron trapping. In other words the applied voltage must vary sufficiently slowly to allow for
an adequate portion of free electrons in the plasma bulk to reach the dielectrically coated anode such that these electrons can then induce sufficient change in the memory voltage to balance out the changing applied voltage. When the barrier capacitance increases, more electrons are needed in order to induce the same change in the memory voltage because \( \Delta Q = CV_m \). To allow for more electrons to reach the instantaneous anode, the applied voltage has to vary more slowly. Therefore the upper frequency reduces as the barrier capacitance increases. On the other hand, the lower frequency bound is due to the mismatch between the electron drift time and the half period of the applied voltage. These two parameters are not affected by the barrier capacitance and therefore the lower frequency remains relatively unchanged.

Another obvious geometrical parameter is the electrode gap distance. Numerical examples suggest that as the electrode gap increases both the lower frequency and upper frequency bounds decrease. At low frequencies, a larger electrode gap increases the electron drift time and so the applied voltage can vary more slowly without causing too much mismatch with the changing rate of the memory voltage. In other words the lower frequency bound becomes smaller. At high frequencies, a larger electrode gap makes it easier to trap electrons at any given frequency and as such the upper frequency bound must decrease to avoid too much electron trapping.

To explore the effect of plasma chemistry, we note that both the lower and the upper frequency bounds are extended when the background gas is changed from helium-nitrogen to nitrogen. Also we simulate the helium DBD with the nitrogen content between 0% and 0.65%, and find that both the lower and the upper frequency bounds change markedly as shown in figure 6.9 and 6.10. As the nitrogen content increases, the Penning ionization is progressively enhanced as confirmed numerically by an increase in the electric field. At low frequencies, the increase of the electric field accelerates the electron drift towards the instantaneous anode and as a result the applied voltage must change faster in order to react to the change of the memory voltage. Therefore the lower frequency bound increases as the nitrogen content increases as
shown in figure 6.9.

Figure 6.9: Effect of N₂ content in the gas mixture on the low frequency bound.

Figure 6.10: Effect of N₂ content in the gas mixture on the high frequency bound.
At high frequencies on the other hand, the increase of the electric field increases the electron displacement (see eq.(6.7)) and as such relieve the degree of electron trapping. This in turns allows for an increase in the upper frequency bound, as clearly suggested in figure 6.10. It is therefore evident that plasma chemistry impacts significantly on the specific range of the excitation frequency for plasma stability.

6.4 Summary

Plasma stability of atmospheric dielectric-barrier discharges has been studied under sinusoidal excitation at different frequencies. Through numerical simulation, it has been shown that the frequency range of plasma stability is from 5.2kHz to 112kHz for a helium-nitrogen DBD and from 0.6kHz and 200kHz for a pure nitrogen DBD. These frequency ranges vary with the geometry of plasma reactor and the plasma chemistry. Stability disruption mechanisms have also been studied for these two atmospheric DBDs. It has been established that the mismatch of the rise time of the memory voltage and the applied voltage become irreversibly too large when the excitation frequency is too low. This mismatch leads to a too large memory voltage compared to the applied voltage, and as such the gas voltage is rapidly reduced leading to a premature plasma quenching. On the other hand, electrons produced in the plasma bulk become trapped in the interelectrode gap without being able to reach the electrodes if the excitation frequency is too high. As a result the memory voltage increases little and is unable to maintain a dynamic balance with the applied voltage. This also leads to premature plasma quenching. These two stability disruption mechanisms are confirmed for both the helium DBD and the nitrogen DBD, and are therefore generic. They offer additional insight into the mechanisms for stable generation and operation of atmospheric glow discharges particularly nonthermal atmospheric DBD. In addition the frequency range established for plasma stability will allow for informed choice of power sources from commercial products for DBD production and facilitate design considerations for future power sources. Ultimately
this generic dependence will contribute to system optimization of atmospheric dielectric-barrier discharge devices with tailored characteristics for DBD dynamics and for power source matching.
Reference


Chapter 7

APGD-Based Decontamination

7.1 Introduction

As reviewed in many literatures, gas discharge plasmas are widely used in many applications, for example etching and deposition in semiconductor devices\textsuperscript{7,1}, surface treatment on polymeric materials, plasma display and lighting\textsuperscript{2,3}, and decontamination of medical devices\textsuperscript{7,4,7,7}. In this chapter, the emphasis is to assess sterilization achieved with APGD so as to establish efficacy of plasma decontamination.

Sterilization is defined as any process or procedure designed to entirely eliminate microorganisms from a material or medium\textsuperscript{7,8}. The microorganisms usually include bacteria, viruses and fungi. An ideal sterilization method would: 1) be able to destroy all types of microorganisms effectively and efficiently; 2) not cause any negative effects on the articles to be sterilized; 3) not leave harmful residue to the personnel and environment during and after sterilization process; 4) be cost-effective. Conventionally, sterilization is achieved through physical or chemical methods\textsuperscript{7,8}, such as dry heat, steam, toxic gases, electromagnetic radiation, and particle and \(\gamma\)-ray radiation. Most of these techniques are associated with either some level of damage to the material or medium supporting the microorganisms, or toxicity to the surrounding environment.
For example, autoclaving and ethylene oxide are two widely used conventional sterilization methods to treat medical instruments\cite{7,10}. Autoclaving process generates pressurized steam within a sealed chamber, and it can sterilize numerous items that are heat stable\cite{7,10}. Because the temperature of the steam inside autoclaves is required to be at least 121°C\cite{7,10}, this method is not suitable for those non-heat-tolerant articles for the reason that the high temperature steam might damage them. In modern medical practice, a variety of instruments and materials are heat-sensitive, thus cold sterilization techniques are preferred. By far, cold sterilization is currently performed by means of toxic gases - pure ethylene oxide or its mixture with fluorochlorocarbons\cite{7,10}. The drawbacks of this method are the toxicity of gas, which presents serious threat for both personnel and environment\cite{7,10,7,11}. Also many conventional strategies are rather time-consuming. The autoclaving process normally requires more than 1 hour to achieve proper decontamination; while EtO (ethylene oxide) sterilization require a much longer process time, sometimes more than 24 hours, to allow for an adequate aeration process (up to 24 hours)\cite{7,11}. The disadvantages of conventional methods lead to a drive to develop new sterilization techniques.

Recently, low-pressure gas discharge plasmas have been used as a low-temperature sterilizing agent\cite{7,10,7,11}. The works in this area show some advantages of the plasma sterilization method. For example, plasma sterilization can be performed at a relatively low temperature, less than 70°C, and in a relatively short period from several minutes to about one hour\cite{7,10}. The active agents that are important for sterilization exist only after the discharge ignites, and they disappear almost immediately after the discharge is turned off. The low-pressure plasma sterilization method overcomes the drawbacks of conventional sterilization techniques mentioned before. Nagatsu’s study\cite{7,10} shows that the bacillus stearothermophilus spores with a population of $1.5 \times 10^6 \text{cm}^{-3}$ can be perfectly sterilized after 3 minutes irradiation of oxygen plasma. The shape and size of killed spores were clearly changed after the sterilization process. But the low-pressure discharge system requires a vacuum system, which is both expensive and complex in terms of its sterilization process. The sterilization techniques based on
APGD can overcome this problem whilst being capable of achieving similar biological efficacy as low-pressure plasmas. Table 7.1 gives a cost comparison between conventional and discharge plasma decontamination methods, and all the price are shown in deutsche mark (DM). This is based on the calculation of Adler’s work\textsuperscript{12} on the sterilization methods of steam, ethylene oxide and low-pressure plasma. One sterilization unit is defined as: 30cm×30cm×60cm=54L. Because the vacuum pumping system is no longer necessary for the atmospheric pressure glow discharge, the time and personnel spent on the vacuum system can both be saved from the low-pressure plasma sterilization. Therefore we can conservatively estimate that the process time and cost in APGD sterilization are both much lower than that in the low-pressure plasma sterilization.

Table 7.1: Costs of the sterilization procedures in GBP per sterilization unit.

<table>
<thead>
<tr>
<th></th>
<th>Steam</th>
<th>Ethylene Oxide</th>
<th>Low-pressure plasmas</th>
<th>APGD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat Damage</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Toxic Residue</td>
<td>No</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Vacuum System</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Process Time</td>
<td>&gt;1 Hour</td>
<td>~24 Hours</td>
<td>Minutes ~1 Hour</td>
<td>&lt;&lt;1 Hour</td>
</tr>
</tbody>
</table>

Today, atmospheric pressure glow discharge can be generated by various means, which includes: the dielectric barrier discharge (DBD)\textsuperscript{7,13,14} the resistive barrier discharge (RBD)\textsuperscript{7,15}, and the atmospheric pressure plasma jet (APPJ)\textsuperscript{7,16}. The driven power source varies from DC to AC, and the frequency varies from kHz to MHz. The plasma produced via these means have its electron density typically in the range of $10^6\text{cm}^{-3} - 10^{11}\text{cm}^{-3}$, the plasma power density in the range of 10 to 300mW/cm\textsuperscript{2}, and the gas temperatures normally below 100°C\textsuperscript{7,17,18}. The generated plasmas are sources of UV, visible, IR radiation, free charged particles, and free radicals, which play important
roles in destructing microorganisms. In 1857, Siemens used a corona discharge to generate ozone to disinfect water; in 1970's, Menashi used a corona discharge to sterilize the surface of materials; and more recently in mid-1990s Laroussi used an atmospheric DBD to decontaminate biological media.

In this chapter, an atmospheric pressure glow discharge generated in a reactor with two parallel plane bare stainless steel electrodes is used for sterilization. The background gases used is helium mixed with very small amount of oxygen. The treated samples in this experiment are two representative types of microorganisms in food industry: Enterobacter agglomerans and Bacillus Subtilis spores. This study aims to show the generation of stable atmospheric pressure glow discharge in helium-oxygen gas mixture and its sterilization capability.

7.2 An Atmospheric Glow Plasma Apparatus

The APGD system set up for plasma sterilization is sketched in figure 7.1, which consists of a power supply, an impedance matching network, a water-cooling system and a plasma reactor. The power supply (RFPP LF50 Advanced Energy) provides the power for plasma generation and sustainment. The frequency of this machine varies from 50kHz to 500kHz, and 460kHz is the frequency used in all experiments reported in this chapter. From the standpoint of an equivalent circuit, the plasma reactor works as a capacitor in parallel with a resistor. With the plasma ignited, the impedance of the plasma reactor varies in a very large range, from several kilo Ohm to several hundred Ohm. So when the plasma reactor and the power supply are not suitably matched, the capacitive plasma reactor reflects a large fraction of the input power back to the power supply. In this circumstance, only a small part of the output power from power supply can be delivered to the plasma reactor. The large amount reflected power does not contribute to plasma formation, and so plasma generation requires an expensive and overrated power supply. In order to reduce the reflected power and have the maximum power delivered to the plasma, an impedance matching network is
essential for generating an atmospheric pressure glow discharge. As there is usually significant electrical power reflected back to the power supply, a water-cooling system is often required to cool down the heated power generator. The power generator used in this work has an auto-protection function, with which the power supply shuts down automatically whenever the power supply is over-heated.

![Figure 7.1: Schematic of an atmospheric pressure glow discharge system.](image)

The plasma reactor, see figure 7.2, consists of two parallel bare stainless steel electrodes enclosed in a transparent Perspex box to minimize the possible environmental interference and to maximize the control over the background gas. The box is not airtight but with two openings used as the gas inlet and the gas outlet. The gap between electrodes is adjustable, 1 - 3mm in this experiment. The top electrode, which is grounded, is a round stainless steel plate whose diameter varies from 0.5cm to 5cm. A top electrode with 2cm diameter is used in this experiment. The bottom electrode is a 5×10cm² stainless steel plate and connected to the power supply via the matching network. This reactor is different from that one simulated computationally in previous chapters, in which the two electrodes are covered by thin dielectric layers. The working gas is fed into the reactor box from the gas inlet, and the exhaust gas is led out of the reactor from the gas outlet (see figure 7.1).
After the samples is put on the top of the bottom electrode and before the power is switched on, the gas flow is left to persist for several minutes to ensure that the majority of air originally contained in the rig is flushed out and replaced with helium-oxygen mixture. This process ensures the stable glow discharge to be generated very soon after the power is switched on, and avoids the generation of an arc plasma that can affect the final sterilization result. The reason for this is because that the existence of superfluous impurity in the gas mixture may cause the instability of discharge and it is very difficult to generate the glow discharge in air. The working gas used here is helium-oxygen mixture, which is mixed by 99.85% helium with flow rate of 2L/min and 0.15% oxygen with flow rate of 0.003L/min. The reasons of using helium-oxygen mixture as the background gas are following: 1) helium is one of the few nobel gases in which the stable APGD can be generated very easily\textsuperscript{7,19}; 2) oxygen composition in the background gas mixture has been proved to be very important in killing microorganisms\textsuperscript{7,8,10}. As the power supplying to plasma reactor increases, the working gas between the two electrodes reaches the breakdown point and an illuminant
gas discharge region is formed as shown in figure 7.3. This picture shows a stable atmospheric pressure glow discharge generated under following conditions: (a) the electrode gap distance is 1.5mm; (b) the input power is 2 watt at 460kHz. The generated luminous discharge is uniformly distributed over the entire electrode with a constant light intensity radially on a plane parallel to the electrodes. The generated discharge is half transparent, whose colour varies from pure purple for pure helium discharge (see figure 7.4) to purple-white for helium-oxygen discharge (see figure 7.3). The axial distribution of the generated plasma in the gas gap is also shown clearly, and is similar to that of a typical low-pressure glow discharge\(^{7,20}\). In the low-pressure glow discharge, from the cathode to the anode, there are different regions with different light intensities including the Aston dark space, the cathode glow, the cathode dark space, the negative glow, the Faraday dark space, the positive column, the anode glow and the anode dark space as shown in figure 7.5. These spatial distributions are also observed by many other research groups\(^{7,7,13}\).

![Figure 7.3: Stable APGD generated between two parallel plane steel electrodes in helium-oxygen mixture. Gas gap is 1.5mm and the top disk electrode has a diameter of 2cm.](image)
Figure 7.4: Stable APGD generated in pure helium gas with a top electrode of 5cm diameter and a gas gap of 3mm.

Figure 7.5: Spatial characteristics of typical glow discharge.
7.3 Sterilization of Microorganism on Biofilms

7.3.1 Enterobacter agglomerans

The name for this microorganism was first published by M. W. Beijerinck as Bacillus agglomerans in 1888. Later in 1972, W. H. Ewing and M. A. Fife changed the name to Enterobacter agglomerans. Enterobacter agglomerans is one of the most commonly encountered microflora on fruits and vegetables, and it is largely responsible for the spoilage of the fresh food product. Thus, this microorganism is widely used as an indicator organism for those tests associated with vegetation in laboratory.

To prepare the sample of this microorganism, the well-sterilized white cellulose nitrate filters used as substrate are put on top of a ready-to-used agar Petri dish. Agar is beef extract, yeast extract and peptone, and it is a germ food that can be used to grow bacteria. Then an overnight culture of agglomerans is put on top of the filter, and left to grow for some time. The growth is strongly dependent on the environment, for example the temperature. The longer time the samples are left to grow, the more they grow. During the growth of microorganisms, biofilms are generated and these are gel layers that help to adhere microorganisms to filter surface. Figure 7.6 shows a ready sample, in which the grown-up Enterobacter agglomerans lies in the centred light yellow part, and the white fringe is the filter. The thickness and colour of samples vary with their age.
By exposing the samples in a helium flow or even in stationary air, the gel-like biofilm on the filter surface dries up and shrinks at the same time. The tension caused by this rolls the thin filter up. If the sample is put in the centre area of the plasma, the rolled-up filter may change the configuration of the gas bulk between the two electrodes and so affect the generation of the stable APGD. Even without putting the filter sample on the centre of gas bulk instead of putting it aside of plasma region, the rolled-up filter still affects the sterilization process on the microorganisms. Because the rolled-up section may change the flow of plasma species around the samples, it interferes the reactions of the microorganisms to plasma species. Also it is possible for the rolled-up filter to be blown away by the gas flow. To tackle these practical problems, we fix the filter sample on the bottom electrode in a region immediately outside of the generated plasma, and simply use tapes to hold it down to the bottom electrode thus preventing it from rolling up as much as possible (see figure 7.7). Although the generated plasma is unable to reach the samples directly, reactive plasma species such as atomic oxygen and ozone are able to reach microorganisms by the background gas flow. This method also allow minimization of the possible heat effects of the plasma on the microorganisms.
Figure 7.7: Sterilization treatment on Enterobacter agglomerans samples: (a) Plasma region; (b) Overall picture.

After the samples have been treated by the atmospheric plasma, we need to recover those microorganisms left on the filter in order to establish the level of survived microorganisms. The treated samples are put into a sterile plastic bag called stomacher bag with 10ml MRD (maximum recovery diluent) inside. The bag is then put into the stomacher machine (see figure 7.8 (a)) and pounded by the paddles inside for 1 minute. This treatment helps to transfer all cells left on the filter to MRD liquid and mix the cells evenly with the diluent liquid. One portion (1ml) dilution from the stomacher bag is transferred to a sterile universal containing 9ml MRD. The universal is whirlimixed by a whirli mixer (figure 7.8 (b)) to form a $10^1$ dilution. Then 1ml of the $10^1$ dilution is transferred to another sterile universal and mixed with 9ml MRD to form a $10^2$ dilution. This operation is repeated six times in this study. One portion, 1ml, of the final dilution is spread on an agar plate, and the plate is incubated for 24
hours. After 24 hours, we can see colonies grown from the remaining cells (see figure 7.9). The number of colonies counted from the Petri dish is the actual number of the microorganisms contained in the 1ml final dilution. Therefore we can find out the total number of microorganisms left on the filter after plasma sterilization processes.

Figure 7.8: Machines used for recovery: (a) Stomacher; (b) Whirli mixer.

Figure 7.9: Colonies of Enterobacter agglomerans.
7.3.2 Bacillus subtilis spores

In October 2001, several letters containing Bacillus anthracis spores were sent through the U.S. Postal Service to recipients in government and private-sector buildings. Consequently, 23 human inhalational or cutaneous anthrax infections occurred, and five of the 11 inhalational anthrax infections were fatal. Even more seriously, several post offices, mailrooms in government buildings, and private office buildings were contaminated with Bacillus anthracis spores. These not only interrupted the regular work of these government departments, but also threaten the health and life of people who work there. This kind of contamination has heightened concerns about the use of spores as an agent of biowarfare or bioterrorism. Thus, a safe, efficient decontamination procedure that can inactivate spores of Bacillus anthracis or other similar microorganisms with minimal harm to equipment and personnel is required. Such procedures would contribute to the protection of individual, the decontamination of equipment and installations and would reduce the impact of a biological attack with spores.

Spore is a living cell that can grow on a non-selective medium. For example in our experiments, they are grown on stainless steel coupons. It is not repressed by exposure to air, and it is heat resistant. Thus spore can survive harsh physical and chemical treatments and remain in a dormant state for long period. These properties make spores very difficult to be killed, and the inactivation of such microorganisms becomes a representative target for biological sterilization. If spores can be killed efficiently by one method, then other microorganisms can be safely assumed to be killed efficiently by the same method. For the research in this area, Bacillus Subtilis spores are chosen as the test organism for evaluating the efficacy of biological sterilization. The most important reason for this is because Bacillus Subtilis spores are non-pathogenic surrogate organisms, and also there are sufficient genetic information and techniques available for this bacterium. Also, the sterilization of Bacillus Subtilis spores is important in the food preservation industry.
Chapter 7

The Bacillus Subtilis spores are grown on stainless steel coupons in our experiments, because they have a very strong living ability and can survive lots of environment. Similar to the growth of Enterobacter agglomerans on filter, the longer time the samples are left to grow, the more they grow. Figure 7.10 shows a ready-to-treat sample, in which the grown-up Bacillus Subtilis spores are centred on the coupon.

Figure 7.10: Ready-to-treat microorganisms samples: Bacillus Subtilis spores on a stainless steel coupon.

As the Bacillus Subtilis spores are placed on the stainless steel coupons, the coupons with microorganisms on can be placed anywhere on the bottom electrode. When it is put exactly under the top electrode (see figure 7.11 (a)), the discharge is produced exactly on top of the coupon because the gap distance between the top surface of the coupon and the top electrode is the smallest in the entire region between the two electrodes. The stainless steel coupon works as the bottom electrode in this case. The cross area of the discharge is the same as the coupon size. When the coupon is put aside the plasma region (see figure 7.11 (b)), plasma species are blown towards the coupon’s surface by the background gas flow. In this case, the cross area of the discharge is same as the size of the top electrode.
Figure 7.11: Sterilization treatment on Bacillus Subtilis spores samples: (a) Sample centred case; (b) Sample aside case.
After the sterilization processes, the treated coupon is put into a sterile universal containing 10ml MRD in it. The sterile universal is put on a whirlymixer and processed for about 5 seconds. This helps to release all the remaining cells on the coupon to the MRD liquid and mix the cells evenly with the diluent liquid. Then the diluent liquid is diluted several more times in a similar way to that needed for treatment of Enterobacter agglomerans. This is repeated until the desired dilution is achieved, and our experiments require four consecutive dilutions. Again, 1 ml final dilution is spread to an agar-ready Petri dish, and let to incubate for 24 hours in an environment with temperature of 35°C. The total amount of spores survived from plasma treatment can be calculated from the number of spores colonies counted from the Petri dish.

7.4 Result and Discussion

7.4.1 Effects caused by gas flow

Without the plasma generated in the rig, the gas flow inside it does not contain any charged or reactive species that may inactivate microorganisms. The microorganisms lost in this operation are entirely caused by the gas flow. Although the gas mixture is injected to the rig in a relatively low rate, the gas flow inside the rig can still take some microorganisms away from the sample. The experimental result shows that the rate of microorganisms' loss is reversely proportional to the age of samples. Table 7.2 shows the relationship between the sample's age and the loss rate for Enterobacter agglomerans case. As mentioned before, the gel-like biofilms come into being on the surface of samples as the Enterobacter agglomerans grow up on the white cellulose nitrate filter in the agar plate, which give certain protection to the microorganisms from being blown away from the sample filter. The longer the microorganisms grow, the thicker the biofilm is and the stronger the adhesion is between microorganisms and
filter. This agrees to the fact that the older the samples are, the less microorganisms are blown away after 1 hour process in the same gas flow.

Table 7.2: Loss of E. Agglomerans caused by gas flow

<table>
<thead>
<tr>
<th>Age of E. Agglomerans</th>
<th>E. Agglomerans Remained on Filter after 1 hour Treatment</th>
<th>E. Agglomerans Loss after 1 hour Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 Day</td>
<td>13.98%</td>
<td>86.02%</td>
</tr>
<tr>
<td>1 Day</td>
<td>87.27%</td>
<td>12.73%</td>
</tr>
<tr>
<td>6 Days</td>
<td>97.95%</td>
<td>2.05%</td>
</tr>
</tbody>
</table>

In the case of Bacillus Subtilis spore samples, an interesting observation is that the effect caused by the gas flow to the microorganisms on the substrate in the “sample-in-plasma” case is slighter than that in the “sample-outside-plasma” case. When the sample is put at the centre of the electrode, 15.81% of the original cells on the sample get lost after one hour, while 66.50% are lost when the sample is put aside the electrode. Table 7.3 gives the comparison. We may understand this by looking at the geometry of the plasma reactor. As the gap between two electrode is very small, the gas flow may be blocked off to some extent by the top electrode, and changes its flow direction and speed when it reach the near side of the top electrode to the gas inlet. Also the gas flow in the gap may be blocked off again by the steel substrate although it is not very thick. In the “sample-outside-plasma” case, the obstruction to the gas flow is much less. To overcome this problem, it would be a good idea to modify the current rig regarding the position of the gas inlet and the gas outlet, as well as the way of leaking the working gas in and out of the rig.

Table 7.3: Loss of B. Subtilis spores caused by gas flow

<table>
<thead>
<tr>
<th>Position of B. Subtilis spores</th>
<th>B. Subtilis spores Remained on Filter after 1 hour Treatment</th>
<th>B. Subtilis spores Loss after 1 hour Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Centred</td>
<td>84.19%</td>
<td>15.81%</td>
</tr>
<tr>
<td>Aside</td>
<td>33.50%</td>
<td>66.50%</td>
</tr>
</tbody>
</table>
7.4.2 Effects caused by sample’s age

As what has been discussed in the previous section, the effect caused by the flow of the working gas without plasma is reversely proportional to the age of samples. Figure 7.12 shows the result of microorganisms’ loss rate in the case that the discharge is ignited in the rig, where $N_r$ is the number of microorganisms survived after the plasma treatment, and $N_0$ the number of microorganisms on the original samples. It is noticed that the relationship between the loss rate and the sample’s age is as same as that caused by the pure gas flow. This is understandable because the young microorganisms are not as strong as the old ones, and the young microorganisms do not have same strength to fight with the external force as those mature ones, no matter what this external force is. On the other hand, the sterilization treatment done to the same microorganism samples via UV light has a consistent trend of the loss rate as shown in figure 7.13.

![Figure 7.12: Relationship between the survived Enterobacter agglomerans from plasma treatment and their age.](image)

```latex
\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure7_12.png}
\caption{Relationship between the survived Enterobacter agglomerans from plasma treatment and their age.}
\end{figure}
```
Figure 7.13: Relationship between the survived Enterobacter agglomerans from UV treatment and their age.

7.4.3 Comparison to UV light sterilization

Figure 7.14 shows the comparison between the sterilization processes done to the 12-hour-old Enterobacter agglomerans samples by the atmospheric pressure glow discharge and that by UV light. With plasma treatment, about 97% of the microorganisms are killed in just 5 minutes. In the subsequent 55 minutes, only additional 2.95% of microorganisms are killed. Thus plasma inactivation of Enterobacter agglomerans is very efficient in the first 5 minutes. With in UV light, there is only 20% of microorganism killed after the first 5 minutes treatment and then the microorganisms are inactivated in a nearly linear rate during the first 25 minutes treatment. After 1 hour process, the sample treated by plasma has much less survived microorganisms (only 0.052% survived), than the sample treated by UV light (15.05% of cells survived). Thus, the atmospheric pressure glow discharge is more efficient than the UV light in killing Enterobacter agglomerans.
Figure 7.14: Comparison between plasma and UV light treatment to 12-hour-old Enterobacter agglomerans.

Table 7.4 summarises all the sterilization treatment on Enterobacter agglomerans done by the UV radiation and the atmospheric pressure glow discharge. We can see that the plasma treatment generally has better result than the UV light treatment. This table also clearly shows how the age of microorganisms affect the sterilization result in both plasma and UV light treatment.

<table>
<thead>
<tr>
<th>Sample microorganism</th>
<th>Age</th>
<th>Treatment environment</th>
<th>Log reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>E. agglomerans</td>
<td>12-hour</td>
<td>UV inactivation</td>
<td>0.82</td>
</tr>
<tr>
<td></td>
<td>2-day</td>
<td>UV inactivation</td>
<td>0.73</td>
</tr>
<tr>
<td></td>
<td>6-day</td>
<td>UV inactivation</td>
<td>0.58</td>
</tr>
<tr>
<td></td>
<td>12-hour</td>
<td>APGD afterglow</td>
<td>3.28</td>
</tr>
<tr>
<td></td>
<td>1-day</td>
<td>APGD afterglow</td>
<td>1.36</td>
</tr>
<tr>
<td></td>
<td>6-day</td>
<td>APGD afterglow</td>
<td>0.60</td>
</tr>
</tbody>
</table>
For the treatment done to those Bacillus Subtilis spores samples, sterilization efficacies of these two methods are not very different from each other, both achieving 70% reduction in survival cells after 15 minutes. Table 7.5 summarises all the sterilization treatment on Bacillus Subtilis spores done by the UV radiation and the atmospheric pressure glow discharge. After one-hour treatment, the UV light treatment can reach up to 1.5 log reduction, while only 0.76 for the plasma treatment. It is also noted that the sterilization processes done in direct discharge and discharge afterglow give similar result, but the afterglow one is more effective in the first 20 minutes than the direct discharge one.

Table 7.5: Loss of B. Subtilis spores by UV and plasma treatment

<table>
<thead>
<tr>
<th>Sample microorganism</th>
<th>Age</th>
<th>Treatment environment</th>
<th>Log reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>B. Subtilis spores</td>
<td>3-hour</td>
<td>UV inactivation</td>
<td>1.50</td>
</tr>
<tr>
<td></td>
<td>2-week</td>
<td>UV inactivation</td>
<td>1.04</td>
</tr>
<tr>
<td></td>
<td>3-hour</td>
<td>APGD afterglow</td>
<td>0.74</td>
</tr>
<tr>
<td></td>
<td>3-hour</td>
<td>APGD</td>
<td>0.76</td>
</tr>
</tbody>
</table>

It is expected that a greater oxygen content in the background gas mixture should increase the density of oxidising plasma agents produced in the plasma (e.g. atomic oxygen and ozone). In turn this should improve the capability of the APGD to inactivate B. Subtilis spores. While this is outside the scope of this thesis and require a systematic study in future, the results of our preliminary experiments highlight unambiguously the capability of APGD for decontamination and sterilization.

7.5 Summary

In this chapter, stable atmospheric pressure glow discharges have been generated in pure helium and helium-oxygen mixture. The produced discharges have been used to inactivate two common indicator microorganisms that often exist in food: Enterobacter
agglomerans and Bacillus Subtilis spores. The results are promising, showing that this kind of plasma is capable of decontaminating microorganisms and that sterilization achieved by APGDs is better than the UV light for the Enterobacter agglomerans. These experiments offer clear indication of key issues to be addressed in the future. For example, the current plasma reactor configuration highlights practical issues that prevent direct plasma treatment of samples. Secondly, although we have now established that APGD is capable of killing microorganisms, the detailed killing mechanisms are still unknown. Therefore, our existing experimental results inspire us to modify the current plasma system, to make it more suitable for the decontamination, and to perform further research for a better understanding of plasma sterilization.
Reference


Chapter 8

Conclusions and Further Work

8.1 Conclusions

In recent years, atmospheric pressure glow discharges attract a huge amount of interests in both academic and industrial sectors, and the dielectric barrier discharges are especially attractive because of their capability in generating easily stable glow discharges at atmospheric pressure. This project focuses on APGD through computational and experimental studies to provide valuable insights into their electrical properties and dynamics.

8.1.1 Numerical study

The mathematical model used in this work consists of a series of governing equations: the electric circuit equation which is used to describe the circuitry of the whole discharge system, a set of convection-diffusion equations for different species considered in the simulation, in which the flow of particles in the discharge is viewed as a fluid, and Poisson’s equation which describes the electric field within the generated plasma. The solution to this set of equations under certain boundary and initial conditions provides us a clear picture of the characteristics of atmospheric dielectric
Chapter 8  Conclusions and Further Work

barrier discharges. These characteristics include the spatiotemporal properties of the electric field, the number density of plasma species, and the temporal variations of the voltage and the discharge current. Two discharge cases are studied, namely APGD generated in pure helium and helium-nitrogen mixture respectively. The simulation results achieved are in good agreement with relevant experimental results, thus offering accurate prediction of plasma dynamics. The study of helium-nitrogen APGD confirms the important role that the small amount of impurity gas plays in electron production, and in the generation and sustainment of APGDs.

The second contribution of the numerical simulation of this work is the study on power efficiency and on the frequency range for stable APGD. Studied in depth are techniques that can be used to reduce the power consumed in generating and sustaining APGD. Three different pulsed excitation waveforms are considered in the study, namely peak-levelled sinusoidal, peak-levelled and tail-trimmed sinusoidal, and Gaussian-tailed sinusoidal excitations. Our simulation results show that the plasma power can be reduced by more than 40% without much reduction in densities of electrons, ions and metastables. This suggests that the power reduction does not affect the generation of plasma, and that what has been reduced is the power used in sustaining the plasma. The pulsed excitations should be useful for those applications in which power consumption is essential, for example industrial-scale material processing.

The issue of the frequency range for stable APGD is also considered. The study not only provides a specific frequency range in which stable APGD can be generated, but also gives a clear explanation of plasma disruption mechanisms outside such frequency range. APGDs generated in both helium-nitrogen mixture and pure nitrogen are studied, and two stability disruption mechanisms on both high frequency bound and low frequency bound are unravelled. The frequency range established for stable plasmas should aid an informed choice of power sources from the commercial products for APGD production, and contribute to system optimisation of APGD devices.
8.1.2 Experiments and applications

The most attractive aspect of atmospheric pressure glow discharges is their capability for wide-ranging applications, for example surface treatment and sterilization. The experiments performed during this project focus on food decontamination. We generated an atmospheric pressure glow discharge between two parallel stainless steel plates with helium and helium-oxygen mixture as the reactant gases. The discharges produced in this environment are quite stable and uniformly distributed. We used the produced discharge to treat two common indicator microorganisms: Enterobacter agglomerans and Bacillus Subtilis spores. The result shows that our discharges are capable of killing microorganisms, and are better than UV light for inactivation of Enterobacter agglomerans. These early results are very promising for food decontamination.

8.2 Further Works

After three years of working on the subject of atmospheric pressure glow discharge, the initial objectives of this project have been achieved. Atmospheric dielectric barrier discharge is a subject with huge potential, so that continuing the study on this subject is both exciting and beneficial. In this section, some brief suggestions on both numerical simulation and experiments are given for the future study.

8.2.1 Improvement on numerical study

The numerical study undertaken in this project employs an important assumption: local field approximation, with which the electrons are assumed to be in equilibrium with the local electric field and as such the ionization coefficient and other reaction coefficients are treated as a function of the electric field. However this is not fully accurate in reality. Because the electron energy may not always be in equilibrium with the local electric field, the local field approximation may not describe the properties of the plasmas properly. Thus, it would be valuable for the modelling study on
atmospheric dielectric barrier glow discharges to consider their non-equilibrium effect. The specific operation would involve the calculation of the electron energy distribution. The ionization coefficient and other reaction coefficients would then be functions of the electron energy. It is anticipated that the consideration of the non-equilibrium effect can offer better accuracy for plasma simulation, and provide more quantitative information of the simulated plasma.

8.2.2 Development of experiments and applications

In the present experiment, the largest discharge obtained has a volume of about 23.5 cm³ (=π × 5 × 2 × 0.3 cm³). The gap distance of 0.3 cm between the two electrodes restricts more potential applications. The current problem for this is that the increase in the gap distance makes it difficult to generate a uniform discharge. One possible reason is that the system is not matched very well by the present impedance matching box, thus the sufficient power needed for an increased gap cannot be delivered to the plasma. Therefore a matching network with better performance would be the solution to the small distance problem. An alternative solution is DBD, which require a power source of tens kHz. In this way, the system can be matched better than that with a high frequency power source. The second problem is the gas composition. Currently, only a very small amount of oxygen, up to 0.15%, can be fed into the plasma reactor without disrupting plasma stability. This amount of oxygen might not be enough for an efficient decontamination process. To address this problem, we may again need to improve our plasma reactor with dielectric-barriered electrodes. For decontamination, it is important to apply plasma treatment to more microorganisms, and to establish the relationship between sterilization efficacy and plasma conditions.
Appendix 2-A Derivation of eq. (2.11)

We start from the following equations:

\[ C = \varepsilon_0 \varepsilon_r \frac{s}{L} \]  \hspace{1cm} (2.1)

\[ \frac{1}{C_{ds}} = \frac{1}{C_{ds1}} + \frac{1}{C_{ds2}} \]  \hspace{1cm} (2.2)

\[ V_s(t) = V_{ds1}(t) + V_g(t) + V_{ds2}(t) = V_g(t) + V_m(t) \] \hspace{1cm} (2.4)

\[ V_m(t) = V_{ds}(t) = \frac{C_k}{C_{ds}} \left\{ V_g(t) - \frac{1}{\varepsilon_0 \varepsilon_r} \int_0^t \int j(x,t) dx dt \right\} + \left( 1 + \frac{C_k}{C_{ds}} \right) V_m(0) \] \hspace{1cm} (2.10)

Substituting eq. (2.10) into eq. (2.4):

\[ V_s(t) = V_g(t) + V_m(t) \]

\[ = V_g(t) + \frac{C_k}{C_{ds}} \left\{ V_g(t) - \frac{1}{\varepsilon_0 \varepsilon_r} \int_0^t \int j(x,t) dx dt \right\} + \left( 1 + \frac{C_k}{C_{ds}} \right) V_m(0) \]
We have

\[ \left(1 + \frac{C_g}{C_{ds}}\right) V_g(t) = V_a(t) + \frac{C_g}{C_{ds}} \frac{1}{C_{es}C_g} \int_0^t j(x,t)dxdt - \left(1 + \frac{C_g}{C_{ds}}\right) V_n(0) \]

\[ V_g(t) = \frac{C_{ds}}{C_{ds} + C_g} \left[ V_a(t) + \frac{C_g}{C_{ds}} \frac{1}{C_{es}C_g} \int_0^t j(x,t)dxdt \right] - \frac{C_{ds}}{C_{ds} + C_g} \left(1 + \frac{C_g}{C_{ds}}\right) V_n(0) \]

\[ = \frac{C_{ds}}{C_{ds} + C_g} \left[ V_a(t) + \frac{C_g}{C_{ds}} \frac{1}{C_{es}C_g} \int_0^t j(x,t)dxdt \right] - V_n(0) \]

so:

\[ V_g(t) = \frac{C_{ds}}{C_{ds} + C_g} \left[ V_a(t) + \frac{S}{C_{ds}C_g} \int_0^t j(x,t)dxdt \right] - V_n(0) \]  \hspace{1cm} (2.11)

At \( t = 0 \), the above equation becomes

\[ V_g(0) = \frac{C_{ds}}{C_{ds} + C_g} V_a(0) - V_n(0) = -V_n(0) \]

which satisfies eq. (2.4) at \( t = 0 \).
Appendix 2-B Derivation of eq. (2.19)

We start from the equation
\[ \int \left( m \vec{v} \frac{\partial f_k}{\partial t} + m \vec{v} \cdot \nabla, f_k \pm m \frac{\vec{F}}{m} \cdot \nabla, f_k \right) d\vec{v} = \int m \vec{v} \left( \frac{\partial f_k}{\partial t} \right)_{\text{col}} d\vec{v} \]  
(2-B-1)

By using the particle density
\[ n_k (\vec{r}, t) = \int f_k (\vec{r}, \vec{v}, t) d\vec{v} \]  
(2-B-2)

and the average velocity:
\[ \vec{u}(\vec{r}, t) = \frac{1}{n_k (\vec{r}, t)} \int \vec{v} f_k (\vec{r}, \vec{v}, t) d\vec{v} \]  
(2-B-3)

Eq. (2-B-1) becomes:
\[ \frac{\partial}{\partial t} \left[ m n_k \left( \frac{1}{n_k} \int \vec{v} f_k d\vec{v} \right) \right] + \nabla \cdot \left[ m n_k \left( \frac{1}{n_k} \int \vec{vf_k} d\vec{v} \right) \right] \pm \vec{F} \cdot m \nabla, f_k d\vec{v} = \int m \vec{v} \left( \frac{\partial f_k}{\partial t} \right)_{\text{col}} d\vec{v} \]

(2-B-4)

On the RHS of eq. (2-B-4), \( \vec{R}_m = \left. \int m \vec{v} \frac{\partial f}{\partial t} \right|_{\text{collision}} d\vec{v} = \pm m n_k \vec{u} \vec{v} = \pm m \vec{v} \vec{v}_m \) is defined as the momentum creation or loss term caused only by the collisions among the plasma species, and plus and minus signs are used to denote the creation and loss term respectively. \( \vec{v}_m \) is the effective momentum transfer frequency. There is only momentum loss term with only the internal particle collision. Therefore in eq. (2-B-4), the momentum loss term
\[ \vec{R}_m = -m \vec{v} \vec{v}_m. \]
The third term on LHS of eq. (2-B-4) can be derived as

\[ \vec{F} \cdot \left[ \nabla \nabla \cdot f_k d v \right] = F_x \hat{x} \cdot \left[ v_x \frac{\partial f_k}{\partial v_x} + F_y \hat{y} \cdot \left[ \int v_y \frac{\partial f_k}{\partial v_y} + F_z \hat{z} \cdot \left[ \int v_z \frac{\partial f_k}{\partial v_z} \right] \right] \]

So eq. (2-B-4) becomes

\[ \frac{\partial}{\partial t} (\rho \vec{u} \cdot (mn_k \vec{u} \cdot \nabla)) + n_k \vec{F} = \vec{R}_m \]  (2-B-5)

The velocity \( \vec{v} \) can be represented by the sum of two components:

\[ \vec{v} = \vec{u} + \vec{v}_i \]

where \( \vec{v}_i \) is a thermal component, which averages to zero. \( \vec{u} \) is due to either the electric field, the spatial gradient of the density of the species under consideration or both. So it does not average to zero. So we have eq. (2-B-5) further written as:

\[ \frac{\partial}{\partial t} (\rho \vec{u} \cdot (mn_k \vec{u} \cdot \nabla)) + n_k \vec{F} = \vec{R}_m \]  (2-B-6)

where the pressure tensor is defined as \( \vec{P} = n_k m \vec{v} \cdot \vec{v}_i \).

The second term on LHS of eq. (2-B-6) can be decomposed as:

\[ \nabla \cdot (n \vec{u} \cdot \nabla \cdot (n \vec{u} \cdot \nabla \cdot \vec{u})) + n_k (\vec{u} \cdot \nabla \cdot \vec{u}) = \vec{u} \nabla \cdot \vec{j} + (\vec{j} \cdot \nabla \cdot \vec{j}) \]  (2-B-7)

with an average flux vector defined as:

\[ \vec{j} = n_k \vec{u} \]  (2-B-8)

With this definition, the mass balance equation (2.18) becomes

\[ \frac{\partial}{\partial t} n_k + \vec{v} \cdot \vec{j} = R_e - R_i \]  (2-B-9)

The time derivative of the product \( (n_k \vec{u}) \) (the first term on LHS of eq. (2-B-6) can be decomposed as:

\[ \frac{\partial}{\partial t} (n_k \vec{u}) = n_k \vec{u} \cdot \nabla \vec{u} + \vec{u} \cdot \nabla n_k \]  (2-B-10)
Substituting eq. (2-B-7), (2-B-8), (2-B-9) and (2-B-10) into eq. (2-B-6)

\[ m[n_k \partial_t \tilde{u} + \tilde{u} \partial_t n_k] + m[\tilde{u} \nabla_r \cdot \tilde{J} + (n_k \tilde{u} \cdot \nabla_r) \tilde{u}] + \nabla_r \cdot \tilde{P} + n_k \tilde{F} = \tilde{R}_m \]

\[ m n_k d_t \tilde{u} + m \tilde{u} (\tilde{R}_r - \tilde{R}_i) + \nabla_r \cdot \tilde{P} + n_k \tilde{F} = \tilde{R}_m \]  \hspace{1cm} (2-B-11)

where \( d_t = \partial_t + (\tilde{u} \cdot \nabla_r) \).

For a Maxwellian distribution\(^{2,19,23,6} \),

\[ \tilde{P} = 2 n_k \tilde{e}_t / 3 \]  \hspace{1cm} (2-B-12)

where \( \tilde{e}_t = \frac{1}{2} m \tilde{v} \tilde{v}_t \) is the thermal component of the energy.

Defining:

The density creation term: \( R_c = \int (\tilde{v})^0 \frac{\partial f}{\partial t} d\tilde{v} = n_k = K_c N n_k \) where \( N \) is the neutral density.

The density loss term: \( R_l = \int (\tilde{v})^0 \frac{\partial f}{\partial t} d\tilde{v} = -n_k = -K_l N n_k \), and again the minus sign here denotes the density loss.

The creation or loss rate: \( K = \frac{\nu}{N} \) where \( \nu \) is the reaction frequencies.

By using these definitions with eq. (2-B-8) and eq. (2-B-12), the momentum balance of eq. (2-B-11) becomes:

\[ m n_k d_t \tilde{u} + m \tilde{u} (K_c N n_k - K_i N n_k) + m \nabla_r (n_k m \tilde{v} \tilde{v}_t / 3) \mp n_k e \tilde{E} = -m n_k \tilde{u} \tilde{v}_m \]

\[ \frac{\partial_t \tilde{u}}{\nu_m} + \frac{\tilde{u} \nabla_r \tilde{u}}{\nu_m} + \frac{\tilde{u} (\nu_c - \nu_i)}{\nu_m} + \nabla_r \left( \frac{n_k D_k}{\nu_m} \right) \mp \mu \tilde{E} = -\tilde{u} \]  \hspace{1cm} (2-B-13)

with the diffusion coefficient: \( D = \frac{m \tilde{v}_t \tilde{v}_t}{3 \nu_m} \), and the mobility: \( \mu = \frac{e}{m \nu_m} \).

Considering the above calculation in one dimension, the following assumptions can be made to simplify the eq. (2-B-13) in the case of APGDs:

1) The creation and loss frequencies are much smaller than the momentum transfer frequency, i.e., \( (\nu_c - \nu_i) / \nu_m << 1 \). This assumption allows us to neglect the third term on LHS of eq. (2-B-13). At atmospheric pressure, both
the creation frequency \( v_c \) and the loss frequency \( v_l \) are at the order of \( 10^7 \) Hz \(^{236}\), and the momentum transfer frequency can be calculated as:

\[
\nu_m = \frac{e}{m\mu} = \frac{1.6 \times 10^{-19}}{9.1 \times 10^{-31} \times (1 \times 10^2/760)} = 1.34 \times 10^{12} \text{Hz},
\]

with the mobility \( \mu = 1 \times 10^2/760 \text{ m}^2\text{V}^{-1}\text{s}^{-1} \). Therefore the assumption of \((v_l - v_m)/v_m << 1\) is valid at atmospheric pressure.

2) The drift velocity is smaller than or at most at the same order of magnitude as the thermal velocity. This assumption permits us to neglect the second term on LHS of eq. (2-B-13). At atmospheric pressure, the drift velocity can be approximated to be \( W = \mu E = 1 \times 10^2 \times 760 \times 10^4 = 1.3 \times 10^3 \text{ m/s} \) with \( \mu = 1 \times 10^2/760 \text{ m}^2\text{V}^{-1}\text{s}^{-1} \) and \( E = 10^4 \text{ V/cm} \), and the thermal velocity calculated from \( v_t = \sqrt{3D \nu_m} = \sqrt{3 \times 0.1737 \times 1.34 \times 10^{12}} = 8.36 \times 10^5 \text{ m/s} \) with \( D = 0.1737 \text{ m}^2\text{s}^{-1} \). Thus this assumption is valid at atmospheric pressure.

3) The angular frequency \( \omega \) is much less than the momentum transfer frequency \( \nu_m \). This assumption permits to neglect the first term on LHS of eq. (2-B-13).

For atmospheric pressure DBD, the angular frequency \( \omega = 2\pi f \) is at most at the order of \( 10^5 \) with the frequency \( f = 100 \text{ kHz} \), and it is much less than the momentum transfer frequency \( \nu_m \). This ensures the validation of this assumption.

Then eq. (2-B-13) becomes:

\[
n_k \ddot{u} = n_k \ddot{W}_k - \nabla_s (n_k \ddot{D}_k)
\]

(2-B-14)

This is identical to eq. (2-19) with the drift velocity \( \dot{W} = \dot{\mu} \dot{E} \).
Appendix 2-C Derivation of eq. (2.28)

We start from the convection-diffusion equation for any species:

$$\frac{\partial n_k(\bar{r}, t)}{\partial t} + \frac{\partial}{\partial \bar{r}} \left[ n_k(\bar{r}, t)w_k(\bar{r}, t) \right] = \frac{\partial}{\partial \bar{r}} \left[ \frac{\partial D_k(\bar{r}, t)n_k(\bar{r}, t)}{\partial \bar{r}} \right] + S_k(\bar{r}, t). \quad (2.26)$$

Replacing $n_k(\bar{r}, t)$, $w_k(\bar{r}, t)$, $D_k(\bar{r}, t)$ and $S_k(\bar{r}, t)$ by $n$, $W$, $D$ and $S$ for simplicity, the above equation can be written as following for one dimensional cases:

$$\frac{\partial n}{\partial t} + \frac{\partial}{\partial x} [nW] = \frac{\partial}{\partial x} \left[ \frac{\partial (Dn)}{\partial x} \right] + S \quad (2-C-1)$$

Integrating the above equation over time and space (noting that $i$ represents the space step and $j$ represents the time step):
We define $\|x, y\|$ is a maximum operator, so $\|x, y\| = \begin{cases} x & \text{if } x > y \\ y & \text{if } x < y \end{cases}$.

So the value of $[nW]_e$ and $[nW]_o$ can be defined as

$$
[nW]_e = n_1 \|W_e, 0\| - n_{i-1} \|W_e, 0\| \\
[nW]_o = n_{i-1} \|W_o, 0\| - n_i \|W_o, 0\|
$$

(2-C-3)

Substituting eq. (2-C-3) into eq. (2-C-2) and applying (2.26)

$$
\int_{t=t}^{t=t+\Delta t} n dt = [f(n(t) + (1 - f)n(t - \Delta t))]dt
$$

(2.27)

Eq. (2-C-2) becomes

$$
\int \frac{\partial}{\partial x} [D_1 \frac{\partial n}{\partial x}] dx dt = \int \frac{1}{\Delta x} \left[ n \frac{\partial}{\partial x} \left[ D_0 \frac{\partial n}{\partial x} \right] - D_0 \frac{\partial n}{\partial x} \right] \Delta x dt
$$

$$
= \int D_e \frac{n_{i+1} - n_i}{\Delta x} - D_o \frac{n_i - n_{i-1}}{\Delta x} dt
$$

$$
= \frac{D_e}{\Delta x} \left[ n_{i+1} - n_i \right] dt - \frac{D_o}{\Delta x} \left[ n_i - n_{i-1} \right] dt
$$

$$
= \frac{D_e}{\Delta x} \left[ fn_{i+1} + (1 - f)n_{i+1} - fn_i - (1 - f)n_i \right] dt
$$

$$
- \frac{D_o}{\Delta x} \left[ fn_i + (1 - f)n_{i-1} - fn_{i+1} - (1 - f)n_{i+1} \right] dt
$$

4) The term on the RHS of eq. (2-C-1)

$$
\int_{t=t}^{t=t+\Delta t} n dt = [f(n(t) + (1 - f)n(t - \Delta t))]dt
$$

(2.27)
\[ \int S_1' \, dx \, dt = S_1' / \Delta x \Delta t \]

From 1), 2), 3), and 4), the convection-diffusion equation can be discretized to:
\[
(n_i' - n_i'^{-1}) \Delta x + \Delta t \left[ W_o, 0 \right] \left[ fn_{i+1} + (1 - f) n_i'^{-1} \right] - \left[ - W_o, 0 \right] \left[ fn_i + (1 - f) n_i'^{-1} \right]
- \left[ W_o, 0 \right] \left[ fn_{i-1} + (1 - f) n_i'^{-1} \right] + \left[ - W_o, 0 \right] \left[ fn_i + (1 - f) n_i'^{-1} \right]
\]
\[= \frac{D_o}{\Delta x} \left[ fn_{i+1} + (1 - f) n_i'^{-1} - fn_i - (1 - f) n_i'^{-1} \right] \Delta t + S_1' / \Delta x \Delta t \]

\[
\frac{\Delta x}{\Delta t} (n_i' - n_i'^{-1}) = fn_{i+1} \left[ \frac{D_o}{\Delta x} + \left[ - W_o, 0 \right] \right] + (1 - f) n_i'^{-1} \left[ \frac{D_o}{\Delta x} + \left[ - W_o, 0 \right] \right]
+ fn_i \left[ \frac{D_o}{\Delta x} + \left[ W_o, 0 \right] \right] + (1 - f) n_i'^{-1} \left[ \frac{D_o}{\Delta x} + \left[ W_o, 0 \right] \right]
+ fn_{i-1} \left[ \frac{D_o}{\Delta x} - \frac{D_o}{\Delta x} + \left[ - W_o, 0 \right] - \left[ - W_o, 0 \right] \right] + S_1' \Delta x
\]

By using the implicit scheme \((f = 1)\), the above equation becomes
\[
\frac{\Delta x}{\Delta t} (n_i' - n_i'^{-1}) = n_{i+1} \left[ \frac{D_o}{\Delta x} + \left[ - W_o, 0 \right] \right] + n_i'^{-1} \left[ \frac{D_o}{\Delta x} + \left[ W_o, 0 \right] \right]
+ n_i \left[ \frac{D_o}{\Delta x} - \frac{D_o}{\Delta x} - \left[ W_o, 0 \right] - \left[ - W_o, 0 \right] \right] + S_1' \Delta x
\]

(2.28)

The discretization of eq. (2.26) finally becomes:
\[
a_i' n_i' = b_i' n_{i+1}' + c_i' n_{i-1}' + d_i'
\]

(2.30)

where: the coefficient of upstream neighbour:
\[ b_i' = \frac{D_o}{\Delta x} + \left[ - W_o, 0 \right] \]

the coefficient of downstream neighbour:
\[ c_i' = \frac{D_o}{\Delta x} + \left[ W_o, 0 \right] \]

the coefficient of present grid point:
\[ a_i' = b_i' + c_i' + W_o - W_o + \frac{\Delta x}{\Delta t} \]

the other source influenced present grid point:
\[ d_i' = \frac{\Delta x}{\Delta t} n_i'^{-1} + S_1' / \Delta x \]
Appendix 2-D  Operation procedure of TDMA\textsuperscript{2,23}

We start with the following discretization equation

\[
a_i^l n_i^l = b_i^l n_{i+1}^l + c_i^l n_{i-1}^l + d_i^l
\] (2-30)

It can be expressed in a matrix format

\[
\begin{bmatrix}
a_1^l & -b_1^l & 0 & 0 & \cdots & \cdots & 0 & 0 & 0 & 0 & \left[ n_1^l \right] & \left[ d_1^l \right] \\
-c_2^l & a_2^l & -b_2^l & 0 & 0 & \cdots & \cdots & 0 & 0 & n_2^l & d_2^l \\
0 & -c_3^l & a_3^l & -b_3^l & 0 & \cdots & \cdots & \cdots & \cdots & 0 & n_3^l & d_3^l \\
\vdots & \vdots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots \\
0 & \cdots & \cdots & 0 & -c_N^{-2} & a_N^{-2} & -b_N^{-2} & 0 & n_N^{-2} & d_N^{-2} \\
0 & 0 & \cdots & \cdots & 0 & 0 & -c_N^{-1} & a_N^{-1} & -b_N^{-1} & n_N^{-1} & d_N^{-1} \\
0 & 0 & 0 & \cdots & \cdots & 0 & 0 & -c_N & a_N & n_N & d_N
\end{bmatrix} = \begin{bmatrix}
\end{bmatrix}
\]

or in a format of simultaneous linear equations

\[
\begin{align*}
a_i^l n_i^l - b_i^l n_{i+1}^l - c_i^l n_{i-1}^l + d_i^l & = d_i^l \\
-c_2^l a_2^l + a_2^l n_2^l - b_2^l & = d_2^l \\
0 & = d_3^l \\
0 - c_3^l a_3^l + a_3^l n_3^l - b_3^l & = d_4^l \\
0 & = d_5 \\
& \vdots
\end{align*}
\]
Appendix

and the coefficients can be evaluated as:

\[ i = 1, \quad n_{i} = \frac{b_{1}}{a_{1}}n_{2} + \frac{d_{1}}{a_{1}} = P_{1}n_{2} + Q_{1} \]

\[ i = 2, \quad n_{2} = \frac{b_{2}}{a_{2}} \frac{b_{1}}{a_{1}}n_{3} + \frac{d_{2} + c_{2}Q_{2}}{a_{2} - c_{2}P_{1}} = \frac{b_{2}}{a_{2} - c_{2}P_{1}}n_{3} + \frac{d_{2} + c_{2}Q_{2}}{a_{2} - c_{2}P_{1}} = P_{2}n_{3} + Q_{2} \]

\[ i = 3, \quad n_{3} = \frac{b_{3}}{a_{3}} \frac{b_{2}}{a_{2}}n_{4} + \frac{d_{3} + c_{3}Q_{3}}{a_{3} - c_{3}P_{2}} = \frac{b_{3}}{a_{3} - c_{3}P_{2}}n_{4} + \frac{d_{3} + c_{3}Q_{3}}{a_{3} - c_{3}P_{2}} = P_{3}n_{4} + Q_{3} \]

\[ \vdots \]

\[ i = i, \quad n_{i} = \frac{b_{i}}{a_{i} - c_{i}P_{i-1}}n_{i+1} + \frac{d_{i} + c_{i}Q_{i-1}}{a_{i} - c_{i}P_{i-1}} = P_{i}n_{i+1} + Q_{i} \]

\[ \vdots \]

\[ i = N, \quad n_{N} = \frac{b_{N}}{a_{N} - c_{N}P_{N-1}}n_{N+1} + \frac{d_{N} + c_{N}Q_{N-1}}{a_{N} - c_{N}P_{N-1}} = P_{N}n_{N+1} + Q_{N} = Q_{N} (\because b_{N} = 0) \]

So the procedural steps of the TDMA algorithm are

1. Define coefficients of final discretization equation over the whole space for a specific time step;

2. Calculate \( P \) & \( Q \) values from coefficient \( a, b, c \) and \( d \);

3. Set \( n_{N} = Q_{N} \);

4. Calculate backward \( n_{N-1} \ldots n_{1} \) via the relation: \( n_{N-1} = P_{N-1}n_{N} + Q_{N-1} \).