Fundamental Understanding of Plasma Discharge Formation in Liquid and Multiphase Configurations Through Multiphysics Modeling

Ali Charchi Aghdam

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Fundamental understanding of plasma discharge formation in liquid and multiphase configurations through multiphysics modeling

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2020

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Dedication

Dedicated to my parents Narmin and Yousef,
my sister Nazanin
and
My Love, Nazli
ACKNOWLEDGMENTS

This dissertation would not have been possible without the help, support, and advice of many people.

I’m deeply indebted to my advisor, Dr. Tanvir Farouk. Thank you for all the support and encouragement you gave me during these years. Without your guidance and constant feedback this Ph.D. would not have been achievable.

I would like to extend my sincere thanks to the members of my Ph.D. committee, Dr. Jamil Khan, Dr. Sourav Banerjee, Dr. Sang Hee Won and Dr. Shamia Houqe for their helpful suggestions. I would also like to acknowledge the financial support from the National Science Foundation.

I am grateful to the members of RASAER lab with whom I had the pleasure to work throughout the past 6 years. Particularly, Farhan, Sudipta, Tahiyat and Fahd, who all helped me in numerous ways during various stages of my Ph.D.. My special thanks go to my Iranian friends in Columbia for their friendship and support.

I wish to express my sincere gratitude to my family, specially my parents for the unconditional love and care they provided. I am also grateful to my sister, mother-in-law, father-in-law and brother-in-law for their love and support. I love them so much, and I would not have made it this far without them.

Finally, I wish to thank my wife, my love, and my soulmate, Nazli, for her constant support. She has made countless sacrifices to help me get to this point. Thank you for being my best friend. I owe you everything.
ABSTRACT

During the last two decades, non-thermal plasma discharges in and in contact with liquids have received significant attention due to their wide range of applications including chemical analysis, medical, water treatment, fuel processing, etc. Despite the tremendous interest and advances attained in the experimental studies, modeling efforts providing a comprehensive understanding of the underlying physicochemical processes are limited. There is still no unified theory on plasma formation in dense medium and various theories have been proposed such as the presence of bubbles and tunneling which are topics of debate. In the first part of this study, a mathematical model is proposed to simulate the initiation and propagation of plasma in a liquid medium. An in-house numerical framework consisting of a compressible fluid solver together with the charged species conservation and Poisson’s equation solver is employed for the simulations. The effects of electrostatic, polarization and electrostrictive ponderomotive forces are studied on the initial stage of plasma discharge. The simulation results of the proposed model show that under the influence of nanosecond voltage rise, the liquid experiences the formation of negative pressure region near the vicinity of the powered electrode and surpasses the cavitation threshold pressure. The cavitation locations initiate as sub-micron regions and then extend up to a few microns. These sub-micron low-density regions act as plasma nucleation sites. The second part focuses in assessing the kinetic aspects of plasma formation in liquid water. A chemical kinetic model is proposed and utilized in the simulations. To solve the detailed chemistry problem, a novel operator-splitting scheme is developed. It has been shown that other than water ionization via Zener tunneling,
electron detachment from negative OH ions is an important ionization pathway for liquid molecules. The electrons react with liquid water and generate aqueous ions and radicals. The kinetic analysis of plasma interaction with water shows that at lower voltages, OH ionization is the primary source of electrons while at elevated voltages almost all of electrons are generated via H₂O ionization. Finally, formation of plasma in multi-liquid configuration is investigated. Compared to a single liquid, it has been found that plasma discharge can be achieved at lower voltages thus proving to be an energy efficient method for plasma generation. A multiphase fluid model is proposed to study the electrical forces and plasma discharge in multi-liquid configurations. The effect of interface location as well as the applied voltage profile on discharge probability is studied.
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Chapter 1

Introduction

1.1 Plasmas

A *plasma* is a mixture of charged and neutral particles moving in random directions[1]. The term plasma is often referred to as the fourth state of matter. As temperature increases, molecules become more energetic and transform from solid to liquid and then to gas. If the temperature is sufficiently high, the molecules in the gas dissociate to form a gas of atoms and then a gas of freely moving charged particles, electrons, and positive ions. This state is referred to as the plasma state. The word plasma was first coined by Langmuir to describe the region of a discharge not influenced by walls and electrodes [2]. Example of this state is the stars, in which the plasma species are in thermal equilibrium, i.e. the electron temperature is equal to the temperature of ions and neutral particles.

On the other hand, non-thermal plasma is the state of plasma in which the particles are not in thermal equilibrium with each other or with their surroundings. These discharges are electrically driven (i.e. electric field) and the ionization of neutrals sustains the plasma in the steady state. The medium is weakly ionized that is, the plasma density is only a small fraction of the neutral particles. Briefly, the applied power heats the light and mobile electrons while the heavy charged particles exchange energy by collisions with the background gas (or liquid). Therefore the temperature of these heavy particles in non-thermal plasma is significantly lower than electron temperature [1].
Ionization of atoms and molecules takes place via the elementary processes: electron impact, electron attachment to atoms or molecules, and ion-molecule reactions. These elementary reactive collisions, as well as electron-ion and ion-ion recombination, excitation and dissociation of neutral species by electron impact, electron detachment and destruction of ions, determine the plasma behavior [2].

Typically, a plasma discharge in gas consists of a voltage source and the gas between two conducting electrodes. Once the electric field reaches a certain critical value, the gas breaks down to form a plasma [1]. Electric breakdown is the point that a non-conducting material transforms into a conducting material by applying external electric field. As the field strength increases, the generation of electrons by elementary processes like electron impact ionization, detachment, etc gradually increase. As the rate of ionization increase, the obstacle or loss mechanisms also increases. Transport of electrons towards the electrodes and walls, attachment and recombination are examples of these loss mechanisms. The competition of ionization with loss mechanisms determine the possibility of break down and sustaining the plasma in a quasi-steady state. If the field is raised to the threshold value, a dramatic increase in ionization rates occur and the discharge is generated [3].

1.2 Plasma in liquids

Plasma in liquids is relatively newer and less popular compared to gaseous plasmas. The higher density and shorter mean path of electrons means stronger loss mechanisms in liquids and hence, higher voltages are required for breakdown. However, it has been observed that liquid breakdown is possible at fields slightly higher that for atmospheric gases. Considering the significant difference in density and therefore in $|E|/N$ value of gas and liquid, this is explained by the crack mechanism in liquids [2]. It is shown that under the effect of electric field, the liquid cracks and vapor micro-voids are formed. [4, 5]. These micro-voids grow into bubbles which have
lower density and act as ionization seeding zone. Different theories suggest that the bubble is formed either by joule heating or cavitation. Typically discharge in liquids is carried out in point-to-plane of point-to-point electrode configurations [2]. The advantage of these electrodes are their curved shapes that produce higher local field near the curved zone at the same voltage compared to parallel plate configuration.

Plasma discharge in water is associated with the generation of reactive species such as OH, O and H$_2$O$_2$, making it attractive for many applications like water treatment and disinfection. In some of the applications, discharge is not directly generated in water but initiated in the gas in contact with liquid and the reactive species are delivered into the water.

1.3 Motivation

During the last two decades non-thermal plasma discharges in liquids have received significant attention in view of their wide range of application. Despite the tremendous interest and advances attained in the experimental studies, modeling efforts providing a comprehensive understanding of the underlying physicochemical processes is limited.

The processes involved in the initial stages of discharge in liquids is the major matter of debate among the researchers. While some studies have shown the generation of bubbles at the beginning of the discharge because of joule heating, new evidences have been provided to support the generation of bubbles with non-thermal mechanisms. Furthermore, the primary source of the electrons claimed to be ionization of water and/or Hydroxide ion via Zener tunneling, electron impact ionization of gas inside the bubbles, etc. Finally, the use multi-liquid configuration for obtaining discharge in lower voltages have been proposed recently.
Detailed modeling of this phenomena can provide insight into the interplaying physico-chemical processes and provide better understanding of the effect of these processes in formation and sustainability of plasma.

1.4 Objectives

This dissertation focuses on the development of multi-dimensional multi-physics model to study the plasma discharge in liquids. The objectives are as follows:

- Develop a multi-physics simulation framework for studying the initiation of plasma discharge in liquids.
- Develop a numerical tool to study the hydrodynamic aspects of plasma in liquid.
- Develop a comprehensive plasma code to incorporate detailed chemistry mechanism of discharge in liquids.
- Develop a multi-phase plasma simulation code to investigative plasma properties in multi-liquid configurations.
- Investigate the effect of different parameters such as voltage profile and ionization paths on the discharge characteristics.

1.5 Organization of the thesis

In Chapter 2 a review of literature is presented followed by the problem statement and significance of this work.

Chapter 3, is dedicated to the detailed discussion of the numerical methodology used throughout the rest of the thesis. Simulation algorithms, numerical schemes and mathematics models used in this work is presented in this chapter.

Chapter 4 contains the results for the initial stage of plasma discharge in liquid water. The major focus in this stage will be on the electrical forces acting on the
liquid, facilitating the formation of low density zones. A simple chemistry model is considered in this stage.

Chapter 5 is dedicated to investigation of different ionization mechanisms and inclusion of detailed aqueous plasma chemistry in the model.

In chapter 6, the numerical study of hydrodynamics and chemistry of plasma discharge in multi-liquid configurations is discussed.

Finally, chapter 7 serves as the closure highlighting the findings and recommendations for future works.


CHAPTER 2

BACKGROUND AND LITERATURE REVIEW

2.1 BACKGROUND

The applications of strong electric fields in liquids (e.g. water and organic liquids) have been studied by the electrical engineering community for many years because of its importance in pulsed power and high voltage applications [6, 7]. In recent years, the interest on the non-thermal plasma in liquids has increased exponentially, driven by their application in biological, environmental and biomedical technologies [8–10]. Due to the same advantageous properties, plasma discharges in liquid medium have also immense potential for novel technologies such as nanoparticle synthesis, liquid fuel reforming, etc. Plasma in dense media such as liquids and supercritical fluids is a relatively new area and in its development stage [11]. Even though there has been tremendous growth in the application side; the fundamental understanding of plasma discharges in liquids is limited. There is still no unified theory on plasma formation in dense medium and various theories have been proposed such as the presence of bubbles [12] and tunneling [13] which are topics of debate. Mathematical models capable of predicting plasma formation in liquids is therefore critical in understanding the basic coupled and inter-playing mechanisms driving the plasma phenomena. These models are vital tools for the development of future applications in the coming decades.

Discharges in liquids are typically initiated by the application of a high electric field in a configuration where both the electrodes are submerged in the liquid phase. In this simplest configuration, discharges in the liquid can be classified into
two broad categories a) partial or incomplete discharges i.e. coronas and streamers (non-thermal) and b) complete discharges i.e. arcs and sparks (thermal). The characteristic that dictates the difference between these two types of discharge is whether the plasma wave travels the entire inter-electrode distance or bridges the gap between the electrodes. The difference between these two types of discharges is governed by the deposited power. Incomplete discharges (coronas, streamers) have significantly lower power density in comparison to the complete discharges (arcs, sparks). The non-thermal corona or streamer discharges are almost always generated by pulsed excitation. The most commonly used excitation method is the discharging of a capacitor using a spark gap or another triggering device [10, 14–16]. In most cases, the corona and streamer discharges are not believed to be associated with the phase change of the liquid (i.e. no vaporization and bubble formation) [17] whereas sparks and arcs are always coupled with phase change and bubble formation due to their thermal nature [8].

One of the earliest works in liquid phase plasma was conducted by Dakin and Berg [18] reporting corona discharges in oils. Luminous spots were observed near submerged electrodes, hypothesized to be a result of localized field emission. Gzowski and coworkers [19] reported similar luminescence in hexane under the pulsing electrical field. Shammas et al. [20] reported the first sets of photographs of corona like discharges in liquid hexane. Oils were the first choice of these studies since the breakdown mechanism in oil medium is not associated with any electrolysis due to its non-polar characteristics which make the process less complex. In recent years discharges in cryogenic liquids have also been successfully demonstrated. Li et al. [21] studied the formation of a negative corona in liquid helium. The measured line spectra from the light emission indicated the discharge to be non-thermal; however, the measured temperature was found to be higher than the boiling point of the liquid. As such the formation of bubbles in the discharge was speculated.
Plasma discharge in water is a recent development driven by decontamination and sterilization applications. The review articles of Locke et al. [8, 9] and Bruggeman and Leys [11] summarized a comprehensive set of work on plasma discharge in water. Most of the plasma discharges reported by Locke et al. [8] is an incomplete streamer corona type discharge and measured temperatures indicating that they are operating in the thermal mode. Only recently An et al. [15] and Staack et al. [17] showed the development of non-thermal streamer-corona discharge in liquid water. An et al. [15] employed fast rise time voltages and their high temporal resolution image diagnostics denoted two distinct stages in the streamer-corona formation. In the first stage, the streamer is found to propagate in an almost symmetrical branching structure. A second stage is observed after hundreds of nanoseconds; a secondary streamer is formed from an intensified branch of the first streamer. Spectroscopic measurements denoted the secondary streamer to have a temperature of \( \sim 1000^\circ C \), operating in the thermal mode. In comparison to An et al. [15], Staack et al. [17] employed both nanosecond pulse duration and nanoscale electrodes to generate non-thermal primary streamer at a very early stage.

2.2 Initial stage of plasma discharge in liquid

The formation and presence of vapor phase bubbles for the generation of non-thermal plasma discharge in the liquid phase is a matter of contention in which experimental and numerical verification is incomplete. One major unresolved issue is the formation and propagation of the very first vapor phase bubble that initiates the primary streamer. Among the different theories, Lewis [4] proposed that the water essentially cracks under the high dielectrophoretic stresses which leave a void due to electric fields. Qian et al. [22] and Joshi et al. [13] referred to heating of liquid to vaporization for bubble formation. In addition, Joshi et al. [13] proposed the possibility of electron tunneling effects in the liquid phase plasma discharges. Bunkin et al. [23,
proposed the theory of preexisting \textit{bubbles stabilized by ions}, and their role in non-thermal plasma formation in the liquid phase. Šimek and coworkers [25] have utilized intensified charge-coupled device (ICCD) microscopy and spectroscopy to study the micro-discharge in liquids and found that the nano-second discharge initiation does not involve the formation of vapor bubbles.

Shneider and coworkers [5] conducted a theoretical analysis in determining the initiation mechanism of the sub-nanosecond pulsed breakdown in liquid dielectrics. They proposed that the electrostrictive forces near the electrode could result in a rupture in the continuity of the fluid forming nanopores acting as plasma initiation sites. The experiments conducted by Pekker et al. [26] and Marinov et al. [27] observed the formation of cavitation under the influence of electrostrictive forces as pre-breakdown phenomena supportive of this theory. Also, Shneider and Pekker [28] have proposed a pure hydrodynamic model for initiation of breakdown. In their model, electrostrictive force density is included in a compressible momentum equation. They have used an analytical solution of the poison’s equation in the prolate spheroidal coordinates to calculate the electric field distribution in a needlelike electrode configuration and solved the fluid flow equations numerically. However, they have neglected the polarization and electrostatic forces as well as the kinetic effects. As can be seen in Figure 2.1, the obtained negative pressures are sufficient to crack the fluid and initiate cavitation. In their other papers [29, 30], they have studied the development of pre-breakdown cavitation nanopores near the electrode using the Zel’dovich-Fisher theory [31, 32].

Discharge formation in non-polar liquids (e.g. oils) and liquid noble gas has been numerically modeled in the past. In these models, the presence of phase change has been ignored. Simulations of positive streamers in liquid argon and xenon have been conducted by Babaeva and Naidis [33]. Their study drew a comparison between streamers in gas and liquid media. Jadidian et al. [34] developed an electrother-
Figure 2.1: Longitudinal distributions of the total pressure along the symmetry axis for the linear voltage for the time moments $t/t_0 = 0.25$ (curve 1), $t/t_0 = 0.5$ (curve 2), $t/t_0 = 0.75$ (curve 3), and $t/t_0 = 1$ (curve 4). The dashed line shows the pressure threshold for cavitation of water [28].

mal model to simulate streamer propagation in liquid transformer oil. Their model included the conservation equation for electrons, positive and negative ions. Zener electron tunneling model, as well as attachment and recombination reactions, were employed for the ionization rate. Their model indicated temperatures significantly higher than the boiling point of the oil.

2.3 Plasma chemistry

The most challenging part of modeling of discharge in liquids is the implementation of kinetic effects. As emphasized by Starikovskiy et al. [35], there is no solid theoretical approach to model the discharge in dense media. However, many researchers have used either dense gas or semiconductor approximations or combination of both approaches. The dense gas approximation assumes that the liquid is a gas with high particle number density and the semi-conductor approach considers the liquid as a solid-state crystal for which the electron tunneling is applicable. Although both ap-
approaches have certain drawbacks, at least qualitative results can be obtained using the above-mentioned approaches. For example, in the works of Qian et al. [36] and Jadidian et al. [34], it is assumed that the plasma is generated by field ionization of liquid via Zener tunneling. They have also included constant rate attachment and recombination reactions.

Most of the aqueous plasma chemistry studies are done for plasma jet in contact with water in which the ionized gas collides the water surface. The electrons, ions and radicals generated in gas is then diffuse into water and react with water molecules. Van Gils et al. [37] have studied the efficiency of radio-frequency atmospheric pressure argon plasma jet in bacteria inactivation. They have combined their measurements with a zero-dimensional kinetics model to address the aqueous reactions for disinfection applications. Their results indicate that the reactive nitrogen species (RNS) as well as H$_2$O$_2$ play an important role in bacterial inactivation. They have also observed a decrease in pH for non-buffered solutions. Hamaguchi [38] has used a simplified reactor model to investigate plasma-initiated electrochemistry in water. In his work, plasma is formed in air and reactive species are exposed to water. Machala et al. [39] has also investigated the role of RNS and ROS in treatment of water, electro-sprayed through spark discharge in air. In the work of Tian and Kushner [40] a two-dimensional computational model is used to study the generation of active species during treatment of biological tissues by atmospheric pressure dielectric barrier discharges (DBDs). They have assumed that the plasma forms the active species in gas phase and diffuse into water, solvated by water molecules and the solvated species react with water and each other through in-water reactions.

Among the works on underwater discharge, Šunka et al. [41] have used optical emission spectroscopy to confirm the formation of active species during underwater corona discharge. They have also shown that Fe$_2^+$ is oxidized to Fe$_3^+$ in underwater discharge proving formation of hydrogen peroxide. Formation of reactive species in
aqueous solutions under pulsed corona discharge is studied by Joshi et al. [42]. They calculated the rate of formation of aqueous electrons and hydrogen peroxide by fitting the experimental data for phenol degradation to their kinetic model. Grymonpré et al. [43] investigated the Fenton’s reaction chemistry in degradation of phenol, in liquid phase pulsed corona reactors. Fenton’s reaction is the combination of H$_2$O$_2$ and a ferrous salt to produce hydroxyl radicals. They concluded that the rate of hydrogen peroxide formation in the pulsed corona reactor is dependent upon both the solution conductivity and the applied electrical potential. Mededovic and Locke [44] have proposed a mathematical model for the chemical processes occurring in discharges in water. They have divided discharge channel into the core and the recombination region. They assumed that high temperature initiation reactions take place in the core and the additional reactions such as hydrogen peroxide formation take place in the recombination zone. They have found that 79% of molecular hydrogen is formed in the core at high temperature while hydrogen peroxide is formed in the recombination region.

Since the underwater discharge involves excitation, ionization, and dissociation of water, the reaction mechanism may be similar to those in water radiolysis such
as γ-radiation which produce radical and molecular species through excitation and ionization of water [42]. Therefore most of the studies on the reactions driven by electrons in aqueous systems are done by radiolysis of water. As shown in Figure 2.2, the electrons become hydrated by water, and H₂O⁺ disproportionates to form H₃O⁺ and OH on time scales faster than 1 ps. The radicals and ionic species react with water and other species in the solution to form other species like H₂, H₂O₂, and OH⁻ [45]. Detailed discussion of reaction mechanisms for radiolysis of water is given in review papers of Buxton et al. [46], Garrett et al. [45], and Madden and Mezyk [47]. Tian and Kushner [40] have developed a reaction mechanism from the literature. They have considered hydration reactions for electrons and ions, aqueous chemistry, photon reactions and, reactions of radicals with hydrocarbons.

2.4 Multi-phase plasmas

Multi-phase plasma discharge refers to discharges in which more than one phases are involved, i.e gas-liquid or two liquids configuration. In some of the studies mentioned in section 2.3, the plasma is formed in gas phase and the active species are transported into water. Therefore, formation of these species only depend on gas properties. However, in multi-phase systems, the difference in properties of two fluids has an important effect on plasma characteristics.

Non-thermal plasma discharge in liquids has found several applications during the recent years. Plasma discharges generated directly in liquid medium require much

Figure 2.3: Oscillation of gas bubbles submerged in water [48].
higher breakdown electric fields due to very high liquid densities compared to densities in a gas. Significant field enhancement takes place in the phase boundary due to sharp change of dielectric constants, triggering the discharge in lower voltages. Therefore, one proposed method of facilitating discharge in liquids is to inject gas bubbles into the liquid and generate the plasma in the gas bubbles. This approach has been studied extensively both experimentally and computationally [49, 50]. Sommers and Foster [48] have investigated the formation of plasma in a single, isolated gas bubble submerged in water by trapping the bubble in an acoustic field. In their studies they utilized AC voltage to make the bubble oscillate into nonlinear shapes and explained the observed discharge enhancement as a combined result of shape and volume effects. The shape effect is the enhancement of local electric field by distortion of phase boundary and the volume effect is the decrease in internal pressure of bubble due to expansion. Based on their simulations, the electric field is enhanced up to 53% higher than the case of a sphere. Figure 2.3 shows an oscillation cycle of a bubble subject to AC electric field. The model of Babaeva and Kushner [12] assumes stationary bubbles immersed in non-ionizing liquid. They have shown that the properties of streamers propagating inside bubbles varies for different dielectric constant ratios and conductivities. Similar stationary bubble approach was employed by Sharma et al. [50] to simulate the experiments of Hamdan and Cha [51]. The model of Qian et al. [36] considers single and multiple stationary bubbles in which the electrons are generated by ionization of gas and delivered to the liquid. Hayashi et al. [52] studied the effect of fine bubbles on pulsed discharge in water and pointed out the benefit of injecting bubbles to liquid as an aid to breakdown, lowering the discharge inception voltage and avoiding joule heating.

Although the breakdown voltage can be lowered with gaseous bubbles, the interaction between the plasma and liquid is limited because the discharge occurs in the gaseous bubbles. Hamdan and Cha [53] used a low-dielectric layer of n-Heptane
Figure 2.4: a) The experimental setup of Hamdan and Cha. b) Discharge probability as a function of the position of the interface [53].

over the water to take advantage of dielectric material discontinuity to increase local electric field. Their experimental setup is shown in Figure 2.4a. They defined the discharge probability (DP) as the percentage of successful discharges out of more than 200 applied pulses for a given interfacial position at a given electrode gap \((d)\) and pulse amplitude \((V_a)\). Figure 2.4b shows the variation of DP with interface position. As the interface was moved down closer to the tip of the anode, DP increased and reached 100%. However, DP dropped suddenly when \(h\) approached the tip of the anode \((h = 0)\). In conclusion, the DP in water can be increased by simply adding a covering layer of n-Heptane slightly above the tip of the anode to obtain high processing efficiency, i.e. reaching discharge in lower voltages.

2.5 **Significance of present work**

The discharge of plasma in liquids is an open field of research and has found many practical applications. The need for numerical simulation comes from the fact that the discharge phenomena happens in small time and space scales which makes the experiments difficult. Based on the literature review presented before, a full understanding of the physics of the phenomena have not been available yet. So, the
mathematical modeling can be used as an essential tool for understanding underlying physics as well as enhancing the practical aspects. As such, the problem statement makes it an ideal platform for conducting theoretical studies.

In the current work, a numerical study is performed considering all three components of electrical force acting on the liquid in presence of electric field. To the best of our knowledge, this is the first attempt to include all these forces in the initiation model without simplifying assumptions. Also, for the first time, the chemistry of aqueous plasma is also studied in a simulation coupled with full hydrodynamics of the system. Finally, discharge in a multi-liquid configuration is computational studied using the Volume of fluid interface capturing method. The results of this study will provide better understanding of the underlying mechanisms in liquid and multi-phase plasmas.
Chapter 3

Mathematical model

In this chapter the mathematical model used to simulate plasma discharge formation in single and multi-phase liquid system is presented. In the first section the hydrodynamic model with a limited set of kinetic steps are considered. The primary objective of this study is to computationally investigate the plasma initiation process in the liquid phase in the nano-second time scales and the associated density variation of the medium due to the electric field, charges and the associated forces. The next section covers the details of full chemistry integration algorithm. Finally, the multi-fluid plasma model is presented.

3.1 Plasma initiation model

The mathematical model proposed consists of the fluid dynamic equations of the mass, momentum and energy conservation for the bulk medium in compressible form, species conservation equations for each of the species considered (electrons $n_e$, positive ions $n_p$ and negative ions $n_n$) and the Poisson’s equation for the electric field. A local field approximation is employed to determine the electron temperature as a function of the reduced electric field ($|E|/N$).

3.1.1 Governing equations

The mass, momentum and energy conservation of a compressible Newtonian fluid is described by the following equations:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{U}) = 0$$  \hspace{1cm} (3.1)
\[
\frac{\partial \rho \mathbf{U}}{\partial t} + \nabla \cdot (\rho \mathbf{U} \mathbf{U}) = \mu \nabla^2 \mathbf{U} - \nabla p + \mathbf{F} \tag{3.2}
\]
\[
\frac{\partial \rho E_{tot}}{\partial t} + \nabla \cdot (\rho \mathbf{U} E_{tot}) + \nabla \cdot (\mathbf{U} \mathbf{p}) = -\nabla \cdot \mathbf{q} + \nabla \cdot (\tau \cdot \mathbf{U}) + \rho g \mathbf{U} + \mathbf{J}_{ion} \cdot \mathbf{E} \tag{3.3}
\]

where, \( \rho \) is the liquid density, \( \mathbf{U} \) is the velocity vector, \( \mu \) is the viscosity, \( p \) is the hydrodynamic pressure and \( \mathbf{F} \) is the electrical force vector and \( \psi \) is compressibility of the medium. In the energy conservation equation \( E_{tot} \) is the total energy, \( \mathbf{q} \) is the conductive heat flux, \( \tau \) is the viscous stress tensor and \( \mathbf{J}_{ion} \) is the ion current density.

The electrical force vector \( \mathbf{F} \) contains three terms and has the following form:

\[
\mathbf{F} = q \mathbf{E} - \frac{\epsilon_0}{2} \mathbf{E}^2 \nabla \epsilon + \frac{\epsilon_0}{2} \nabla \left( \mathbf{E}^2 \frac{\partial \epsilon}{\partial \rho} \right) \tag{3.4}
\]

where, \( q \) is the charge density, \( \epsilon_0 \) is the vacuum dielectric permittivity, \( \epsilon \) is the relative permittivity and \( \mathbf{E} \) is the electric field vector. The first term in the right hand side of equation (3.4) is the electrostatic force i.e. the force acting on the free charges, the second term is the force associated with the non-uniformity of the permittivity and the third term is the force due to electric field gradient. The second and third terms are customarily termed as polarization and electrostrictive ponderomotive forces, respectively [28]. The term \( \frac{\partial \epsilon}{\partial \rho} \) is a fluid property. For polar dielectrics like water, it has been shown in [54] that at a constant temperature, the variation in permittivity as a function of density can be expressed in the following form:

\[
\epsilon = \epsilon_l \left( \frac{\rho}{\rho_0} \right)^a \tag{3.5}
\]

where, \( \epsilon_l \) is the relative permittivity of water at atmospheric pressure and room temperature and has a value of 80.79, \( \rho_l \) is the associated liquid density and \( a \) is constant having a value of 1.34 for water. The last term in equation (3.4) can be simplified for a polar liquid as suggested in [28]:

\[
\frac{\partial \epsilon}{\partial \rho} \rho \approx a \epsilon \tag{3.6}
\]
The Tait equation of state [55] is often used to relate the pressure to the density of water.

\[ p = (p_0 + B) \left( \frac{\rho}{\rho_0} \right)^\gamma - B \]  

(3.7)

Here, \( \rho_0 = 1000 \text{ kg m}^{-3} \), \( p_0 = 10^5 \text{ Pa} \), \( B = 3.5 \times 10^5 \text{ Pa} \) and \( \gamma = 7.5 \). However, to simplify the pressure-momentum coupling, instead of the Tait equation a linear compressibility model is used:

\[ \rho = \rho_0 + \psi p \]  

(3.8)

The symbol \( \psi \) is referred to as the compressibility of the medium and is defined as:

\[ \psi = \left( \frac{\partial \rho}{\partial p} \right)_s \]  

(3.9)

The compressibility of a medium is directly related to the speed of sound (\( \psi = 1/c^2 \)). Assuming a constant speed of sound in water over the range of pressure of our interest, the compressibility of water is found to have a value of \( \psi = 4.54 \times 10^{-7} \text{ s}^2 \text{ m}^{-2} \) obtained from linear regression of the Tait expression over a pressure range of \( \pm 100 \text{ MPa} \). As discussed in [56], the deviation between acoustic and Tait equation of state in the aforementioned range is not more than 1%. The pressure gradient term in equation (3.2) can then be expressed in terms of a density gradient \( \nabla p = \frac{1}{\psi} \nabla \rho \).

The total pressure acting on the fluid is the sum of thermodynamic pressure and the pressure associated with the electrical force ((3.4)), which we refer to as electrical pressure. If the electrical pressure only had contribution from ponderomotive forces, the expression could be analytically integrated to obtain the expression for the electrical pressure. However, since the contribution of electrostatic and polarization forces are also being considered, the electrical pressure term is integrated numerically. For convenience, the numerical integration is performed by converting the electrical pressure expression into an elliptic partial differential equation through divergence operation. The equation being solved has the following form:

\[ \nabla \cdot (\nabla p_E) = -\nabla \cdot \mathbf{F} \]  

(3.10)
The species transport equation employed has the following form:

\[
\frac{\partial n_k}{\partial t} + \nabla \cdot (n_k \mathbf{U}) \pm \nabla \cdot (\mu_k \mathbf{E} n_k) = \nabla \cdot (D_k \nabla n_k) + \dot{n}_k
\]  

(3.11)

where, \( n_k \) is the number density of \( k \)th species and \( k = \) electrons (e), positive (p) and negative (n) ions, \( \mu_k \) and \( D_k \) is the mobility and the diffusion coefficient for \( k \)th species respectively and \( \dot{n}_k \) is the source term. The second term in equation (3.11) represents the flux of species due to the bulk fluid motion.

Cross section data of elastic scattering, electron impact ionization and electron attachment were obtained from Itikawa and Mason [57] to generate the electron transport properties and reaction rates over a range of reduced electric field (\(|\mathbf{E}|/N\)) by BOLSIG+ [58]. As an approximation, the liquid media is assumed to be a dense gas with high particle number density [35] and the electron transport properties are evaluated at the corresponding \(|\mathbf{E}|/N\) values for such gas. For the positive and negative ions, mobility values of \( \mu_p = 3.5 \times 10^{-7} \text{m}^2\text{V}^{-1}\text{s}^{-1} \), \( \mu_n = 2.0 \times 10^{-7} \text{m}^2\text{V}^{-1}\text{s}^{-1} \) from [36] and diffusivity values of \( D_{k=p,n} = 10^{-9} \text{m}^2\text{s}^{-1} \) from [9] were used.

Source terms in the species transport equations are determined based on chemical reaction rates in kinetic processes. The source terms for the electrons, positive and negative ions are expressed as follows:

\[
\dot{n}_e = Z_I + k_{\text{ion}}n_e n_{\text{neut}} - k_{\text{attach}}n_e n_{\text{neut}} - k_{\text{recomb1}}n_e n_p
\]  

(3.12)

\[
\dot{n}_p = Z_I + k_{\text{ion}}n_e n_{\text{neut}} - k_{\text{recomb2}}n_p n_n - k_{\text{recomb1}}n_e n_p
\]  

(3.13)

\[
\dot{n}_n = k_{\text{attach}}n_e n_{\text{neut}} - k_{\text{recomb}}n_p n_n
\]  

(3.14)

The kinetic processes considered are field dependent ionization (\( Z_I \)), electron impact ionization (\( k_{\text{ion}} \)), electron attachment (\( k_{\text{attach}} \)), electron-ion recombination (\( k_{\text{recomb1}} \)) and ion-ion recombination (\( k_{\text{recomb2}} \)). For the kinetic processes till now it is common practice to consider the liquid as a dense medium for qualitative description of the phenomena since there is no definitive theoretical understanding/interpretation of
the ongoing kinetic processes [35]. We consider both the electron impact ionization and electron tunneling processes and assume that the overall ionization occurs as a combination of both. Due to the very small-time scale and the associated small mean free path of liquids the avalanche ionization seems to be less likely for the conditions of interest.

The attachment and ionization coefficients are tabulated as lookup tables for a range of reduced electric field ($|E|/N$). For the electron-ion ($k_{recomb1}$) and ion-ion ($k_{recomb2}$) recombination a constant rate constant of $10^{-19} m^{-3} s^{-1}$ is used, similar to the work of Qian et al. [36]. The field dependent ionization rate which corresponds to ionization due to Zener tunneling is previously used by Qian et al. [36] for water and is expressed in the following form:

$$Z_I(E) = \beta n_{neut} \frac{q|E|d}{h} \exp\left(-\frac{m_e d \pi^2 \Delta^2}{q|E|h^2}\right)$$

(3.15)

where, $\beta$ is the fraction of ionizable species, $n_{neut}$ is the number density of neutral species obtained from the density of the fluid, $d$ is the molecular separation distance (0.31 nm for water), $h$ is the Planck’s constant, $m_e$ is the effective electron mass and $\Delta$ is the ionization energy barrier for water. An ionization energy barrier of 4 eV [59, 60] is employed.

The electric field is obtained from the Poisson’s equation expressed in the following form:

$$-\nabla \cdot (\epsilon \nabla \phi) = \frac{e}{\epsilon_0} (n_p - n_n - n_e)$$

(3.16)

where, $\phi$ is the electric potential and $e$ is the electron charge.

3.1.2 Solution of compressible Navier-Stokes equations

The flow solver used here is based on sonicLiquidFOAM, a part of OpenFOAM framework. The fluid velocity and the pressure are obtained by solving the coupled continuity and momentum equation together with the sonic pressure-density equation
of state. For pressure-velocity coupling, the PISO (Pressure-Implicit with Splitting Operators) algorithm [61] is used. In order to derive the pressure equation, a semi-discretized form of momentum equation (Eq. (3.2)) is used, which means all terms are discretized except the pressure gradient. The integral form of the momentum equation is discretized by finite-volume procedure, and the resulting matrix form is decomposed to the following form:

$$ A \mathbf{U} = \mathcal{H} - \nabla p $$

(3.17)

where $A$ is a diagonal matrix containing the matrix coefficients of owner cell and $\mathcal{H}$ consists of coefficients for neighbor cells and all source terms except the pressure gradient [62]. Multiplying (3.17) by $\frac{1}{A}$ yields:

$$ \mathbf{U} = \frac{\mathcal{H}}{A} - \frac{1}{A} \nabla p $$

(3.18)

Eq.(3.18) can not be solved at this point, because the pressure field in not known. However, if the pressure gradient term is dropped, or the pressure from the previous time step is used, an initial guess of velocity can be obtained and the pressure is corrected by an iterative procedure. This stage is called “momentum predictor”:

$$ \mathbf{U}^* = \frac{\mathcal{H}}{A} $$

(3.19)

The advantage of using the decomposed form (3.17) can be seen now: Since $A$ is a diagonal matrix, it can be inverted by simply inverting its diagonal elements. During the iterative procedure, inversion of dense matrix is avoided by using Eq.(3.17) which only requires inversion of $A$. The next step is the “pressure solution”. To derive the pressure equation, Eq. (3.18) is combined with continuity equation (Eq. (3.1)) to get:

$$ \frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{U}) = \frac{\partial \rho}{\partial t} + \nabla \cdot (\frac{\rho}{A}) \mathcal{H} - \nabla \cdot (\frac{\rho}{A} \nabla p) = 0 $$

(3.20)

Combining Eq. (3.20) with (3.8) and (3.19) gives:

$$ \frac{\partial (\psi p)}{\partial t} + \nabla \cdot ((\psi \mathbf{U}^*) f) - \nabla \cdot (\frac{\rho}{A} \nabla p) = -\nabla \cdot (\rho_0 \mathbf{U}^*) $$

(3.21)
in which, subscript $f$ denotes the face interpolation. In order to calculate the face fluxes for solving momentum equation, face interpolation of velocity is required. As described in [62] for collocated grid, similar to Rhie and Chow [63], the face interpolation is done as:

$$ U_f = \left( \frac{H}{A} \right)_f - \left( \frac{1}{A} \right)_f (\nabla p)_f $$

(3.22)

$U^*$ satisfies the momentum conservation but not continuity. Once the pressure is corrected, the velocity should also be corrected. This stage is the “velocity correction”. This is done by adding the calculated pressure gradient to the estimated velocity:

$$ U = U^* - \frac{1}{A} \nabla (p) $$

(3.23)

The above procedure is repeated until the velocities and pressure satisfy both momentum and mass conservation. Note that, momentum equation is only solved once and iteration is carried out over pressure correction to reach convergence.

### 3.1.3 Boundary conditions

Standard no-slip and zero gradient boundary conditions were utilized for velocity and density respectively at all the boundaries. For energy equation, adiabatic wall boundary condition was prescribed. The electric potential at the grounded electrode is set to zero and a time varying potential representative of nano-second pulse is prescribed at the powered electrode. Flux boundary conditions were used for species at the electrodes. The flux of electrons and ions at the electrode walls are given as:

$$ \Gamma_e = \frac{1}{4} n_e u_{th} - \gamma_{se} \sum_i q_i \Gamma_i $$

(3.24)

$$ \Gamma_i = \frac{1}{4} n_i u_{th,i} + b q_i E n_i $$

(3.25)

where $u_{th}$ is the thermal velocity and $\gamma_{se}$ is the secondary electron emission coefficient having a value of 0.01 and $q$ is the sign of the ion charge. In equation (3.25), $b = 0$
for the powered electrode and \( b = 1.0 \) for the grounded electrode. All the other boundaries are treated as zero-flux boundaries for all species.

A boundary condition is required for the electric pressure (equation (3.10)). Since \( \epsilon \) is a function of liquid density only and as already noted, \( \nabla \rho = 0 \) at all the boundaries, the polarization force is zero in all the boundaries. Assuming the electrostatic forces to be negligible at the boundaries and ponderomotive forces being prominent, the following boundary condition for electric pressure is obtained:

\[
p_E = \frac{\epsilon_0}{2} \alpha E^2
\]

(3.26)

3.1.4 Numerical scheme

The numerical scheme for solving the governing equations is based on the finite volume approach. The sets of equations are assembled and solved in the OpenFOAM framework [64]. The discretized equations are solved in a sequential manner. The Poisson’s equation is solved with a semi-implicit solver for the electric field which allows calculating the electric forces and obtaining the force terms for the momentum equations. First-order implicit Euler scheme is used for time integration of all the partial differential equations with a variable time stepping and the maximum time step size limited to \( 10^{-12} \) s. Divergence terms in momentum and species equations were treated with the flux-limited scheme and linear interpolation with orthogonal correction was used for discretizing the Laplacian terms. The individual species transport equation and the energy conservation equation is then solved. Species source terms were included in the species conservation equations using OpenFOAM’s implicit/explicit source switching feature. This feature automatically switches between an implicit and explicit mode for source term to ensure the diagonal dominance of the matrix. The discretized momentum, pressure, energy and species equations are solved using stabilized preconditioned conjugate gradient solver with diagonal incomplete LU preconditioner. Poisson’s equation is solved by geometric agglomerated
algebraic multigrid solver. Iterations are done until a desired residual, of $10^{-8}$ for momentum and energy and $10^{-12}$ for pressure and electric potential is attained.

### 3.2 Plasma chemistry model

Consider the following general expression for the chemical reaction:

$$
\sum_{k=0}^{N_s-1} v_{ki}^r n_k \rightarrow \sum_{k=0}^{N_s-1} v_{ki}^{''} n_k
$$

(3.27)

where $N_s$ is the number of species. Note that only the forward reactions are considered. The production rate of $kth$ specie is given by:

$$
\dot{n}_k = \sum_{i=0}^{N_r-1} u_{ki} q_i
$$

(3.28)

where $N_r$ is the number of species, $v_{ki}$ is given by

$$
v_{ki} = v_{ki}^{''} - v_{ki}^r
$$

(3.29)

$q_i$ is the rate of progress variable for the $i$th reaction and is given by

$$q_i = k_{fi} \prod_{k=0}^{N_s-1} n_k^{v_{ki}^r}
$$

(3.30)

The rate of reactions (3.27) ($k_{fi}$) can be a constant value or functions of $|E|$ or $|E|/N$. Generally $|E|$ can not be assumed constant in each time step. Therefore, components of electric field vector is assumed to vary in each cell of domain over each fluid time step linearly, i.e. $E_j(t) = c_j t + d_j$, $j = x, y, z$; where $j$ is the components of electric field vector. Values of $c_j$ are calculated by using the values of $E_j$ in two consecutive times. The differential equation is then obtained as:

$$
\frac{d|E|}{dt} = \frac{d|E|}{dE_x} \frac{dE_x}{dt} + \frac{d|E|}{dE_y} \frac{dE_y}{dt} + \frac{d|E|}{dE_z} \frac{dE_z}{dt} = \sum_j c_j \frac{E_j}{|E|} = \sum_j \frac{c_j (c_j t + d_j)}{\sqrt{\sum_k (c_k t + d_k)^2}} \quad j, k = x, y, z
$$

(3.31)
The initial value problem to be solved can be represented in the following vector format:

\[
y' = f(y) = \begin{bmatrix}
    \frac{dn_0}{dt} \\
    \frac{dn_1}{dt} \\
    \vdots \\
    \frac{dn_{N_s-1}}{dt} \\
    \frac{d|E|}{dt}
\end{bmatrix} = \begin{bmatrix}
    \dot{n}_0 \\
    \dot{n}_1 \\
    \vdots \\
    \dot{n}_{N_s-1}
\end{bmatrix} \quad (3.32)
\]

where the vector of unknowns is \( y = [n_0, n_1, \ldots, n_{N_s-1}, |E|^T] \).

The reaction source terms in Eq.(3.11), \((\dot{n}_k)\), were implicitly included and integrated along with the other terms with implicit Euler method in section 3.1. This approach is suitable for problems involving small number of reactions of first or lower orders. For the reactions of higher orders, discretization of source terms will generate non-linear terms, which will introduce additional difficulty in the solution procedure. Also, a common issue in solving reactive systems, is that the reactions have significantly different time scales. This situation is referred to as stiffness in which the forward integration will not converge in reasonable computation time [65]. To overcome these difficulties, operator splitting method is used. These schemes split the governing equation into the sub-equations, usually with each having a single operator capturing only a portion of the physics present, and integrate each separately and sequentially in time to advance to the next time step [66]. In that way reaction terms can be solved with specialized solvers for stiff problems while keeping the simple integration scheme for transport terms.

Let’s consider the numerical solution of the time dependent reaction–transport systems described by the following set of nonlinear ordinary differential equations [66, 67]:

\[
\frac{dr}{dt} = S(r) + M(r, t) \quad (3.33)
\]
where \( \mathbf{r} \) is the vector of dependent variables (here, species number densities and electric field), \( \mathbf{S}(\mathbf{r}) \) the vector of rates of change of \( \mathbf{r} \) due to chemical reactions and \( \mathbf{M}(\mathbf{r}, t) \) the vector of rates of change of \( \mathbf{r} \) due to transport processes. In order to solve Eq. (3.33) numerically, the time is discretized in increments \( \Delta t \), and the integration in time is then performed using the Strang splitting scheme [68]. According to this approach, reaction is separated from the transport process and the numerical integration is performed in three sub-steps:

Sub-step 1. The reaction terms are integrated over a time interval \( \Delta t/2 \) by solving

\[
\frac{d\mathbf{r}^a}{dt} = \mathbf{S}(\mathbf{r}^a)
\]  

The initial condition \( \mathbf{r}^a(0) \) is taken to be the final state \( \mathbf{r} \) from the previous time step, and the solution to Eq. (3.34) is denoted by \( \mathbf{r}(\Delta t/2) \).

Sub-step 2. The transport terms are integrated over a time interval \( \Delta t \) by solving

\[
\frac{d\mathbf{r}^b}{dt} = \mathbf{M}(\mathbf{r}^b, t)
\]  

The initial condition \( \mathbf{r}^b(0) \) corresponds to the final state of the system from the previous sub-step, \( \mathbf{r}^a(\Delta t/2) \), and the solution to Eq. (3.35) is denoted by \( \mathbf{r}^b(\Delta t) \).

Sub-step 3. A sub-step identical to Sub-step 1 is performed taking as the initial condition the final state of the system from Sub-step 2, \( \mathbf{r}^b(\Delta t) \). At the completion of this sub-step, the final state of the system is given by \( \mathbf{r}^c(\Delta t/2) \). This is the solution at the end of the current time step and serves as the initial condition for the next time step.

It can be shown that if each of the three sub-steps in the above splitting procedure is solved accurately (with at least second-order accuracy in time), the Strang splitting scheme is second-order accurate in time [66]. Integration of reaction terms (steps 1 and 3) should be done with a method capable of handling stiff equations. Backward Differentiation Formula (BDF) is an implicit method widely used for integration of stiff reactive systems. SUNDIALS (SUite of Nonlinear and DIfferential/ALgebraic
equation Solvers) package developed at Lawrence Livermore national laboratory by Hindmarsh et al. [69] is a collection of tools for solving wide range of differential equations. It comes with a variable-order, variable-step, multi-step ODE solver based on BDF which has been widely used in study of reactive systems.

To solve the reaction terms, CVODE solver from SUNDIALS package was coupled with OpenFOAM. In each flow time step, i.e. step taken to solve flow field, electric potential, etc., Eq.(3.32) is solved twice according to the Strang splitting procedure described earlier. BDF integration with SPGMR (Scaled, Preconditioned, Generalized Minimum Residual) linear solver was used in all calculations. Internal numerical approximation of Jacobin matrix by SUNDIALS was used.

3.2.1 Calculation of transport properties

Diffusion coefficients can be calculated from Nernst-Einstein equation [70] if the limiting molar conductivity of ion ($\Lambda^0_{m,k}$) is available. This equation reads:

$$D_k = \frac{RT}{Z_k^2 F^2} \Lambda^0_{m,k}$$

(3.36)

where $R$ is the gas constant, $T$ is the temperature, $Z_k$ is the charge number and $F$ is the Faraday’s constant. Einstein equation relates the ionic mobility to diffusion coefficient [70]:

$$\mu_k = \frac{D_k e Z}{k_B T}$$

(3.37)

$e$ is the elementary charge, $k_B$ is the Boltzmann’s constant. For neutrals species, Stocks-Einstein equation is used to estimate the diffusion coefficient [71]:

$$D_k = \frac{k_B T}{6\pi\mu r_0}$$

(3.38)

where $\mu$ is the solvent viscosity and $r_0$ is the solute radius.

To calculate the diffusion and mobility coefficients of electrons, the liquid media is assumed to be a dense gas with high particle number density [35] and the electron
transport properties are evaluated at the corresponding $|E|/N$ values for such gas by BOLSIG+ [58] Boltzmann solver. The diffusion coefficient of solvated electrons ($e_{aq}$) is reported by [72] as $4.74 \times 10^{-9} \text{ m}^2/\text{s}$ at room temperature. Drift coefficient can be calculated by Eq. (3.37).

### 3.3 Multi-liquid configuration

In this section, the multi-phase flow field is resolved using interFOAM solver, the incompressible Volume of Fluid (VOF) code of OpenFOAM framework for modeling two-phase flow systems. In the VOF approach, the liquid volume fraction ($\alpha$) is used to reconstruct and evolve the interface. As demonstrated in Figure 3.1 $\alpha$ for each phase varies between the constant value one in full cells to zero in empty cells, while mixed cells with an intermediate value of $\alpha$ define the transition region where the interface is located [73, 74]. The following equation describes the advection of volume fraction by velocity:

$$\frac{\partial \alpha_i}{\partial t} + \nabla \cdot (U \alpha_i) = 0 \quad i = 1, 2$$

(3.39)

where $\alpha_i$ is the volume fraction of phase $i$ and indices 1 and 2 indicates the property is associated to phase 1 and 2 (aqueous and organic), respectively. Velocity field is calculated by solving continuity and momentum equations. Momentum equation for

![Table 3.1](image_url)

Figure 3.1: Two fluids and volume fractions value for each cell of the mesh [75].
the two-phase system is:

\[
\frac{\partial \rho \mathbf{U}}{\partial t} + \nabla \cdot (\rho \mathbf{U} \mathbf{U}) = \nabla p + \left[ \nabla \cdot (\mu \nabla \mathbf{U}) + \nabla \mathbf{U} \cdot \nabla \mu \right] + \mathbf{F} + \rho \mathbf{g} + \int_{\Gamma} \sigma \kappa \delta (\mathbf{x} - \mathbf{x}_s) \, d\Gamma(\mathbf{x}_s)
\]

where \( \mathbf{F} \) is the electrical force density, \( \mathbf{g} \) is gravitational acceleration, \( \sigma \) is the surface tension, \( \delta (\mathbf{x} - \mathbf{x}_s) \) is the three-dimensional Dirac delta function, \( \kappa \) is the local interfacial curvature, and \( \Gamma \) is the gas–liquid interface.

The integral term basically interprets the interfacial tension force as a continuous force density by distributing it force over a transition zone. This approach is based on continuum surface force (CSF) model of Brackbill et al [76]. By definition, surface tension is defined by Laplace’s equation which gives the fluid pressure jump in to interface under the action of surface tension:

\[
\Delta p = \sigma \kappa
\]

Direct application of Eq. (3.41) to VOF multiphase model requires reconstruction of the interface for accurate calculation of curvature. In CSF, surface tension is treated as a volumetric body force near the interface instead of pressure jump. Since \( \alpha_i \) is discontinuous on the interface, a smooth variation of \( \alpha_i \) is used to apply the surface tension force. The smoothing is done in such a way that \( \alpha_i \) varies across a transition zone of finite thickness near the interface. This transition zone is now aligned with the grid, but typically chosen as the normal distance of one or two grid size from the interface. Note that the line integral of smooth surface tension force is approximately equal to the pressure jump given bu Eq. (3.41) . The local interface curvature is calculated from:

\[
\kappa = - \nabla \cdot \mathbf{n}
\]

And the unit normal to the surface is calculated from the phase fraction field [76]:

\[
\mathbf{n} = - \frac{\nabla \alpha_i}{|\nabla \alpha_i|}
\]
Because of discontinuous nature of $\alpha_i$ functions, some modifications are necessary to limit the numerical diffusion and preserve the sharpness of the interface [73]. In \textit{interFOAM}, this is done by modifying the advection term in Eq. (3.39) and introducing an interfacial compression flux. This flux is adjusted by MULES (Multidimensional Universal Limiter with Explicit Solution) procedure to efficiently reduce the numerical diffusion at the interface. The solution of the momentum and equation is done by Pressure Implicit with Splitting of Operators (PISO) procedure [61]. A predicted velocity field is constructed and then corrected by implicit pressure correction procedure to time advance the pressure and velocity fields. More details on VOF and MULES can be found in [73–75, 77].

3.3.1 Calculation of electric forces

Mixture properties are related to properties of each phase in pure state by weighted averaging using $\alpha_i$ as weighting factor:

$$\rho = \alpha_1 \rho_1 + \alpha_2 \rho_2$$  \hspace{1cm} (3.44)

$$\epsilon = \alpha_1 \epsilon_1 + \alpha_2 \epsilon_2$$  \hspace{1cm} (3.45)

The force term in Eq. (3.40) is given in Eq. (3.4) and must be modified for multi-phase system. Polarization force can be derived for two phase system by taking the gradient of Eq.(3.45) as:

$$\nabla \epsilon = \nabla \left( \sum_{i=1,2} (\alpha_i \epsilon_i) \right) = (\epsilon_1 - \epsilon_2) \nabla \alpha_1 + \alpha_1 \nabla \epsilon_1 + \alpha_2 \nabla \epsilon_2$$  \hspace{1cm} (3.46)

Assuming both phases to be incompressible, dielectric permittivity of each phase is constant; therefore, second and third terms on the right-hand side of Eq.(3.46) is negligible and polarization force for two-liquid field is given by:

$$\mathbf{F}_{pol} = -\frac{\epsilon_0}{2} (\epsilon_1 - \epsilon_2) \mathbf{E}^2 \nabla \alpha_1$$  \hspace{1cm} (3.47)
To derive an expression for ponderomotive force, an expression for the term \( \rho \frac{\partial \epsilon}{\partial \rho} \) should be found first. This expression can be written as:

\[
\rho \frac{\partial \epsilon}{\partial \rho} = \rho \frac{\partial}{\partial \rho} \left( \sum_{i=1,2} (\alpha_i \epsilon_i) \right) = \rho \sum_{i=1,2} \left( \epsilon_i \frac{\partial \alpha_i}{\partial \rho} + \alpha_i \frac{\partial \epsilon_i}{\partial \rho} \right)
\]  

(3.48)

As discussed in section 3.1, Eq. (3.6) can be used to evaluate term \( \frac{\partial \epsilon_i}{\partial \rho} \) for polar dielectrics. For non-polar media, the Clausius-Mossotti relation [28] can be used to relate the permittivity to density:

\[
\rho \frac{\partial \epsilon_2}{\partial \rho} = \frac{(\epsilon_2 - 1)(\epsilon_2 + 1)}{3}
\]  

(3.49)

Rewriting Eq. (3.44) as an expression for \( \alpha_1 \):

\[
\alpha_1 = \frac{\rho - \rho_2}{\rho_1 - \rho_2}
\]  

(3.50)

Taking partial derivative with respect to \( \rho \):

\[
\frac{\partial \alpha_1}{\partial \rho} = \frac{1}{\rho_1 - \rho_2}
\]  

(3.51)

Similarly, for \( \alpha_2 \) we will get:

\[
\frac{\partial \alpha_2}{\partial \rho} = \frac{-1}{\rho_1 - \rho_2}
\]  

(3.52)

Substituting equations (3.6) and (3.49) to (3.52) into Eq. (3.48):

\[
\rho \frac{\partial \epsilon}{\partial \rho} = \frac{\epsilon_1 - \epsilon_2}{\rho_1 - \rho_2} \rho + \alpha_1 a \epsilon_1 + \alpha_2 \frac{(\epsilon_2 - 1)(\epsilon_2 + 1)}{3}
\]  

(3.53)

The expression for ponderomotive force is found as:

\[
\mathbf{F}_{pon} = \frac{\epsilon_0}{2} \nabla \left[ \mathbf{E}^2 \left( \frac{\epsilon_1 - \epsilon_2}{\rho_1 - \rho_2} \rho + \alpha_1 a \epsilon_1 + \alpha_2 \frac{(\epsilon_2 - 1)(\epsilon_2 + 1)}{3} \right) \right]
\]  

(3.54)

Electric field is obtained by solving Poisson’s equation for potential (Eq. (3.16)). Relative permittivity in Eq. (3.16) is calculated from Eq. (3.45) using the most recent values for phase fractions. Chemical source splitting procedure described in section 3.2 is used to integrate the species conservation.
3.3.2 Numerical scheme

The Poisson’s equation is solved and the electric forces is obtained for multi-liquid configuration. First-order implicit Euler scheme is used for time integration of all the partial differential equations. Divergence terms in momentum and species equations is treated with the flux-limited scheme. Van-Leer scheme is used for discretizing the divergence of phase fraction. Cell-limited scheme is used for treatment of gradient in electrical forces. Linear interpolation with orthogonal correction was used for discretizing the Laplacian terms. Species source terms were integrated with Cvode package according to Strang splitting procedure. Iterations are done until a desired residual, of $10^{-8}$ for momentum and energy and $10^{-12}$ for pressure and electric potential is attained.
Chapter 4

Multiphysics simulation of the initial stage of plasma discharge formation in liquids

In this chapter results from plasma initiation simulations in homogenous liquids in response to $\sim 3.0 - 5.0$ ns voltage pulse is presented. The simulations are conducted for a needle-like powered electrode with two different voltage profiles – linear and exponential increase. The model predictions show that under the influence of nanosecond voltage rise the liquid experiences the formation of negative pressure region near the vicinity of the powered electrode and surpasses the cavitation threshold pressure. The cavitation locations initiate as sub-micron regions and then extends up to a few microns. The electrical forces which is a combination of electrostatic, polarization and electrostrictive ponderomotive forces contributes significantly in cavitating the medium and forming low-density region. The ponderomotive forces have the highest impact followed by the polarization forces. The effect of electrostatic forces only become significant when sufficient free charges are formed. Despite the formation of low-density region, the ionization process is still predominantly driven by field dependent ionization – Zener tunneling; as the electric field across the sub-micron to micron scale low-density regions are not sufficient for electron impact ionization to be significant. A parametric study on maximum driving voltage and voltage profile is conducted. The results indicate that at higher voltage both the exponential and linear voltage profile form a compression wave and an associated high-density region in the medium. The magnitude of the compressive waves is not representative of
shock waves. The bulk liquid velocity can reach hundreds of meters per second but maintains subsonic conditions when the maximum driving voltage is increased by a factor of 2.5 to 15 kV suggesting shock like conditions will be formed under higher electric field conditions\(^1\).

4.1 PROBLEM GEOMETRY

Figure 4.1a depicts the computational domain for the liquid phase plasma discharge simulations. The discharge is initiated with a needle like electrode that is powered. Due to symmetry, only half of the geometry is simulated. The line a-b is the axis of symmetry. The boundary a-d denotes the powered electrode. The boundary b-c is the grounded electrode. The smallest distance between the powered and grounded electrode is 60 µm (ab). The length of c-d is chosen to be 180 µm along which zero gradient boundary conditions are prescribed. A structured non-uniform mesh of 89000 cells was employed with denser grids present near the powered electrode and shortest inter-electrode separation distance Figure 4.1b. The meshing operation is performed with the Gmsh package [78].

Two different pulse profiles were applied to the powered electrode Figure 4.1c: “linear ramp” and “rapid pulse”. In the linear ramp case, the electrode was subject to a linearly ascending ramp and in the rapid pulse case, the applied voltage was increased exponentially. The prescribed time-varying voltage on the powered electrode for linear ramp case is given by:

\[
V(t) = V_{\text{max}} \left(\frac{t}{t_n}\right)
\]  

where $t_n = 5 \times 10^{-9}$. For the rapid pulse case, voltage on the powered electrode is determined from the following relation:

$$V(t) = \begin{cases} 
V_{\text{max}} \frac{\delta}{1-\delta} \left[ \exp \left( -\log(\delta) \left( \frac{t}{\tau_1} \right) \right) - 1 \right] & t \leq \tau_1 \\
V_{\text{max}} \left( \frac{t-\tau_2}{\tau_1-\tau_2} \right) & t > \tau_1 
\end{cases} \quad (4.2)$$

where $\delta = 0.01$, $\tau_1 = 3 \times 10^{-9}$ and $\tau_2 = 10^{-8}$. It should be noted that both profiles had identical maximum voltage of 7 kV. However, unlike the rapid pulse case where the voltage starts to decrease once the peak voltage is attained, the maximum voltage is maintained for the linear ramp case.

Figure 4.1: a) Schematic of the problem geometry, b) computational mesh considered in the present study and c) two different voltage profile employed at the powered electrode
4.2 Results and discussions

Simulations have been conducted for plasma initiation in distilled water for a powered needle-like electrode. The needle electrode either exposed to a linear ramp or a pulsed profile as shown in Figure 4.1c. For the base case, the maximum voltage for both the voltage profiles is 7 kV which was chosen to be consistent with the work of Shneider and Pekker [28]. Figures 4.2a and 4.2b show the spatial variation of the bulk fluid velocity magnitude and total pressure \( p_{\text{total}} = p + p_E \) in the domain at different time instances. For both voltage profiles a negative pressure region near the electrode is progressively formed within 5 nanoseconds. The low-pressure region is formed as a result of the contributions from electrical forces. The magnitude of the negative pressure region for the two cases are not identical despite the identical maximum voltage value. For the pulse case the total pressure had a lowest value of \( \sim -180 \text{ MPa} \) which was \( \sim -115 \text{ MPa} \) for the linear ramp. Apart from the magnitude of the total pressure, a far more distinctive characteristic related to the low-pressure region is observed between the two cases. Under linear ramping, the low-pressure region remains stationary adjacent to the powered electrode, whereas with a pulsed profile, a propagating low-pressure wave followed by a high-pressure region is seen. The time response of the hydrodynamic pressure has an initial buildup period. If the hydrodynamic pressure is of higher magnitude it can compensate any possible negative electric pressure contributions. For the pulse case, as the electric field strength decreases after the peak voltage, the electric pressure starts to decrease; however, the hydrodynamic pressure continues to grow resulting in a propagating high-pressure wave. The resulting velocity magnitude for the two different driving voltage profiles indicates the formation of a high velocity region near the powered electrode. The peak velocity magnitude is in the range of tens of meter per second; subsonic flow condition. It should be noted though that the bulk fluid velocity of the domain is dictated by the peak value of the applied voltage as well the voltage.
profile. For the same peak voltage, a pulsed profile results in a peak velocity which is a factor of two higher than that of the linear ramp case. The resulting bulk fluid temperature is found to increase by $\sim 1K$ only (not shown here).

Figure 4.2: Spatio-temporal contour plots of velocity magnitude and total pressure for (a) linear ramp case and (b) pulse case ($V_{\text{max}} = 7.0kV, \beta = 1.0$). The inset shows a zoomed view very close to the electrode tip.

The center line distribution of hydrodynamic and electric pressure for the same linear ramp and pulsed case are presented in Figure 4.3. For both the voltage profiles there is a buildup of the hydrodynamic pressure near the electrode surface. This high-pressure region is indicative of the bulk fluid undergoing compression. This high-pressure region extends to $\sim 4 \mu m$ from the electrode surface. The hydrodynamic pressure also undergoes a distinctive pressure reversal (i.e. formation of negative
Figure 4.3: Center line distribution of hydrodynamic and electric pressure at different time instances for the linear ramp (a and b) and pulsed case (c and d). ($V_{\text{max}} = 7.0 \text{kV}$, $\beta = 1.0$).

For the linear ramp, where the magnitude of the negative hydrodynamic pressure is lower, the pressure has a significantly lower gradient in comparison to the pulse case. Both these reversals occur at $\sim 4 \mu m$ from the electrode surface and extends up to $\sim 3 \mu m$. On the other hand, the electric pressure having predominant contribution from the polarization and ponderomotive forces have very large negative pressure near the electrode. The electric pressure maintains very sharp gradients within $\sim 5 \mu m$ and then asymptotically diminishes. The negative electric pressure region extends to almost $\sim 20 \mu m$ when the maximum driving voltage is attained.

The distribution of the polarization ($F_{\text{pol}}$) and ponderomotive ($F_{\text{pon}}$) and electrostatic forces ($F_{\text{es}}$) along the centerline is presented in Figure 4.4f. It can be seen that the $F_{\text{pon}}$ which results from the electric field gradients, has the maximum contribution. On the other hand, the polarization force depends on the gradient of the
dielectric permittivity which is a function of medium density. As a result, \( F_{\text{pol}} \) is in effect only after a density gradient is established by the other forces. The strong dependence of the \( F_{\text{pol}} \) on the density field leads to its slower response to voltage changes in the domain. Compared to \( F_{\text{pon}} \), \( F_{\text{pol}} \) force is effective in a smaller region range near the powered electrode surface. For both the ramp and pulse case, \( F_{\text{pon}} \) is an order of magnitude higher than that of the \( F_{\text{pol}} \). For the linear ramp case, \( F_{\text{pon}} \) continues to increase while for a pulsed voltage it decreases once the driving voltage starts to decrease. Between the two cases a noticeable difference is seen in the \( F_{\text{pol}} \) profile as well. A sharp increase in \( F_{\text{pol}} \) is observed only for the pulse due to due to propagating high pressure wave (Fig. 4c) and the associated increase in the density. From the distribution of the different electrical forces it is evident that magnitude of \( F_{e.s} \) is not comparable to either \( F_{\text{pol}} \) and \( F_{\text{pon}} \) initially. Once ionization takes place it has comparable magnitude as that of \( F_{\text{pol}} \) due to the presence of the charged species.

![Figure 4.4](image_url)

**Figure 4.4:** Spatial evolution of polarization (a, d), ponderomotive (b, e) and electrostatic (c, f) forces along the center line at different time instances. Forces for the linear ramp case are presented in a, b and c. Figures d, e and f represent pulsed case. (\( V_{\text{max}} = 7.0 \text{kV}, \ \beta = 1.0 \)).
Figure 4.5 presents the transient evolution of the centerline profile of the fluid density and axial component of the velocity. The fluid density increases to its maximum in the vicinity of the electrode tip as a result of compressive stresses (Figure 4.3a, 4.3c). A small region of rarefaction spanning \(\sim 3\,\mu m\) occurs due to the fluid motion and stretching under the influence of both polarization and ponderomotive forces. For both the driving voltage profiles, the fluid density increases by \(\sim 10\%\). However, the decrease in the density hence the degree of rarefaction is distinctively different between the two. In case of the pulsed voltage, the density decreases by \(\sim 2\%\) unlike the linear ramp where it does not even approach a percentage. In addition, a sharp gradient in the rarefaction is not observed under linear ramp condition rather the density decreases in a gradual fashion. The axial velocity evolution clearly shows that electrical forces drives the flow towards the electrodes. Under pulsed condition when the driving voltage starts to decrease an outward flow is established due to the formation of a high-pressure wave (Figure 4.3c). For a maximum driving voltage of 7 kV the fluid velocity is found to remain in the subsonic regime.

To assess if the resulting pressure field is conducive of cavitation and possible rupture of the fluid, the evolution of the total pressure along the center line was analyzed. The center line profiles of \(p_{\text{total}}\) at different time instances are presented in Figure 4.6. Simulations were also conducted with and without the inclusion of polarization forces to investigate the relative influence of polarization and ponderomotive forces. The predicted \(p_{\text{total}}\) for those conditions are also summarized in Figure 4.6. The threshold pressure limit for water to rupture and cavitation is dependent upon a number of parameters, including the presence of dissolved gases, the degree of purity of the fluid, possible debris particles. Experiments [79] have demonstrated that at nominal ambient conditions (i.e. room temperature and atmospheric pressure) -0.15 MPa is sufficient to rupture the water under slower tension. However, under rapid stretching the threshold pressure limit increases significantly. The comprehensive
Figure 4.5: Center line distribution of fluid density and axial velocity at different time instances for the linear ramp (a and b) and pulsed case (c and d). ($V_{\text{max}} = 7.0\text{kV}, \beta = 1.0$).

Experimental study of Herbert et al. [80] reports that the threshold pressure limit for cavitation monotonically varies between -26 MPa to -17 MPa for a temperature range of 0.1°C – 80°C. Under room temperature condition the threshold value was experimentally determined to be approximately -24 MPa. For our study, following Shneider and Pekker [28] we consider the threshold pressure limit for cavitation to be -30 MPa. The spatio-temporal evolution of $p_{\text{tot}}$ clearly shows that for both the voltage profiles where the maximum voltage is reached in between 2.5–5 ns, conditions are favorable for cavitation to occur. However, for the linear ramp case (Figure 4.5a) the threshold pressure condition is surpassed at 2.5 ns; before the maximum driving voltage condition (i.e. 5 ns Figure 4.1c). Additionally, the negative pressure region is formed gradually and is observed to have lower spatial gradients. In contrast, the negative pressure region for the pulsed voltage has sharper gradients spatially with
smaller region of influence. The comparison between the voltage suggests that the cavitation size is strongly dictated by the driving voltage profiles and nano voids can be formed with sharp voltage rise. The total pressure distribution further shows that the polarization force which has a slower response to change in electric field does not have an effect initially but becomes important later. Polarization force is directly dependent on the gradient of the dielectric permittivity and fluid density. As a result, its impact only becomes significant when a density gradient is established. Interestingly, it can be seen that due to the absence of polarization forces a pulsed voltage forms a stronger compressive pressure wave.

The evolution of electron number density, $n_e$ for the two different voltage profiles are summarized in figures 4.7 and 4.8. The impact of $\beta$, fraction of ionizable species on $n_e$ distribution is also shown. The $\beta$ term denotes the fraction of neutral species that can be undergo field dependent ionization i.e. ionization through Zener tunneling process. A higher $\beta$ denotes that a higher fraction of the neutral species is available for field dependent ionization and vice versa. Since the field dependent ionization is directly related to $\beta$, an increase in the $\beta$ value results in higher electron number

![Figure 4.6: Center line distribution of total pressure at different time instances for a) linear ramp and b) pulse case. ($V_{\text{max}} = 7.0kV, \beta = 1.0$). The impact of polarization and ponderomotive forces on the total pressure is also shown. The dashed horizontal line represents the threshold pressure for cavitation of water.](image)
density. For both the voltage profiles the $n_e$ are concentrated near the powered electrode. The peak $n_e$ associated with $\beta = 1.0$ is found to be $2.2 \times 10^{23}$ and $1.5 \times 10^{23}$ for the pulsed and linearly ramped voltage profile respectively. The maximum ionization degree of the systems is $\sim 5 \times 10^{-6}$. The ionization is predominantly driven by field dependent ionization. As discussed by Kolb et al [81], due to the higher density of liquid the scattering rates are high and mean free paths are low. As a result, the probability of mobile charges reaching ionization energy threshold is low.
unless a very high external electric field is introduced. However, the lack of strong lattice structure in liquids, allows ionization through Zener tunneling process possible at lower threshold values. For a peak voltage of 7 kV the electron impact ionization is insignificant due to low $|E|/N$ values. The peak $|E|/N$ (not shown here) remains around $\sim 22 \text{Td}$ and $\sim 25 \text{Td}$ respectively for the linear ramp and pulsed case. For the electron impact ionization channel to be effective, $|E|/N$ values need to exceed $\sim 70 \text{Td}$.

Figure 4.8: Spatio-temporal contour plots of electron number density for different values of fraction of ionizable species, under pulsed condition, $V_{\text{max}} = 7kV$. 

45
Simulations were also conducted with a higher maximum driving voltage to determine its impact on the overall characteristics of the system. For these cases the $V_{\text{max}}$ was set at 15 kV with identical rise time and profiles as that of the 7 kV cases. The spatial contours of the electron number density, total pressure and velocity magnitude for the linear voltage ramp is presented in Figure 4.9. It is evident that for a higher temporal gradient of the voltage (i.e. $3 \text{kV/} ns$) a traveling ionization and pressure wave is formed and the bulk fluid velocity is increased significantly. The velocity magnitude is observed to reach a maximum value of $\sim 145 \text{m/s}$ but still maintains subsonic conditions. The fluid velocity is directed towards the electrode till $2.50 \text{ns}$ after which there is a reversal in the flow direction (Figure 4.10b). Unlike the 7 kV case where a compression in the total pressure is completely absent, for the 15 kV linear ramp a positive $p_{\text{total}}$ is present. The lowest $p_{\text{total}}$ is $\sim -650 \text{MPa}$ which is well below the cavitation threshold limit and differs by a factor of $\sim 6$ than that of the 7 kV case. The peak $n_e$ is $\sim 4 \times 10^{24} \text{m}^{-3}$ and the electron formation route is predominantly driven by the field dependent ionization (Figure 4.10d). The field dependent ionization overlaps with the maximum reduced electric field location. The reduced electric field profiles suggest that under these conditions the electron impact ionization process still remains insignificant as the maximum $|E|/N$ is $\sim 25 \text{Td}$ (Figure 4.10c). The variation in the center line density profiles presented in Figure 4.10a shows that the density undergoes sharp variations. The compression and expansion regions are initiated at $3.50 \text{ns}$ with a sub-micron low-density region near the electrode surface followed by a high-density region. The density increases and decreases by $\sim 15\%$ and $\sim 8\%$ respectively. The alternating low-high density region propagates further downstream at $5 \text{ns}$ and has a larger spatial influence. The decrease in $|E|/N$ overlaps with the region of high density. Despite the formation of the low-density region the electric field across this region is not sufficient for electron impact ionization.
of water to be dominant. The ionization at this stage is still driven by field dependent ionization process.

Figure 4.9: Spatio-temporal contour plots of electron number density, total pressure and velocity magnitude for a linearly increasing voltage $V_{\text{max}} = 15.0\,\text{kV}$, $\beta = 1.0$

The contour plots of electron number density, total pressure and velocity magnitude for the pulsed 15 kV voltage for identical time instances as the linear ramp
is presented in Figure 4.10. The peak $n_e$ under pulsed condition is a factor of $\sim 6$ higher than the linear case reaching a value of $\sim 2.4 \times 10^{25} \text{ m}^{-3}$. As the voltage rise time is further reduced in the exponential growth, the peak electron number density increases compared to the linear ramp and at the same time they are advected further downstream from the powered electrode. The downstream advection however takes place during the voltage relaxation (i.e. the linear decay in Figure 4.1c). The bulk fluid velocity magnitude also reaches its peak value after the driving voltage starts to decrease due to the slower response of the liquid medium to electrical forces and the pressure variations. The predicted peak fluid velocity of $\sim 200 \text{ m/s}$ is $12\%$ of the peak electron drift velocity (e.g. $v_d \sim 1550 \text{ m/s}$ for $\sim 30 \text{Td}$) and is comparable to the negative and positive ion drift velocities. In comparison to the linear ramp of 15 kV, the exponential rise generates a stronger compressive wave in the total pressure distribution but at the same time forms a negative pressure that is well below the threshold cavitation pressure limit.

Figure 4.12 presents the center line distribution of density, axial velocity, reduced electric field and the field dependent ionization rate at different time instances for the pulsed voltage profile. The time instances are so chosen to show the temporal evolution right before the peak voltage, during the peak voltage and as the voltage starts decreasing. We can see that the decrease in the density happens before the peak voltage but is confined to a very small region near the electrode surface. The density variation propagates with the variation in the voltage and extends to $\sim 15 \mu \text{m}$ region along the centerline at $5 \text{ns}$. In comparison to the linear ramp case, the density perturbation is lower. The bulk fluid velocity in general is found to travel away from the electrode in the low-density region and is directed towards the powered electrode when the density increases (Figure 4.12b). The maximum reduced electric field $|\mathbf{E}|/N$ under a pulsed voltage is slightly higher (i.e. $\sim 30 \text{Td}$) but still not sufficient to allow significant electron impact ionization to occur. The ionization is dictated by the field
Figure 4.10: Temporal evolution of the center line a) density, b) axial velocity, c) reduced electric field and d) field dependent ionization for a linearly increasing voltage $V_{\text{max}} = 15.0 \text{kV}$, $\beta = 1.0$.

dependent Zener tunneling and is an order of magnitude higher than the linear ramp case (Figure 4.12d).
Figure 4.11: Spatio-temporal contour plots of electron number density, total pressure and velocity magnitude for a pulsed voltage $V_{\text{max}} = 15.0\text{kV}$, $\beta = 1.0$. 
Figure 4.12: Temporal evolution of the center line a) density, b) axial velocity, c) reduced electric field and d) field dependent ionization for a pulsed voltage $V_{\text{max}} = 15.0\,\text{kV}$, $\beta = 1.0$. 
4.3 Conclusions

A multi-dimensional multi-physics model considering liquid phase compressibility has been developed to simulate the early stage of plasma initiation in a liquid medium and obtain insight on the coupled physicochemical process occurring during these extremely small time duration. The simulations were conducted for a powered needle-like electrode where the peak voltage and driving voltage profile was varied to assess its impact on the plasma initiation characteristics. The results show that the electrical body forces – electrostatic, polarization and electrostrictive ponderomotive, play a key role in generating strong density variation during the initial stage. Among the three electrical forces electrostrictive ponderomotive force which is directly dependent on the gradient of the electric field has the strongest contribution. The polarization force only becomes effective when a density variation is established and in general have slower response time. However, for a pulsed profile having exponential rise to the peak driving voltage, an earlier onset of strong polarization forces is observed resulting from fast and sharper variation in the fluid density. The model further shows that the fluid medium exposed to these electrical forces can easily reach cavitation threshold condition and forms lower density region near the vicinity of the powered electrode. These low-density regions initiate on a sub-micron scale and then extends to a few microns during the course of complete voltage rise time.

Parametric study on the driving voltage profiles show that for an exponential voltage rise, the slow response of the fluid results in continuing variation in the fluid phase density and pressure during the voltage decay time. For a linear voltage rise (i.e. slower voltage rise), the resulting fluid velocity is directed towards the powered electrode which undergoes a reversal in direction as the voltage rise time is shortened via an exponential profile. The predicted peak electron number density ranged between $\sim 10^{23}$–$10^{23} m^{-3}$ for the different peak voltage values and voltage profiles considered. The major electron formation route was found to be field dependent –
Zener tunneling based ionization process even though possible low-density fluid region is formed due to cavitation like conditions. The electric field across the low-density region, due to the small spatial and temporal scales do not reach conditions that allow electron impact ionization to be significant and prominent. For higher values of peak driving voltages for both linear and exponential profiles the initial dynamics changes significantly. The fluid undergoes larger variation in density and the formation of stronger compression pressure waves are prevalent. The peak fluid velocity increases to hundreds of meters per second but still maintains subsonic conditions.
Chapter 5

Role of kinetics in liquid phase plasma initiation

In chapter 4 a simple plasma chemistry model was used focusing on the hydrodynamics of the system with the inclusion of limited number of reactions. Here, an attempt is made to improve the chemistry model by including additional reaction pathways and increasing the details in the kinetic scheme. In addition to previously considered ionization of water molecules due to Zener tunneling mechanism, electron detachment from hydroxide ion (OH\(^-\)) under lower electron energy is investigated.

5.1 Source of electrons

As described by Shneider and Pekker [56], the probability of electron detachment from negative OH\(^-\) ions, is higher than probability of field ionization of water molecules. As mentioned in chapter 4, Kolb et al [81] argued that lack of strong lattice structure in liquids, allows ionization of water molecules through Zener tunneling process possible at lower threshold values. Schematic comparison of Zener tunneling for water and OH\(^-\) molecules is shown in Figure 5.1. R1 and R2 refers to the reactions in which electrons are detached from water and OH\(^-\) molecules, respectively. Therefore, additional electron source i.e. tunneling detachment of electrons from OH\(^-\) should be considered in the plasma model. This term is given as [56]:

\[
W_I = n_{OH\tiny{aq}} \frac{\pi A^2 q|E|}{\sqrt{2I_n m}} \cdot exp \left( -\frac{4}{3} \frac{\sqrt{2m} I_n^{3/2}}{qh |E|} \right) \tag{5.1}
\]
in which $I_n$ is the affinity energy of an electron in a negative ion ($2.96 \times 10^{-19}$ joules for OH\textsuperscript{−}). The coefficient $A \sim 1$ depends on the shape of the potential well.

![Figure 5.1: Schematic comparison of rate constants or R1 and R2 reactions as a function of electric field magnitude (R1 and R2 are the rate constant of the tunneling detachment of electrons from water and OH\textsuperscript{−}, respectively ).](image)

\[ \text{OH}^- \text{ ions are present in water due to self-ionization equilibrium reaction:} \]

\[ \text{H}_2\text{O} + \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^- \quad (5.2) \]

At room temperatures, the rates of forward and reverse reactions are $k_f = 2.5 \times 10^{-5} \text{ s}^{-1}$ and $k_r = 1.4 \times 10^{11} \text{ mol}^{-1} \text{s}^{-1}$, respectively [82]. Consequently, the relation $[\text{H}^+][\text{OH}^-] = 10^{-14}$ exists at atmospheric pressure and temperature of 25 °C. Therefore, the equilibrium density of ions in distilled water is about $n_{\text{H}_3\text{O}^+} = n_{\text{OH}^-} = 6 \times 10^{19} \text{m}^{-3}$.

Shneider and Pekker [56] justified that the number of electrons formed by field detachment from OH\textsuperscript{−} ions in a cubic micron of water in 1 ns is $n_e > 15$. In their estimation they have only considered the existing equilibrium OH\textsuperscript{−} ions and subsequent generation of OH\textsuperscript{−} driven by external electric field and associated electron and charged species kinetics is neglected. Therefore, in the presence of a strong field the amount of electrons generated through this channel may increase significantly.
5.2 Kinetic model and transport properties

The proposed chemical kinetics model involving electrons and heavy particle species is summarized in Table 5.3. The model consists of 26 species and 54 reactions. Reactions involving solvated electrons participating in the liquid are considered as they do provide additional heavy particle charged species more specifically OH⁻ that contributes to electron multiplication through the tunneling process. As presented in Table 5.3, R1 and R2 correspond to ionization of H₂O and OH⁻ by tunneling, respectively. R3 - R6 are attachment reactions, R7 is electron-ion recombination reaction, and R8 - R15 are reactions associated with solvation of electrons and ions. R16 - R54 represents aqueous reactions. Reaction rates for R1 and R2 are based on theoretical formulation. The rates for R3 - R6 are calculated from gas phase cross-section data employing a dense gas approximation. These reaction rates are determined using the zero-dimensional Boltzman equation solver BOLSIG+. These reaction rates are obtained over a range of reduced electric (|E|/N) and tabulated in the form of lookup tables. Rates for the solvation and aqueous reactions are obtained from Tian and Kushner [40]. It should be noted that the chemical kinetic model is developed for degassed, deionized, distilled water with no dissolved gases (e.g. nitrogen, oxygen). In addition, the role of photons in the kinetics are not considered.

As discussed in section 3.2.1, diffusion coefficients are calculated from Nernst-Einstein equation [70]:

\[
D_k = \frac{RT}{Z_k^2 F^2} \Lambda_{m,k}^0
\]  

(5.3)

where \( R \) is the gas constant, \( T \) is the temperature, \( Z_k \) is the charge number, \( F \) is the Faraday’s constant, and \( \Lambda_{m,k}^0 \) is the limiting molar conductivity of ion. Einstein equation relates the ionic mobility to diffusion coefficient [70]:

\[
\mu_k = \frac{D_k eZ}{k_B T}
\]  

(5.4)
$e$ is the elementary charge, $k_B$ is the Boltzmann’s constant. For neutrals species, Stocks-Einstein equation is used to estimate the diffusion coefficient [71]:

$$D_k = \frac{k_B T}{6\pi \mu r_0} \quad (5.5)$$

where $\mu$ is the solvent viscosity and $r_0$ is the solute radius.

To calculate the diffusion and mobility coefficients of electrons, the liquid media is assumed to be a dense gas with high particle number density [35] and the electron transport properties are evaluated at the corresponding $|E|/N$ values for such gas by BOLSIG+ [58] Boltzmann solver. The diffusion coefficient of solvated electrons ($e_{aq}$) is reported by [72] as $4.74 \times 10^{-9} \text{ m}^2/\text{s}$ at room temperature. Drift coefficient can be calculated by Eq. (3.37).

Table 5.1: Species considered in the kinetic model

<table>
<thead>
<tr>
<th></th>
<th>H$<em>2$O$</em>{aq}$</th>
<th>e$_{aq}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>e</td>
<td>H</td>
<td>H$_2$</td>
</tr>
<tr>
<td>H</td>
<td>H$_{aq}$</td>
<td>H$_2$</td>
</tr>
<tr>
<td>H$_{2aq}$</td>
<td>O$^-$</td>
<td>O$_{aq}$$^-$</td>
</tr>
<tr>
<td>OH</td>
<td>OH$_{aq}$</td>
<td>H$^+$</td>
</tr>
<tr>
<td>H$<em>2$O$</em>{aq}$</td>
<td>OH$^-$</td>
<td>OH$_{aq}$</td>
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<td>H$<em>3$O$</em>{aq}$</td>
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<td>H$<em>2$O$</em>{aq}$</td>
<td>H$<em>2$O$</em>{2aq}$</td>
</tr>
<tr>
<td>HO$_{2aq}$</td>
<td>O$_{2aq}$</td>
<td>O$_{2aq}$</td>
</tr>
<tr>
<td>O$_{aq}$</td>
<td>HO$_{2aq}$</td>
<td>O$_{3aq}$</td>
</tr>
<tr>
<td>O$_{3aq}$</td>
<td>H$^-$</td>
<td>H$<em>2$O$</em>{aq}$</td>
</tr>
</tbody>
</table>

Table 5.3: Water reaction mechanism (rates are in number density units)

<table>
<thead>
<tr>
<th>#</th>
<th>Reaction</th>
<th>Rate</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H$<em>2$O$</em>{aq}$ $\rightarrow$ H$_2$O$^+$ + e</td>
<td>$Z_{H_2O}(</td>
<td>E</td>
</tr>
<tr>
<td>2</td>
<td>OH$_{aq}$ $\rightarrow$ OH + e</td>
<td>$Z_{OH^-}(</td>
<td>E</td>
</tr>
<tr>
<td>3</td>
<td>e + H$<em>2$O$</em>{aq}$ $\rightarrow$ OH$^-$ + H</td>
<td>$f\left(\frac{</td>
<td>E</td>
</tr>
</tbody>
</table>
Table 5.3: Water reaction mechanism (contd.)

<table>
<thead>
<tr>
<th>#</th>
<th>Reaction</th>
<th>Rate</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>$e + \text{H}<em>2\text{O}</em>{aq} \rightarrow \text{H}_2 + \text{O}^-$</td>
<td>$f\left(\frac{E}{N}\right)$</td>
<td>[57]</td>
</tr>
<tr>
<td>5</td>
<td>$e + \text{H}<em>2\text{O}</em>{aq} \rightarrow \text{OH} + \text{H}^-$</td>
<td>$f\left(\frac{E}{N}\right)$</td>
<td>[57]</td>
</tr>
<tr>
<td>6</td>
<td>$e + \text{H}<em>2\text{O}</em>{aq} \rightarrow \text{H}^+ + \text{OH} + e + e$</td>
<td>$f\left(\frac{E}{N}\right)$</td>
<td>[83]</td>
</tr>
<tr>
<td>7</td>
<td>$\text{H}_2\text{O}^+ + e \rightarrow \text{H}<em>2\text{O}</em>{aq}$</td>
<td>$1 \times 10^{-19}$</td>
<td>[36]</td>
</tr>
<tr>
<td>8</td>
<td>$e + \text{H}<em>2\text{O}</em>{aq} \rightarrow e_{aq} + \text{H}<em>2\text{O}</em>{aq}$</td>
<td>$3.3 \times 10^{-18}$</td>
<td>[40]</td>
</tr>
<tr>
<td>9</td>
<td>$\text{H} + \text{H}<em>2\text{O}</em>{aq} \rightarrow \text{H}_{aq} + \text{H}<em>2\text{O}</em>{aq}$</td>
<td>$5 \times 10^{-21}$</td>
<td>[40]</td>
</tr>
<tr>
<td>10</td>
<td>$\text{H}_2 + \text{H}<em>2\text{O}</em>{aq} \rightarrow \text{H}_2\text{aq} + \text{H}<em>2\text{O}</em>{aq}$</td>
<td>$5 \times 10^{-21}$</td>
<td>[40]</td>
</tr>
<tr>
<td>11</td>
<td>$\text{O}^- + \text{H}<em>2\text{O}</em>{aq} \rightarrow \text{O}_{aq}^- + \text{H}<em>2\text{O}</em>{aq}$</td>
<td>$5 \times 10^{-21}$</td>
<td>[40]</td>
</tr>
<tr>
<td>12</td>
<td>$\text{OH} + \text{H}<em>2\text{O}</em>{aq} \rightarrow \text{OH}_{aq} + \text{H}<em>2\text{O}</em>{aq}$</td>
<td>$5 \times 10^{-21}$</td>
<td>[40]</td>
</tr>
<tr>
<td>13</td>
<td>$\text{H}^+ + \text{H}<em>2\text{O}</em>{aq} \rightarrow \text{H}<em>3\text{O}</em>{aq}^+$</td>
<td>$5 \times 10^{-21}$</td>
<td>[40]</td>
</tr>
<tr>
<td>14</td>
<td>$\text{OH}^- + \text{H}<em>2\text{O}</em>{aq} \rightarrow \text{OH}_{aq}^- + \text{H}<em>2\text{O}</em>{aq}$</td>
<td>$5 \times 10^{-21}$</td>
<td>[40]</td>
</tr>
<tr>
<td>15</td>
<td>$\text{H}_2\text{O}^+ + \text{H}<em>2\text{O}</em>{aq} \rightarrow \text{H}<em>2\text{O}</em>{aq}^+ + \text{H}<em>2\text{O}</em>{aq}$</td>
<td>$5 \times 10^{-21}$</td>
<td>[40]</td>
</tr>
<tr>
<td>16</td>
<td>$e_{aq} + \text{H}<em>2\text{O}</em>{aq} \rightarrow \text{H}<em>{aq} + \text{OH}</em>{aq}^-$</td>
<td>$3.2 \times 10^{-26}$</td>
<td>[40]</td>
</tr>
<tr>
<td>17</td>
<td>$e_{aq} + \text{H}<em>2\text{O}</em>{aq}^+ \rightarrow \text{H}<em>{aq} + \text{OH}</em>{aq}$</td>
<td>$1 \times 10^{-15}$</td>
<td>[40]</td>
</tr>
<tr>
<td>18</td>
<td>$e_{aq} + e_{aq} ( + 2 \text{H}<em>2\text{O}</em>{aq}) \rightarrow \text{H}<em>2\text{aq} + 2 \text{OH}</em>{aq}^-$</td>
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<td>[40]</td>
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<tr>
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<td>$6.9 \times 10^{-44}$</td>
<td>[40]</td>
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<tr>
<td>20</td>
<td>$e_{aq} + \text{OH}<em>{aq} \rightarrow \text{OH}</em>{aq}^-$</td>
<td>$5 \times 10^{-17}$</td>
<td>[40]</td>
</tr>
<tr>
<td>21</td>
<td>$e_{aq} + \text{O}<em>{aq}^- + \text{H}<em>2\text{O}</em>{aq} \rightarrow \text{OH}</em>{aq}^- + \text{OH}_{aq}^-$</td>
<td>$6.1 \times 10^{-44}$</td>
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<tr>
<td>23</td>
<td>$e_{aq} + \text{H}<em>2\text{O}</em>{2aq} \rightarrow \text{OH}<em>{aq} + \text{OH}</em>{aq}^-$</td>
<td>$1.8 \times 10^{-17}$</td>
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<td>24</td>
<td>$e_{aq} + \text{HO}<em>{2aq} + \text{H}<em>2\text{O}</em>{aq} \rightarrow \text{OH}</em>{aq} + \text{OH}<em>{aq}^- + \text{OH}</em>{aq}$</td>
<td>$9.7 \times 10^{-45}$</td>
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Table 5.3: Water reaction mechanism (contd.)

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<td>[40]</td>
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<tr>
<td>26</td>
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<td>[40]</td>
</tr>
<tr>
<td>27</td>
<td>$H_{aq} + H_2O_{aq} \rightarrow H_{2aq} + OH_{aq}$</td>
<td>$1.7 \times 10^{-26}$</td>
<td>[40]</td>
</tr>
<tr>
<td>28</td>
<td>$H_{aq} + H_{aq} \rightarrow H_{2aq}$</td>
<td>$1.2 \times 10^{-17}$</td>
<td>[40]</td>
</tr>
<tr>
<td>29</td>
<td>$H_{aq} + OH_{aq} \rightarrow H_2O_{aq}$</td>
<td>$1.2 \times 10^{-17}$</td>
<td>[40]</td>
</tr>
<tr>
<td>30</td>
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<td>[40]</td>
</tr>
<tr>
<td>31</td>
<td>$H_{aq} + H_2O_{2aq} \rightarrow OH_{aq} + H_2O_{aq}$</td>
<td>$1.5 \times 10^{-19}$</td>
<td>[40]</td>
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<tr>
<td>32</td>
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<td>[40]</td>
</tr>
<tr>
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<td>[40]</td>
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<td>[40]</td>
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<td>[40]</td>
</tr>
<tr>
<td>36</td>
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<td>$5 \times 10^{-18}$</td>
<td>[40]</td>
</tr>
<tr>
<td>37</td>
<td>$OH_{aq} + OH_{aq} \rightarrow H_2O_{2aq}$</td>
<td>$9.1 \times 10^{-18}$</td>
<td>[40]</td>
</tr>
<tr>
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<td>[40]</td>
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<td>[40]</td>
</tr>
<tr>
<td>40</td>
<td>$OH_{aq} + OH_{aq}^- \rightarrow O_{aq}^- + H_2O_{aq}$</td>
<td>$2.2 \times 10^{-17}$</td>
<td>[40]</td>
</tr>
<tr>
<td>41</td>
<td>$OH_{aq} + HO_{2aq} \rightarrow H_2O_{aq} + O_{2aq}$</td>
<td>$1 \times 10^{-17}$</td>
<td>[40]</td>
</tr>
<tr>
<td>42</td>
<td>$OH_{aq} + O_{2aq}^- \rightarrow OH_{aq}^- + O_{2aq}$</td>
<td>$1.3 \times 10^{-17}$</td>
<td>[40]</td>
</tr>
<tr>
<td>43</td>
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<td>$3 \times 10^{-21}$</td>
<td>[40]</td>
</tr>
<tr>
<td>44</td>
<td>$O_{aq}^- + H_{2aq} \rightarrow OH_{aq}^- + H_{aq}$</td>
<td>$1.3 \times 10^{-19}$</td>
<td>[40]</td>
</tr>
<tr>
<td>45</td>
<td>$O_{aq}^- + H_2O_{2aq} \rightarrow O_{2aq} + H_2O_{aq}$</td>
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<td>[40]</td>
</tr>
</tbody>
</table>
Table 5.3: Water reaction mechanism (contd.)

<table>
<thead>
<tr>
<th>#</th>
<th>Reaction</th>
<th>Rate</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>46</td>
<td>$\text{O}^-<em>{aq} + \text{HO}<em>2^-</em>{aq} \rightarrow \text{O}<em>2^-</em>{aq} + \text{OH}</em>{aq}^-$</td>
<td>$6.6 \times 10^{-19}$</td>
<td>[40]</td>
</tr>
<tr>
<td>47</td>
<td>$\text{O}^-<em>{aq} + \text{O}</em>{2aq} \rightarrow \text{O}<em>3^-</em>{aq}$</td>
<td>$6 \times 10^{-18}$</td>
<td>[40]</td>
</tr>
<tr>
<td>48</td>
<td>$\text{O}^-<em>{aq} + \text{O}<em>2^-</em>{aq} + \text{H}<em>2\text{O}</em>{aq} \rightarrow \text{OH}</em>{aq}^- + \text{OH}<em>{aq}^- + \text{O}</em>{2aq}$</td>
<td>$1.7 \times 10^{-45}$</td>
<td>[40]</td>
</tr>
<tr>
<td>49</td>
<td>$\text{OH}_{aq} + \text{H}<em>2\text{O}<em>2</em>{aq} \rightarrow \text{H}<em>2\text{O}</em>{aq} + \text{HO}</em>{2aq}$</td>
<td>$4.5 \times 10^{-20}$</td>
<td>[40]</td>
</tr>
<tr>
<td>50</td>
<td>$\text{OH}<em>{aq} + \text{HO}<em>2^-</em>{aq} \rightarrow \text{OH}</em>{aq}^- + \text{HO}_{2aq}$</td>
<td>$1.2 \times 10^{-17}$</td>
<td>[40]</td>
</tr>
<tr>
<td>51</td>
<td>$\text{H}_2\text{O}<em>2^+</em>{aq} + \text{H}<em>2\text{O}</em>{aq} \rightarrow \text{H}<em>3\text{O}<em>2^+</em>{aq} + \text{OH}</em>{aq}$</td>
<td>$1 \times 10^{-23}$</td>
<td>[40]</td>
</tr>
<tr>
<td>52</td>
<td>$\text{H}<em>3\text{O}^+</em>{aq} + \text{OH}<em>{aq}^- \rightarrow \text{H}</em>{aq}^- + \text{OH}_{aq} + \text{H}<em>2\text{O}</em>{aq}$</td>
<td>$1 \times 10^{-16}$</td>
<td>[40]</td>
</tr>
<tr>
<td>53</td>
<td>$\text{HO}_{2aq} + \text{H}<em>2\text{O}</em>{aq} \rightarrow \text{H}<em>3\text{O}^+</em>{aq} + \text{O}<em>2^-</em>{aq}$</td>
<td>$3.3 \times 10^{-24}$</td>
<td>[40]</td>
</tr>
<tr>
<td>54</td>
<td>$\text{H}<em>3\text{O}^+</em>{aq} + \text{O}<em>2^-</em>{aq} \rightarrow \text{HO}_{2aq} + \text{H}<em>2\text{O}</em>{aq}$</td>
<td>$1 \times 10^{-25}$</td>
<td>[40]</td>
</tr>
</tbody>
</table>

5.3 Problem statement

Simulations were conducted with the proposed kinetic model coupled with multiphysics plasma model described in section 3.1. Due to inclusion of an extended chemical kinetic model, the numerical framework employs the methodology described in section 3.2 for integration and coupling of chemical source terms. The problem geometry and applied voltage profile remain identical to the one presented in Figure 4.1c. To differentiate the role of electron source terms on the initiation process three cases were simulated:

i) Case I: Electrons formed through ionization of water molecules via the Zener tunneling mechanism

ii) Case II: Electrons formed through detachment from negative hydroxyl ions via a tunneling mechanism
iii) Case III: Electrons formed through a combination of ionization of water molecules and detachment from hydroxyl ions via the tunneling mechanism

For each of these cases linear ramp and rapid pulse with a maximum voltage of 15 kV and 20 kV is considered for conducting the simulations.

5.4 Results and discussions

The first cases are simulated for a linear ramp of the voltage. Under the linear ramp condition the maximum voltage is attained at 5 ns. The simulations are conducted by isolating the ionization (i.e. reactions R1 and R2) reactions to determine their independent role on the plasma initiation process.

In Figure 5.2 the distribution of axial velocity along the center line is given. The plots shown in Figures 5.2a and 5.2d are almost identical to 4.12b and 4.10b, respectively. In chapter 4, same problem was dealt with the simple chemistry model including H$_2$O ionization via Zener tunneling (R1). Similar trends and magnitudes are observed here which confirms the dominant role of polarization and ponderomotive forces on velocity field. The polarity of system is slightly changed when considering detailed chemistry which affects the electric field distribution. However, the change is not comparable with the magnitudes of other forces. In the cases having OH$^-$ as the only ionization source (5.2b and 5.2e), different velocity distribution is observed. The positive velocity region (i.e. the region where fluid moves away from the powered electrode) does not appear for OH$^-$, because the ionization degree is lower and less charges are produced. Therefore the alteration of electric field and also increase in electrostatic force is not seen here and the fluid flow is only caused by hydrodynamic effects, i.e. $F_{pon}$ and $F_{pol}$. The discussion given in chapter 4 also stands for Figure 5.2d. Reaction R1 generates electrons and H$_2$O$^+$ ions. Electrons are either transported towards powered electrode or react to form more stable species while H$_2$O$^+$ ions move away from powered electrodes with slower speed. The result is accumu-
lation of positive ions which is responsible for the positive velocity region in Figure 5.2d. Since R2 produces neutral OH radicals in addition to electrons, such behavior is not observed in Figure 5.2e and the bulk fluid is solely driven by hydrodynamic effects.

![Figure 5.2](image-url)

**Figure 5.2:** Center line distribution of axial velocity for a,d) Case I, R1: H₂O ionization via tunneling process, b,e) Case II, R2: electron detachment from OH⁻ ions and c,f) Case III, combined electron formation from both R1 and R2 reactions. Plots in the top row are associated to the cases with ramp and the bottom row are the cases for pulse voltage (\(V_{\text{max}} = 15kV\)).

In Figure 5.3, the special and temporal variation of density is illustrated for ramp and pulse cases with different electron sources. For the OH⁻ ionization cases (Figures 5.3b and 5.3e), the compression wave is close to electrode, while for all other cases, a traveling compression wave is observed. This wave is partly formed by the low-field zone described before. It will be shown later that since positive ions are formed in the reaction zone, electrostatic forces increases and creates different flow pattern, responsible for compression. As mention in previous section, the change in density is reflected in reaction rates by altering \(|E|/N\).
Figure 5.3: Center line distribution of density for a,d) Case I, R1: H$_2$O ionization via tunneling process, b,e) Case II, R2: electron detachment from OH$^-$ ions and c,f) Case III, combined electron formation from both R1 and R2 reactions. Plots in the top row are associated to the cases with ramp and the bottom row are the cases for pulse voltage ($V_{\text{max}} = 15kV$).

The effect of ionization path on hydrodynamics of the plasma can be better explained by examining the distribution of electric forces. In Figure 5.4, center line distribution of the electrostatic, polarization and ponderomotive forces density is given for each of the ionizations paths considered (H$_2$O, OH and combined). This plot is for the case with linear voltage applied and the pulse case is not shown here. Comparing Figure 5.4b with 5.4e and 5.4h shows that electrostatic force is several orders of magnitude smaller than other two forces when ionization is only considered through OH$^-$ channel. Therefore, like the 7 kV cases investigated in chapter 4, the dominant forces for case with hydroxide ionization are $\mathbf{F}_{\text{pon}}$ and $\mathbf{F}_{\text{pol}}$. On the other hand, when water ionization is considered, accumulation of positive ions increases the electrostatic force dramatically (Figure 5.4a). Also, these positive charges reduce
the effective electric field near the powered electrodes and a drop is seen in $F_{pon}$ and $F_{pol}$. This is shown in Figures 5.4d, 5.4g, 5.4f and 5.4i.

The evolution of the electron number density, $n_e$, under the linear ramp condition is presented in Figures 5.5a to 5.5c. The spatio-temporal evolution of $n_e$ shows that due to lower threshold energy, the free electrons from OH$^-$ detachment (Case II) is formed at earlier times when compared to the H$_2$O tunnel ionization channel (Case I). At $t = 1$ ns, when the voltage pulse reaches $3$ kV, the maximum $n_e$ formed by
reaction R2 is around $5 \times 10^{18} \text{ m}^{-3}$ with a clear formation of free electron wave emerging near the vicinity of the powered electrode. In comparison, when electrons are formed through H$_2$O ionization (i.e. reaction R1), under the same voltage the maximum $n_e$ is only $\sim 10^{12} \text{ m}^{-3}$. But at 2 ns, the peak electron number density with only R1 active reaches a value of $\sim 10^{21} \text{ m}^{-3}$, whereas the peak remains constant with only the R2 channel being active. In addition to available electric field/electron energy, the R2 reaction rate is also limited by the presence of available OH$^-$. At the very initial stage, electrons are detached from the pre-existing hydroxyl ion OH$^-$ available in the water, which is $6 \times 10^{19} \text{ m}^{-3}$. These negative hydroxyl ions is rapidly consumed through the R2 channel forming free electrons. This is evident in the OH$^-$ profile at $\sim 1$ns, which shows a sharp decrease in the OH$_{aq}^-$ near the powered electrode (Figure 5.5e). As the $n_e$ wave front propagates forward, the OH$_{aq}^-$ number density in the trailing downstream region continues to increase from the resulting aqueous and solvated electron reactions. The OH$^-$ formation routes generates sufficient negative ions to maintain a quasi-steady concentration and allowing a constant source limited by the available OH$^-$ number density. With electrons forming only through the R1 channel the ionization wave does not start propagating until $\sim 4$ ns. At 4 ns the electron wave formed only through the detachment process (i.e. reaction R2) propagates further downstream to a distance of $\sim 10 \mu m$. In the simultaneous presence of both R1 and R2 channels, at the very initial stage electrons are generated from the detachment reaction alone, until the available OH$^-$ ions are consumed. As these electrons propagate downstream, electrons are produced near the vicinity of the powered electrode by the tunnel ionization of H$_2$O molecules. The electrons spatio-temporal evolution distinctively show a relatively weaker wave which is followed by a stronger wave.

The centerline distribution of OH$^-$ for the three different cases are also shown in Figures 5.5d to 5.5f. The H$_2$O ionization channel through subsequent reactions
forms sufficient OH\(^-\) ions in the electron wave front. These OH\(^-\) number densities are high enough to allow electrons to form through the detachment reactions (R2). For case II, the formation of electrons from OH\(^-\) detachment is sufficiently faster than the net production of OH\(^-\) as a result the OH\(^-\) gets depleted once the electrons are formed. As seen in Figure 5.5b, the electron wave propagates forward up consuming the down stream OH\(^-\). When both the electron sources are active (Case III), the electrons formed by R1 allows the formation of sufficient OH\(_{aq}\) (Figure 5.5f). At \(\sim 3.0\) ns the OH\(_{aq}\) number density near the powered electrode increases to \(\sim 10^{20}\) m\(^{-3}\)s\(^{-1}\). Therefore the second electron avalanche triggered at \(\sim 3.0\) ns near the powered electrode has contribution from both R1 and R2 channels.

Generation of positive H\(_2\)O\(^+\) ions by reaction R1 in cases I and III has a strong effect on the hydrodynamics and chemistry of the system. By increasing electric field, rate of R1 increases dramatically and generates considerable amount of H\(_2\)O\(^+\). As
shown in Figures 5.6 and 5.7a, both cases I and III, where H₂O ionization is present, show almost identical profiles of H₂O⁺ number density. For both of these cases, peak H₂O⁺ number density value is \(2.95 \times 10^{25} \text{ m}^{-3}\). In case II, H₂O⁺ is not formed, since R1 is not considered.

Figure 5.6: Spatial evolution of H₂O⁺ at the centerline at different time instances for a) Case I, R1: H₂O ionization via tunneling process and b) Case III, combined electron formation from both R1 and R2 reactions. (Linear voltage ramp, \(V_{\text{max}} = 15\text{kV}\)).

Spatio-temporal contour plots of HO₂aq and H₂O₂aq number density at different times are presented in Figures 5.7b and 5.7c. These species are important in decontamination and materials processing. The peak value for HO₂aq was found to be \(1.56 \times 10^{19} \text{ m}^{-3}\) (\(\sim 0.5\text{ppb}\)). For H₂O₂aq, the maximum number density observed was \(1.42 \times 10^{23} \text{ m}^{-3}\) (\(\sim 4\text{ppm}\)).

The reaction mechanism scheme contains the solvation of the plasma generated electrons to the aqueous state. The electron solvation reaction (R8) acts as one of the major loss channels. In the \(n_e\) profile, (Figure 5.5) it is evident that as the electron generation decreases after a few nanoseconds, the electrons are quickly consumed. The time required for electrons to solvate and produce \(e_{\text{aq}}\) is in the order of pico seconds [84]. Other reaction steps associated with electrons consumption routes such as dissociative attachment (R3 – R5), dissociative ionization (R6) are typically only
active in the $|E|/N$ ranges above 50 Td while for the applied voltage of 15kV, $|E|/N$ barely exceeds 30 Td.

In Figure 5.8, the evolution of solvated electrons number density at the centerline for the three different cases are presented. Comparing the electrons and solvated electron profiles for Case I (Figures 5.5a and 5.8a), one can see that in the earlier stages when the electron generation rates are low, the electron solvation rate remains comparable to the electron production rate. As a result most of the electrons formed during the early stage gets solvated. For Case II, when the electrons are generated through the detachment process alone, the generation rate is comparable or lower than the solvation rate. As a consequence, as the electron wave propagates forward it is trailed by the region of solvated electrons (Figures 5.5b and 5.8b) to the downstream of the electron. Once the electrons are solvated it becomes less mobile due to the lower drift and diffusion. It should be noted that reaction R30 also contributes to the formation of solvated electron by converting $H_{aq}$ and $OH_{aq}$ to $e_{aq}$ and $H_2O$. R30 acts as a consumption channel of $OH_{aq}$ reducing the available negative hydroxyl ions for the electron detachment process (R2). With both $n_e$ channels present (i.e. R1 and R2) simultaneously, during the early stages the electrons formed from R2 gets solvated as the electric field increases and R1 is activated, a second high concentration region of $e_{aq}$ emerges and starts to propagate in the liquid. A distinct demarcation between these concentration levels of $e_{aq}$ is present due to the low diffusivity and very short time scales. It has been shown [46, 72, 85] that during water radiolysis in the absence of scavenging species like dissolved oxygen, the solvated electron density decays mainly through reaction R18. However, when considerable amounts of $H_2O^+$ are generated by $H_2O$ ionization (R1), reaction R17 also reduces $e_{aq}$ concentration by converting it to $H_{aq}$ and $OH_{aq}$.

Spatio-temporal contour plots of electrons and solvated electrons for all three cases are presented in Figures 5.9 to 5.11. As shown in Figure 5.11 for case III, the first
wave of electrons is caused by R2 at earlier times and lower electrode voltages followed by second ionization wave via R1. The second wave of electrons have a higher peak number density, despite the higher threshold energy requirement. The reaction rate for R1 depends on the number density of H$_2$O, which is multiple orders of magnitude higher than that of OH$^-$. As a result once the threshold energy is acquired, R1 channel rapidly surpasses the contribution from R2. At $\sim 3$ ns when the peak electron number density from the second wave is $\sim 9 \times 10^{23}$ m$^{-3}$, the contour plots clearly shows that the electron avalanche resulting from R2 continues to propagate down. In addition, as the depleted OH$^-$ near the electrode gets replenished and augmented to allow R2 to become active (Figure 5.5f), the second electron wave is formed. This wave has contribution from both R1 and R2 near the electrode vicinity. The solvated electron number density does not show the presence of multiple peaks. The electrons formed by both R1 and R2 continues to solvate and participate in the aqueous reactions.
Figure 5.7: Spatio-temporal contour plots of $\text{H}_2\text{O}^+$, $\text{HO}_2\text{aq}$ and $\text{H}_2\text{O}_2\text{aq}$ number density for combined $\text{H}_2\text{O}$ and OH$^-$ ionization under linear ramp condition, ($V_{\text{max}} = 15kV$).
Figure 5.8: Spatial evolution of solvated electrons number density ($n_{\text{eaq}}$) at the centerline at different time instances for a) Case I, R1: $\text{H}_2\text{O}$ ionization via tunneling process, b) Case II, R2: electron detachment from $\text{OH}^-$ ions and c) Case III, combined electron formation from both R1 and R2 reactions. (Linear voltage ramp, $V_{\text{max}} = 15kV$).

Figure 5.9: Spatio-temporal contour plots of electron number density for Case I under linear ramp condition, ($V_{\text{max}} = 15kV$).
Figure 5.10: Spatio-temporal contour plots of electron number density for Case II under linear ramp condition, \( (V_{\text{max}} = 15kV) \).
Figure 5.11: Spatio-temporal contour plots of electron number density for Case III under linear ramp condition, ($V_{\text{max}} = 15kV$).
Figure 5.12: Spatio-temporal contour plots of $\text{OH}^-_{\text{aq}}$ and $\text{H}_3\text{O}^+_{\text{aq}}$ number density for combined $\text{H}_2\text{O}$ and OH$^-$ ionization (Case III) under ramp condition, ($V_{\text{max}} = 15kV$).
The influence of the driving voltage profile was investigated by performing simulations with a voltage profile having a rise time of a few nano-seconds. The pulsed voltage profile has an exponential rise to $V_{\text{max}}$ in 3 ns followed by a linear decay. The spatio-temporal evolution of the electron number density ($n_e$), OH$^-$, H$_2$O$^+$ under a pulsed voltage for the aforementioned three cases are shown in Figures 5.13 and 5.14. Under the pulsed condition, the applied voltage at 1 ns is low as a result no significant electron generation is observed from either channels (Figures 5.13a and 5.13c). As the voltage increases to $\sim$ 1.5 kV at 2 ns both R1 and R2 reactions become active and an increase in the electron number density is observed. However compared to the linear ramp case, where at 2 ns the $n_{e,\text{max}}$ generated from either R1 or R2 is comparable, for the pulsed case electrons produced only from H$_2$O tunneling (i.e. R1 reaction) is 9 orders of magnitude lower than that of R2. At 3 ns an ionization front is formed and the profile and $n_{e,\text{max}}$ for the ramp and pulse cases are similar. However under pulsed condition the ionization front propagates further downstream. It should be noted that voltage value for a ramp and a pulse are almost identical at 2.5 ns. The R1 has a larger energy barrier, it is only active in the vicinity of the powered electrode where stronger field is present. After 3 ns as the voltage starts to decay and rate of H$_2$O ionization (R1) decreases resulting in a significant decrease in the $n_{e,\text{max}}$ near the powered electrode at 4 and 5 ns (Figure 5.13a). It is evident that OH$^-$ detachment reaction (R2) is not active until $\sim$ 2 ns. Similar to Case I, under pulse condition the ionization front formed by R2 propagates further downstream. The R2 reactions with its lower energy barrier detaches electrons from the negative hydroxyl ions even in regions far from anode with lower field strength. Two ionization fronts emerges when both R1 and R2 paths are active simultaneously. The first $n_e$ wave emerges from OH$^-$ detachment which requires lower energy and is trailed by a stronger ionization front formed by H$_2$O ionization. The second $n_e$ wave front however has contribution from both R1 and R2 reactions. It is apparent that compared to the linear ramp,
the pulsed voltage generates significantly higher concentration of OH\textsubscript{aq} (Figure 5.13). Therefore in Case III, the R1 channel generating high number density of ne allows the buildup of OH\textsubscript{aq} near the powered electrode. The R2 reaction becomes active and the OH\textsubscript{aq} concentration limit is relaxed. It should be mentioned that under pulsed condition the spatial lag between the two wave fronts are minimized.

![Figure 5.13: Spatial evolution of electrons number density ($n_e$) and OH\textsuperscript{−} at the center-line at different time instances for a) Case I, R1: H\textsubscript{2}O ionization via tunneling process, b) Case II, R2: electron detachment from OH\textsuperscript{−} ions and c) Case III, combined electron formation from both R1 and R2 reactions. (Pulsed voltage, $V_{\text{max}} = 15\text{kV}$).](image)

Distribution of OH\textsubscript{aq} along the center line is also presented in Figure 5.13 for the pulsed voltage. With only R1 active, the OH\textsubscript{aq} is generated in the vicinity of powered electrons mostly by electron reactions such as R16, R18-R21, R23-R24. Most of the electrons needed in these reactions are formed by the ionization of H\textsubscript{2}O supplied by R1. As shown in Figure 5.13, the OH\textsubscript{aq} is rapidly consumed to form free electrons and OH when only R2 reaction is active, OH\textsubscript{aq} is quickly converted to OH via reaction R2. In comparison, the hydroxyl ion concentration in a linear voltage decreases gradually, whereas with a pulse the decrease is initially slow and rapid as the pulse peak is
approached. Shneider and Pekker [56] estimated the number of primary electrons detached from hydroxyl ions via field ionization neglecting the secondary reactions that can recycle OH\(^-\) in the system. They highlighted that in the real systems where electron driven processes generate increased amount of OH\(^-\) than that is already available from water self-ionization, reaction R2 can have a stronger influence on the breakdown process. This is clearly seen in Figure 5.13f when both R1 and R2 are considered to be active (and Figure 5.5f for the ramp case), while the existing hydroxyl ions participate in the detachment reactions, significant OH\(^-\) are formed resulting from the electrons formed via R1 reactions and the participating aqueous reactions. As a result near the vicinity of the powered electrode due to the replenishment and eventual abundance of OH\(^-\), R2 also becomes active.

Spatial evolution of H\(_2\)O\(^+\) at the centerline at different time instances for cases I and III is shown in Figure 5.14. Similar to the cases with linear ramp applied voltage, plots for case I and III are identical, confirming the fact that H\(_2\)O\(^+\) formed from R1 mostly accumulates in the reaction zone. For both of these cases, peak H\(_2\)O\(^+\) number density value is \(1.13 \times 10^{26} \text{ m}^{-3}\).

![Figure 5.14: Spatial evolution of H\(_2\)O\(^+\) at the centerline at different time instances for a) Case I, R1: H\(_2\)O ionization via tunneling process and b) Case III, combined electron formation from both R1 and R2 reactions. (Pulsed voltage, \(V_{\text{max}} = 15kV\).)](image-url)
The contour plots of the electron and solvated electron number density for the pulsed 15 kV for identical time instances as the linear ramp is presented in Figure 5.17. The peak n_e under the pulsed condition is $1.6 \times 10^{24} \text{ m}^{-3}$, which is a factor of 3 higher than the linear case. As the voltage rise time reduces in the exponential growth, not only does the peak electron number density increase at the same time they are advected further downstream from the powered electrode. The downstream advection occurs during the linear decay of the voltage. The bulk fluid velocity also attains the maximum value during the voltage relaxation period (Figure 5.2f). The $n_{\text{eaq}}$ clearly shows the presence of stratified regions of high density $n_{\text{eaq}}$. This is due to the low mobility and diffusivity of the solvated electrons. Regions close to the powered electrode the solvated electrons get advected due to the high bulk fluid velocity. Compared to $n_e$ the $n_{\text{eaq}}$ does not show a steep decrease during the voltage relaxation period.

Spatio-temporal contour plots of HO$_{2\text{aq}}$ and H$_2$O$_{2\text{aq}}$ number density under 15 kv pulse condition at different times are presented in Figures 5.19b and 5.19c. Compared to the case under ramp condition, higher peak values are observed in pulse condition. The peak value for HO$_{2\text{aq}}$ was found to be $2.55 \times 10^{22} \text{ m}^{-3}$ ($\sim 750\text{ ppb}$). For H$_2$O$_{2\text{aq}}$, the maximum number density observed was $2.51 \times 10^{24} \text{ m}^{-3}$ ($\sim 74\text{ ppm}$).
Figure 5.15: Spatio-temporal contour plots of electron number density for Case I under pulse condition, \((V_{\text{max}} = 15kV)\).
Figure 5.16: Spatio-temporal contour plots of electron number density for Case II under pulse condition, ($V_{\text{max}} = 15\text{kV}$).
Figure 5.17: Spatio-temporal contour plots of electron number density for combined H$_2$O and OH$^-$ ionization under pulse condition, ($V_{\text{max}} = 15\text{kV}$).
Figure 5.18: Spatio-temporal contour plots of $\text{OH}^-_{\text{aq}}$ and $\text{H}_3\text{O}^+_{\text{aq}}$ number density for combined $\text{H}_2\text{O}$ and $\text{OH}^-$ ionization (Case III) under pulse condition, ($V_{\text{max}} = 15kV$).
Figure 5.19: Spatio-temporal contour plots of H$_2$O$^+$, HO$_2$aq and H$_2$O$_2$aq number density for combined H$_2$O and OH$^-$ ionization under pulse condition, ($V_{\text{max}} = 15kV$).
In the proposed reaction scheme the rate constant of reactions R1 and R2 strongly depend on the local electric field magnitude. Reactions R3 – R6 are dependent on the local reduced electric field \(|E|/N\) magnitude. Figure 5.20 presents the rate constant for reactions R1 – R6 as a function of the reduced electric field. The ionization of H$_2$O by Zener tunneling requires a higher field strength for initiation compared to the OH$^-$ detachment tunneling process. In addition, the rate constant for R1 is smaller. The rate of production of electron from these two reactions are obtained by $k_{R1} \cdot n_{H_2O}$ and $k_{R2} \cdot n_{OH^-}$ respectively. As a result the rate of the reactions is also limited by the initial number density of the participating species. The initial number density of OH$^-$ in distilled water is $\sim 10^{19}$ m$^{-3}$. However, electron driven reactions can generate OH$^-$ far beyond the equilibrium concentration in the discharge under conducive conditions.

For a peak applied voltage of 15kV, the peak OH$^-$ number density is predicted to be $\sim 10^{21}$ and $10^{26}$ m$^{-3}$ for the ramp and pulse cases, respectively. The number density of H$_2$O is typically $\sim 3.3 \times 10^{28}$ m$^{-3}$. While H$_2$O is abundant throughout the discharge, the OH$^-$ is consumed at a faster rate by R2 and requires recycling in order to sustain the OH$^-$ tunneling route. The rate of electron generation from R1 is considerably smaller compared to R2 at the initial stages of discharge. As OH$^-$ number density drops, most of the electron formation takes place via H$_2$O tunneling when the required electric field is established during the later stages of the discharge.

Figure 5.20 clearly shows that R3 to R5 becomes effective at \(|E|/N\) values of 50 Td and R6 is starts to have significant contribution when \(|E|/N\) exceeds 150 Td.

Figure 5.21, presents the distribution of the reduced electric field at the centerline for different time instances for the 15kv ramp case. From 1 to 3 ns, a gradual increase is observed in \(|E|/N\) distribution due to the linear increase in the applied voltage. This results in higher reaction rates and also higher drift velocity for charged particles. Starting from 4 ns for Cases I and III, where R1 reaction is active a localized decrease in the reduced electric field is observed close to the powered electrode (5 - 6 $\mu$m from
anode). Within a distance of $\sim 5 \, \mu m$ in the downstream direction the $|E|/N$ value shows an increase. This undulated $|E|/N$ profile is associated with the increase and decrease in the density due to the resulting compression and expansion waves generated from the electrical forces (see Figure 5.4). Additionally, accumulation of $H_2O^+$ positive ions near the anode alters the polarity of the region, decreasing the electric field magnitude. These undulations in the $|E|/N$ directly impact the reaction rates, especially R1 and R2 that have strong dependence in the lower range. With only $OH^-$ tunneling (Figure 5.21b), the $|E|/N$ profiles remain free from undulation. The density variation is distinctively different compared to Case I and III (Figure 5.3). Near the anode the density increases by a factor of $\sim 1.4$ at 5 ns and a slight rarefaction in between 85 – 90 $\mu m$ is also observed. At earlier time instances this decrease in density is nearly absent. However, the $|E|/N$ profile do not show large variation that is associated with density changes. Only at $\sim 5$ ns the $|E|/N$ near the anode tip shows an increase, which peaks and then starts to decrease within $\sim 5\mu m$ distance. This is associated with the high density near the anode that also progressively decreases within $\sim 5 \, \mu m$.
Figure 5.21: Variation of reduced electric field (|E|/N) for at the centerline at different time instances for a) Case I, R1: H₂O ionization via tunneling process, b) Case II, R2: electron detachment from OH⁻ ions and c) Case III, combined electron formation from both R1 and R2 reactions. (Linear voltage ramp, \( V_{\text{max}} = 15kV \)).

Figure 5.22 summarizes the spatio-temporal evolution of the R1 and R2 reactions along the centerline under linear voltage ramp. In Figure 5.24, the contour plots of R1 and R2 reactions are given at different times. The peak rate of formation from R1 and R2 at 1 ns are about \( 10^{23} \) and \( 10^{30} \), respectively. The location of the peak rate for R1 is at the vicinity of the powered electrode where \(|E|/N\) is the maximum at 1 ns. The peak R2 rate locates itself \( \sim 1 \, \mu m \) away from electrode, due to the depletion of the hydroxyl ions near the electrode tip (Figure 5.13f). Furthermore, within 1 ns formation of additional OH⁻ near the electrode does not take place. As time progresses the rate of R1 increases drastically due to increase in the applied voltage. In contrast the R2 reaction rate decreases due to the lower concentration of the OH⁻. The R2 rate profile also clearly shows the OH⁻ depleted regions, where the rate remains relatively constant. However, at 3 ns near the anode the R2 rate increases as a result of OH⁻ build up. The rate continues to grow near the electrode at 5 ns due to both increasing electric field and OH⁻ number density. At 5 ns, the R1 reaction rate profile reflects the reduced electric field distribution. The profiles also depict the decrease of R1 in regions far from electrode, whereas R2 continues to remain active due to its low energy barrier and the presence of OH⁻ ions.
Reactions R8 and R30 are the key paths that act as the formation route of solvated electrons (Figure 5.23). It is clear that major source of $n_{\text{eaq}}$ is the hydration reaction R8. Electrons generated from both R1 and R2 participates in the R8 reaction. Reaction R30 does not have significant contribution specially in the higher field regions.

Figure 5.22: Centerline distribution of electron formation rate from R1 and R2 at different time instances for Case III under linear voltage ramp ($V_{\text{max}} = 15kV$)

Figure 5.23: Centerline distribution of solvated electron formation rate from R8 and R30 at different time instances for Case III under linear voltage ramp ($V_{\text{max}} = 15kV$).
Figure 5.24: Spatio-temporal contour plots of R1 (left) and R2 (right) reaction rate for combined H$_2$O and OH$^-$ ionization under linear ramp condition, ($V_{\text{max}} = 15kV$).
The volume averaged reactions rates of the dominant formation and consumption routes for electrons at different time instances for the cases under linear ramp voltage are summarized in Figure 5.25. These rates are volume averaged over the entire solution domain. As mentioned earlier, initially (t = 1 ns), almost all of the ionization happens via R2. At 2 ns, electron formation via R1 is about two orders of magnitude higher than that of R2. The rate of R2 remains almost unchanged from 1 to 2 ns, rate. This is due to the fact that the peak of R2 gradually moves away from the electrode maintaining the same rate as it progresses forward. By further increase in voltage, both reactions volumetrically generate the same amount of electrons. The generated electrons are either hydrated (R8) or react with H$_2$O$^+$ through the recombination reaction R7. The rate of hydration is generally higher than recombination. During the initial stages the recombination reaction is negligible due to the absence of H$_2$O$^+$ ions. We would highlight that in the initial stages the electrons are primarily formed via OH$^-$ detachment tunneling process. Even though H$_2$O$^+$ ions are by R1 in the later stages, the rate of the solvation reactions remains 5 orders of magnitude higher.
Figure 5.25: Volume-averaged reaction rates of the dominant formation and consumption reaction paths of electrons for Case III, under linear voltage ramp conditions ($V_{\text{max}} = 15kV$).
In the system, the solvated electrons are generated by two channels - R8 and R30, with R8 dominating the formation rate by multiple orders of magnitude (Figure 5.26). A close examination of the consumption routes indicates that initially bulk of $e_{aq}$ is consumed via R22 ($e_{aq} + H_3O^+ \rightarrow H_{aq} + H_2O_{aq}$) with the rate of $2.3 \times 10^{21} \text{ m}^{-3}\text{s}^{-1}$, R16 ($e_{aq} + H_2O_{aq} \rightarrow H_{aq} + OH_{aq}$) with the rate of $1.1 \times 10^{21} \text{ m}^{-3}\text{s}^{-1}$, and R18 ($e_{aq} + e_{aq} + 2H_2O_{aq} \rightarrow H_{2aq} + 2OH_{aq}$) with $8.7 \times 10^{20} \text{ m}^{-3}\text{s}^{-1}$. Note that R18 is a second order reaction and its rate only depends on $n_{eaq}$ and not H$_2$O [46]. In R22 the aqueous electrons gets recombined with the hydronium ions (H$_3$O$^+$) to form H$_{aq}$ and H$_2$O$_{aq}$. The initial H$_3$O$^+$ (Hydronium ion) in the aqueous state is present as a product of self ionization of water (H$_2$O + H$_2$O $\rightarrow$ H$^+$ + OH$^-$). As the concentration of H$_3$O$^+$ decreases at later stages, the R22 rate tends to flatten out. R16 and R18 both these $n_{eaq}$ consumption channels contribute to the formation of OH$^-$ in the system. As the system approaches 4 ns, R17 ($e_{aq} + H_2O_{aq}^+ \rightarrow H_{aq} + OH_{aq}$), R18 ($e_{aq} + e_{aq} + 2H_2O_{aq} \rightarrow H_{2aq} + 2OH_{aq}$), R19 ($e_{aq} + H_{aq} + H_2O_{aq} \rightarrow H_{2aq} + OH_{aq}$) and R20 ($e_{aq} + OH_{aq} \rightarrow OH_{aq}$) becomes the main $n_{eaq}$ consumption reactions, having the reaction rates of $1 \times 10^{32}$, $1.7 \times 10^{32}$, $1 \times 10^{32}$ and $4.5 \times 10^{31} \text{ m}^{-3}\text{s}^{-1}$, respectively. Reactions R18, R19 and R20 all contribute to the formation OH$^-_{aq}$ and in R19 and R20 $n_{eaq}$ reacts with H$_2$O$_{aq}$. This suggests if enough solvated electrons are present, sufficient OH$^-_{aq}$ will be formed. These OH$^-_{aq}$ can easily act as the source for electrons when the applied voltage starts to decay.
Figure 5.26: Volume-averaged reaction rates of the prominent formation and consumption reactions of the solvated electrons for Case III, under linear voltage ramp conditions ($V_{\text{max}} = 15kV$).
Figure 5.27 presents the volume averaged reactions rates of the formation and consumption routes of OH\textsubscript{aq} at different time instances for Cases II and III. As illustrated in Figure 5.27b, for Case III where both R1 and R2 electron sources are considered, hydroxide ions are consumed by the average rate of about $4 \times 10^{27}$ m$^{-3}$s$^{-1}$ from 0 to 2 ns, by R2. The second most prominent consumption route is R52 and remains fairly constant at $\sim 3.5 \times 10^{12}$ m$^{-3}$s$^{-1}$ throughout the 5 ns duration. Concentration of H$_3$O$^+$ is the limiting factor for this reaction as both R52 and R22 compete for the H$_3$O$^+$ pool and the generation of H$_3$O$^+$ by R51 and R53 is relatively slow. At 1 ns, 54% and 43% of hydroxyl ions are formed through reactions R16 and R18 and only 3% is formed by R20. As time progresses, a sharp increase is observed in production of OH$^-$ by reactions R18, R19 and R20. These reactions generate 52%, 27% and 21% percents of total OH$^-$ produced, respectively. Similar to the prior works [46, 72, 85] R18 is found to be a the major sink of e\textsubscript{aq} and forming OH$^-$. The comparison further shows that R19 and R20 are not initially significant since the necessary H and OH radicals to proceed are not available at sufficient quantities. The OH radicals are later formed by electron driven reactions, namely R12 and R17. At 5 ns, 33% and 66% of the OH is formed by R12 and R17 respectively. The hydroxyl radical produced in R2 gets solvated in water by R12. R12 is the only source of OH\textsubscript{aq} at earlier times but as OH\textsubscript{aq} concentration decreases, less OH becomes available as well. On the other hand, as the electron number density increases at later times, the R17 recombination reaction becomes the dominant source for OH radical. From 2 to 5 ns, almost all of H radicals are produced by R17, whereas for 0 – 2 ns R52 act as the main source of H generation. In the case with only OH$^-$ ionization (Figure 5.27a), the OH$^-$ production happens through R16, R18 and R19. Similar to the case with both ionization sources, at 1 ns, 52%, 45% and 3% of hydroxide is formed through reactions R16, R18 and R19, respectively. As time progresses these three reactions contributes equally in generating OH$^-$, whereas for Case III R16 has the maximum contribution followed by
by R18. The rate of hydroxide ions formation from all reactions is about $1 \times 10^{23}$ m$^{-3}$s$^{-1}$ for Case II and $1 \times 10^{33}$ m$^{-3}$s$^{-1}$ for Case III.

![Graph](image1)

(a)

![Graph](image2)

(b)

Figure 5.27: Volume-averaged reaction rates of the prominent formation and consumption reactions of OH$^-$ for a) Case II and b) Case III, under linear voltage ramp conditions ($V_{max} = 15kV$).

Apart from electrons and hydroxide ions, there are other important ions and radicals formed during the discharge initiation process. Among these species is the
$\text{H}_2\text{O}^+$, which is formed as product of water ionization via tunneling (R1) and then gets solvated. A small fraction of $\text{H}_2\text{O}^+$ is consumed by recombination reaction (R7). The aqueous $\text{H}_2\text{O}^+$ is ultimately converted to $\text{H}_{\text{aq}}$ and $\text{OH}_{\text{aq}}$ through R17. R51 is another path for $\text{H}_2\text{O}^+$ consumption but generally is much slower and not comparable to R17. Although other reactions are present in table 5.3 for H radical formation, R17 has by far the most contribution. Most of the H is consumed in R19 to form molecular hydrogen and hydroxide ions. Along with R19, R18 generates $\text{H}_2$. The major consumption of $\text{H}_2$ takes place in R39 to recycle H radical. $\text{H}_2\text{O}_2$ is also formed almost completely through R37. $\text{H}_2\text{O}_2$ also contributes to OH$^-$ regeneration from R23, although the amount of hydroxide generated from this path is negligible. It should be noted that the reactions involving ions and neutral radicals of Oxygen was not found to be important here because the initiator for those reactions is the dissolved $\text{O}_2$ in water, which was assumed to be absent in all simulations.

The centerline profiles of reduced electric field ($|\text{E}|/N$) for cases I, II and III under pulsed voltage at different time instances are shown in Figure 5.28. The highest $|\text{E}|/N$ value for all cases is observed at 3 ns, where the applied voltage reaches the peak. In cases, I and III, where $\text{H}_2\text{O}$ ionization is active, $\text{H}_2\text{O}^+$ ions are produced in large amounts resulting in lower electric field magnitude. Also, as discussed before, these ions increase the electrostatic forces acting on the system and increase the fluid density. The combined effect is the decrease in reduced electric field. The drop $|\text{E}|/N$ in case II is mostly because of density variation and is confined to a small region near the electrode surface ($\sim 15\mu$ from the electrode). Compared to the cases with linear applied voltage (Figure 5.21), higher peak $|\text{E}|/N$ values are observed for pulse cases.

Figure 5.29 shows the centerline distribution of electron formation rates by reactions R1 and R2 under pulsed voltage condition. It can be seen that R1 has smaller value at 2 ns compared to R2 because R2 has lower threshold energy. By increasing
Figure 5.28: Variation of reduced electric field (|E|/N) for at the centerline at different time instances for a) Case I, R1: H$_2$O ionization via tunneling process, b) Case II, R2: electron detachment from OH$^-$ ions and c) Case III, combined electron formation from both R1 and R2 reactions. (Pulsed voltage, $V_{\text{max}} = 15kV$).

Voltage to 15 kv, at 3 ns, the rate of R2 falls behind R1. Also, at the initial stage, R2 consumes the pre-existing OH$^-$ ions while fast rise in voltage does not allow the OH$^-$ recycling reaction to recover enough OH$^-$ to sustain R2. At 5 ns, the maximum R2 rate becomes higher that R1. The spacial distribution of R1 and R2 is better shown in contour plots of Figure 5.31. Generally, R1 predecease significantly in regions far from electrode, whereas R2 continues to remain active due to its low energy barrier and the presence of OH$^-$ ions. The travling wave observed in Figure 5.31 for R1 is because of the traveling high density zone described in chapter 4. This wave is only seen in pulse cases. This higher density core results in a higher H$_2$O number density and higher R1 rate. Also, the rate constant for R1 is smaller in the regions behind the wave because of lower electric field magnitude near the electrode (Figure 5.28c).

In Figure 5.30, the formation rate of solvated electrons from R8 and R30 at different time instances along the centerline under linear voltage ramp is presented. Reactions R8 and R30 are the key paths that act as the formation route of solvated electrons. Similar to the linear ramp case, the major source of $n_{\text{eq}}$ is the hydration reaction R8 and reaction R30 does not have significant contribution.
Figure 5.29: Centerline distribution of electron formation rate from R1 and R2 at different time instances for Case III under pulsed voltage, ($V_{\text{max}} = 15kV$)

Figure 5.30: Centerline distribution of solvated electron formation rate from R8 and R30 at different time instances for Case III under pulsed voltage ($V_{\text{max}} = 15kV$).

The volume averaged reactions rates of the dominant formation and consumption routes for electrons at different time instances for the cases under pulsed voltage are shown in Figure 5.32. As already discussed, R2 (electron detachment from OH$^-$) has a higher share in generating electrons at initial stages. At 3 ns, the voltage reaches its peak value and R1 (H$_2$O tunneling) gets ahead of R1. The maximum volume averaged rates of R1 and R2 at 3 ns are $1.9 \times 10^{34}$ and $4.4 \times 10^{33}$ m$^{-3}$s$^{-1}$, respectively. Compared to the corresponding ramp case, these values are about 3 order of magnitude higher. Since the maximum voltage is identical in linear ramp and pulse cases, this difference can be attributed to the high density zones formed
by electric forces which has higher $n_{H_2O}$ and thus, R1 values. Before 3 ns, All of the electrons are generated via R1 while at 3 ns, 80% of electrons are formed by R1 channel. As the voltage decreases after 3 ns, R2 becomes the major channel for electron formation. At 4 and 5 ns, 97 % and 100 % of electrons are formed by R2, respectively. Apart from voltage drop, the low density zone is developed in the region about 15$\mu$m from the electrode (Figure 5.3f). $n_{H_2O}$ is directly related to density and is smaller in that zone. As a result, rate of R1 is lower in this zoned. On the other hand, R2 is active in lower electric fields and farther locations, thus having a higher volume average rate. Examination of consumption rates reveals that very small fraction of electrons are consumed by R7 recombination reaction. The only consumption pathway for electrons is R8 solvation reaction.
Figure 5.31: Spatio-temporal contour plots of R1 (left) and R2 (right) reaction rate for combined H$_2$O and OH$^-$ ionization under pulse condition, ($V_{\text{max}} = 15kV$).
Figure 5.32: Volume-averaged reaction rates of the dominant formation and consumption reaction paths of electrons for Case III, under pulsed voltage conditions ($V_{\text{max}} = 15kV$).
In addition to solvation of electrons (R8), R30 \((H_{aq} + OH_{aq}^{-} \rightarrow e_{aq} + H_{2}O_{aq})\) is the only channel for formation of solvated electrons. As mentioned before, rate of R8 is the highest at the voltage peak, where electron number density is maximum. Compared to R8, \(e_{aq}\) generated by R30 is negligible. At 1 ns, R22 \((e_{aq} + H_{3}O_{aq}^{+} \rightarrow H_{aq} + H_{2}O_{aq})\) and R16 \((e_{aq} + H_{2}O_{aq} \rightarrow H_{aq} + OH_{aq}^{-})\) are the major consumption routes for \(e_{aq}\) with 68 and 32% of total consumption. At 2 ns, R18 \((e_{aq} + e_{aq} ( + 2H_{2}O_{aq}) \rightarrow H_{2aq} + 2OH_{aq})\) also becomes active. At 3 ns, R16 is almost inactive and 77 % of aqueous electrons consumption occurs through R18. As mentioned before rate of R18 has a second order dependence on aqueous electron number density and responds quadratically to the changes in electron number density. At the later stages of simulation, a drop is observed in the rate of R18 while the role of R17 \((e_{aq} + H_{2}O_{aq}^{+} \rightarrow H_{aq} + OH_{aq})\), R19 \((e_{aq} + H_{aq} + H_{2}O_{aq} \rightarrow H_{2aq} + OH_{aq}^{-})\) and R20 \((e_{aq} + OH_{aq} \rightarrow OH_{aq}^{-})\) becomes more important. At \(t = 5\) ns, R17, R19, R20, R21 and R18 consume 23, 21, 20, 20 and 15 % of aqueous electrons, respectively.
Figure 5.33: Volume-averaged reaction rates of the prominent formation and consumption reactions of the solvated electrons for Case III, under pulsed voltage conditions ($V_{\text{max}} = 15\text{kV}$).
Figure 5.34 shows the volume averaged reactions rates of formation and consumption routes of $\text{OH}_{aq}^-$ at different time instances for cases II and III under pulsed voltage. When both R1 and R2 ionization channels are present (Case III), t=1 ns, $\text{OH}_{aq}^-$ is formed by R16 ($e_{aq} + \text{H}_2\text{O}_{aq} \rightarrow \text{H}_{aq} + \text{OH}_{aq}^-$) and R43 ($\text{O}_{aq}^- + \text{H}_2\text{O}_{aq} \rightarrow \text{OH}_{aq}^- + \text{OH}_{aq}$) reactions with the share of 33 and 67 %, respectively (Figure 5.34b). Note that the overall rate of hydroxyl ion production at 1 ns is negligible ($\sim 3 \times 10^{16}$ m$^{-3}$s$^{-1}$). From 2 ns onward, R43 is no longer significant since high number off electrons are available for R16 and R18 to proceed. At 2 ns, the first order reaction R16 is dominant but with increase in electron number density, the second order R18 reaction gains ground. While at 2 ns 53 % of hydroxyl ions are produces by R16, this share almost zero at 3 ns. On the other hand 85 % of $\text{OH}_{aq}^-$ is formed through R18. Also, R19 ($e_{aq} + \text{H}_{aq} + \text{H}_2\text{O}_{aq} \rightarrow \text{H}_2\text{aq} + \text{OH}_{aq}^-$), R20 ($e_{aq} + \text{OH}_{aq} \rightarrow \text{OH}_{aq}$) and R21 ($e_{aq} + \text{O}_{aq}^- + \text{H}_2\text{O}_{aq} \rightarrow \text{OH}_{aq}^- + \text{OH}_{aq}$) are absent initially but gains importance from 3 ns forward, producing 22, 21 and 41 % of hydroxyl ions while only 16 % is generated by R18. The overall rate of formation of $\text{OH}_{aq}^-$ has its highest value at t = 4 ns which is about $5 \times 10^{33}$ m$^{-3}$s$^{-1}$. Same as the cases with linear applied voltage, almost all of hydroxyl ions are consumed by R2. At t = 1 ns the only significant $\text{OH}_{aq}^-$ consumption reaction is R52, because the electric field is not strong enough to overcome the threshold energy of R2. From 2 to 4 ns, R2 is the dominant pathway for aqueous hydroxyl ion consumption. However, at 5 ns, the share of R2 drops down to 35 % and R40 consumes 65 % of $\text{OH}_{aq}^-$. When R2 is the only route for electron generation (Case II, Figure 5.34a), the volume average rates of each reaction as well as the overall $\text{OH}_{aq}^-$ formation rate are identical to case III ($3.3 \times 10^{16}$ m$^{-3}$s$^{-1}$ overall rate). However, the maximum overall hydroxyl ion generation rate is only about $6 \times 10^{22}$ m$^{-3}$s$^{-1}$ compared to $5 \times 10^{33}$ m$^{-3}$s$^{-1}$ for the case with both R1 and R2 channels. At 3 ns, major routes for hydroxyl ion generation are reaction R16 (47%) and R18 (44%). After 3 ns, R20 also becomes considerable. At 5 ns, R16 and R18 has
each 34 % share on OH$_{\text{aq}}$ production while 31 % is being formed through R20. The major difference between case II and III (Figures 5.34a and 5.34b) is the availability of electrons via R1. In case III, considerable amounts of electrons are generated by R1 and electron driven reactions like R18-R21 recover the hydroxyl ions consumed by R2. In the absence of R1, these reactions proceed with much slower rate. Again at t = 1 ns, R52 in only sink for OH$_{\text{aq}}$ because R2 is not active yet. After t = 2 ns, R2 is the major hydroxyl ion consumption channel and share of R52 remains below 1 %.
Figure 5.34: Volume-averaged reaction rates of the prominent formation and consumption reactions of OH\textsubscript{aq} for a) Case II and b) Case III, under pulsed voltage conditions (V\textsubscript{max} = 15kV).
Simulations were also conducted with higher maximum driving voltage to determine its impact on the plasma chemistry. In this section, results of simulations with 20 kV linear ramp are presented. Simulation of 20 kV with pulsed applied voltage was not successful because the code could not handle the sharp time gradients imposed by the fast changing potential boundary condition. Figure 5.35a illustrates the distribution of electron number density along the centerline at different times for 20 kv ramp case with only H$_2$O tunneling as electron source. The peak $n_e$ observed is $5.5 \times 10^{23} \text{ m}^{-3}\text{s}^{-1}$, 57% higher compared to similar case with 15 kv. Comparing Figure 5.35b with Figure 5.5b, shows that the peak value of $n_e$ remains unchanged by increasing maximum applied voltage from 15 to 20 kV. Finally, as shown in Figure 5.35c, the peak $n_e$ is 10 times higher than for corresponding 15 kV case. The different response to increase in driving voltage in these cases is because of the dependence of rates of R1 and R2 to electric field and also the kinetics of hydroxide ion recycling. As mentioned before (Figure 5.20), the raise in rate of R2 with electric field is sharper than R1. However, R2 depends on OH$^-$ ions to sustain, which is supplied by slower aqueous reactions. The rates of these reactions does not increase sufficiently to provide hydroxide for R2 when another electron source is not present. On the other hand, in the case with both ionization channels, the electrons generated by water tunneling facilitate OH$^-$ recycling which leads to higher ionization rates via R2. In all three cases shown in Figure 5.35, the ionization waves have traveled faster and regions far from electrode are affected compared to 15 kV case.

In Figure 5.36, the spatial evolution of H$_2$O$^+$ at the centerline at different time instances for cases I and III with applied 20 kV linear ramp voltage is presented. Peak H$_2$O$^+$ number density values are $5.63 \times 10^{25}$ and $3.13 \times 10^{25} \text{ m}^{-3}$ for cases I and III, respectively. Unlike the 15 kV simulations where R1 (case I) and combined R1 and R2 (case III) cases had identical H$_2$O$^+$ peak values, a slight decrease is observed in case III compared to case I. This is because of the transport of H$_2$O$^+$ ions subject to
stronger electric field. Also, at higher electric fields, higher concentration of H$_2$O$^+$ is formed and consequently reactions R15 and R51 becomes fast enough to convert a higher fraction of H$_2$O$^+$ to H$_3$O$^{+}$.

Same behavior for the reduced electric field ($|E|/N$) is observed for 20 kv case, as seen before for 15 kv. As shown in Figures 5.37a and 5.37c, the reduction in local $|E|/N$ is caused by accumulation of positive ions and also compression of liquid. The former results in decrease in electric field and the later leads to increase in $N$. The highest increase compared to 15 kV cases, is for OH$^-$ tunneling (Figure 5.37b)
where the local decrease in $|\mathbf{E}|/N$ happens later. In the case with both H$_2$O and OH$^-$ tunneling, the maximum $|\mathbf{E}|/N$ was found to be 30 Td.

![Figure 5.37: Variation of reduced electric field ($|\mathbf{E}|/N$) for a) Case I, b) Case II and c) Case III along the center line at different time instances for ramp case ($V_{\text{max}} = 20kV$).](image)

It was also found that for 20 kV maximum applied voltage, the rate of R2 is always higher than R1 while for the 15 kV case, R2 is initially the significant channel for electron generation but later falls behind R1. For the case with both tunneling reactions present, the rate of electron formation is almost the same at 1 ns (about $5 \times 10^{27} \text{ m}^{-3}\text{s}^{-1}$). At 5 ns, the rates are $2 \times 10^{33}$ and $4 \times 10^{34} \text{ m}^{-3}\text{s}^{-1}$ for 15 and 20 kV cases, respectively.

In Figure 5.38, variation of OH$_{aq}$ number density ($n_{OH_{aq}}$) for H$_2$O, OH$^-$ and combined H$_2$O and OH$^-$ ionization along the center line at different time instances is given for 20 kV ramp case. Compared to 15 kV, a slight increase is observed for hydroxide ion concentration for H$_2$O and OH$^-$ cases with $V_{\text{max}}=20$ kV (Figures 5.38a and 5.38b). OH$^-$ number density shows 10 times increase for the case with both H$_2$O and OH$^-$ tunneling channels compared to 15 kV case. Also, in all cases in Figure 5.38 the reaction zone is advanced further (Almost two times for cases a and b) because of higher electric field.

The volume averaged rates of formation and destruction of electrons by different reactions are given in Figure 5.39 for 20 kV ramp case with both R1 and R2 tunneling reactions considered. In contrast to 15 kV case, for 20 kV applied voltage electron
Figure 5.38: Spatial evolution of OH$_{aq}^-$ number density ($n_{OH_{aq}^-}$) for a) Case I, b) Case II and c) Case III along the center line at different time instances for ramp case. ($V_{max} = 20kV$).

generation from R2 is always higher than from R1, except at 2 ns. The reason for different trend at 2 ns is the delay in initiation of OH$^-$ generation reactions. Also, R7 recombination reaction has less contribution in destruction of electrons compared to R8. In other words, in electrons has more chance to get solvated before reacting with H$_3$O$^+$. This is because less H$_3$O$^+$ is produced since the major tunneling reaction is R2 rather than R1.
Figure 5.39: Volume-averaged rates of formation (top) and destruction (bottom) of electrons by different reactions for ramp case with R1 and R2 electron sources ($V_{\text{max}} = 20\,kV$).
Figure 5.40 shows the volume averaged rates of formation and destruction of hydroxide ions by different reactions for 20 kV ramp case with both R1 and R2 tunneling reactions considered. At t = 1 ns, most of OH$^-\,$ is generated with equal shares by R16 and R18. Later, R16 looses its contribution and R18 becomes important. At 5 ns, 68% of hydroxide ion formation is done R20 because large amounts of OH radical is generated by R2. At the same time, 15 and 12% of OH$^-\,$ is formed through R18 and R19, respectively. R2 is the main destruction path for OH$^-\,$. Almost all of the OH$^-\,$ is converted to OH radical now.
Figure 5.40: Volume-averaged rates of formation (top) and destruction (bottom) of OH\(^-\) by different reactions for ramp case with R1 and R2 electron sources (\(V_{\text{max}} = 20kV\)).
5.5 Conclusions

A detailed chemistry modeling approach was implemented to simulate the effect of different field ionization paths. Also, an aqueous chemistry mechanism was included to study the interaction of plasma with water. The simulations were conducted for the same powered needle-like electrode and same ramp and pulse voltage profiles considered in chapter 4. The results show that tunneling detachment of electrons from OH\(^{-}\) happens at lower electric field strengths, whereas by increasing electric field, electron detachment from water molecules becomes the major ionization route. Due to the limit in the availability of OH\(^{-}\) compared to H\(_2\)O, water ionization generates considerably higher number of electrons. Detachment from OH\(^{-}\) is still ongoing, although not significant, when the field magnitude is sufficient for H\(_2\)O to undergo electron detachment. As electron detachment converts pre-existing hydroxide ions to electrons and hydroxyl radicals, more hydroxide is generated by electron processes. In presence of H\(_2\)O tunneling, more electrons are available for recycling of OH\(^{-}\).

It was also found that reaction of e\(_{\text{aq}}\) with water is the major recycling path for hydroxide ions. In presence of H\(_2\)O tunneling, sufficient electrons are produced to sustain the recycling of OH\(^{-}\) and hence OH\(^{-}\) tunneling.

Comparing results of simulations at 15 and 20 kV, showed that electron detachment by tunneling from OH\(^{-}\) is the major source of electrons at higher voltages.

The results further show that the electrostatic force plays a key role in higher degrees of ionization. While polarization and electrostrictive ponderomotive forces are dominant in close to neutral situations, their magnitude is not directly affected by net charge of the system but affected indirectly by the perturbation of electric field caused by alteration of polarity. The velocities calculated with detailed chemistry model and H\(_2\)O ionization mechanism is very close to the results obtained in chapter 4 with simple chemistry.
Results of comparison between linear ramp and rapid pulse voltage profiles applied to powered electrode are in accordance with findings of chapter 4 where a simple chemistry model is considered. In presence of both H\textsubscript{2}O and OH\textsuperscript{–} field ionization routes, two ionization waves are observed where the first one is caused by electron detachment from water and the second one from hydroxide ion. For the ramp case, electron generation is increased by linear increase in electrode voltage and the produced electrons are solvated until reaching a fixed concentration. For pulse case, the rate of electron generation drops after a fast raise. The concentration of solvated reactions responds quickly to the changes in electron concentration.
Plasma discharges generated directly in a liquid medium require much higher breakdown electric fields due to very high liquid densities compared to densities in a gas. One proposed method of facilitating discharge in liquids is to inject low density nucleation site in the liquid in the form of gas bubbles and allow plasma generation in the small encapsulated gas phase. The higher reduced electric field ($|E|/N$) values and significant field enhancement that occurs in the phase boundary due to sharp change of dielectric constants, enables triggering the discharge at lower voltages [12, 36, 49, 50, 52, 53].

Although breakdown voltage can be lowered with gaseous bubbles, the interaction between the plasma and liquid is limited because the discharge occurs in the gaseous medium and requires the species generated in the gas phase to be transported to the liquid medium. Hamdan and Cha [53] proposed to employ two different liquid with dissimilar dielectric properties to take advantage of the discontinuity in the dielectric property at the interface. They considered a non-polar liquid n-heptane, which has a lower dielectric strength, above a water layer. Their experimental setup is shown in Figure 2.4a. They defined the discharge probability (DP) as the percentage of successful discharges out of more than 200 applied pulses for a given interfacial position ($h$) at a given electrode gap ($d$). Figure 2.4b shows the variation of DP with interface position.
The electric field magnitude here is lower than the cases considered in chapters 4 and 5. Therefore, the ionization by electron detachment via tunneling is not likely. In contrast, electron impact ionization in nano-voids created by cavitation could be a possible path for the plasma initiation process. As discussed by Li et al [86], the rate of cavity formation can be related to the negative pressure by classical nucleation theory [30]. The nucleation rate in unit volume per second is given as:

$$\Gamma = \frac{|p_{\text{total}}|^3}{16\pi (\sigma k_\sigma)^{3/2}} \frac{3k_BT}{4\pi h} \exp \left( -\frac{16\pi (\sigma k_\sigma)^3}{3k_BT |p_{\text{total}}|^2} \right)$$ (6.1)

where $T$ is the temperature, $p_{\text{total}}$ is the total pressure, $k_B$ is the Boltzmann’s constant, $\sigma$ is the surface tension and $k_\sigma$ is surface tension correction factor (0.26 for water [30]).

The probability of cavitation ($\Sigma$) can be estimated as

$$\Sigma = 1 - \exp (-\Gamma V_{\exp} \tau_{\exp})$$ (6.2)

where, $V_{\exp}$ and $\tau_{\exp}$ are the experimentally measured volume and time span in which the negative pressure is applied, respectively. ($V_{\exp} \tau_{\exp} = 10^{-11} mm^3.s$) [86]. Equations (6.1) and (6.2) can be used to calculate the cavitation probability from the total pressure.

6.1 Problem statement

A two-fluid system consisting water (phase 1, $\epsilon = 80$) and n-heptane (phase 2, $\epsilon = 2$) is studied. The multi-phase plasma model is used for investigating the effect of interface location and voltage profile on discharge probability. Figure 6.1a depicts the computational domain for the liquid phase plasma discharge simulations. An unstructured mesh was generated by Gmsh [78] (Figure 6.1b) consisting of tetrahedral and hexahedral cells. Total number of cells was 8700.

It is assumed that the discharge probability is directly related to the probability of cavitation parameter introduced in Eq. (6.2). Plasma reaction mechanism consists
of reactions R1, R2 and R7 in table 5.3 is included. The geometry used is similar to the one studied by Hamdan and Cha [53] (Figure 6.1a). The distance between two electrodes is 1.5 mm. \( h \) is defined as the distance of interface from the tip of powered electrode. ‘h’ has a positive value if the interface is located above the anode and has negative value if it is located between two electrodes.

![Figure 6.1: a) Schematic of the problem geometry, b) computational mesh considered in the present study](image)

6.2 RESULTS AND DISCUSSION

To study the electric forces (Eq. (3.4)) and their impact on the hydrodynamics of multi-liquid configuration, a set of simulations were conducted with fixed voltage applied to the powered electrode for a longer time. Typically, in nano-second discharges, the time is so short that the displacement of the interface cannot be distinctly determined. Two cases were simulated with initial interface location above and below the tip of the powered electrode (\( h=1, -0.5 \) mm respectively). A 10 kV fixed voltage was applied for both cases. Figure 6.2 shows the interface location and electric field.
vectors for the two cases at different times. By comparing two cases, a significant difference is observed in the electric field vector field. For the case with $h=1$, the electric field vector is almost parallel to the interface in the vicinity of powered electrode while for $h=-0.5$, the electric field vector is normal to the interface. The electric field magnitude at different times is presented in Figure 6.3. The peak magnitude of electric field for these cases are $6.9 \times 10^7$ and $1.7 \times 10^8 \ V/m$, respectively. Although the peak electric field for the first case is smaller than that of the second case, in the first case ($h=1$), the position of peak electric field is in the water phase with higher dielectric permittivity. From Eq. (3.54), it is evident that the ponderomotive force directly depends on the dielectric permittivity. Therefore, higher ponderomotive force is generated in cases where the interface is located above the anode tip. Besides dielectric permittivity, ponderomotive force depends on the gradient of electric field which always has the highest value near the curved electrode. As a result, the ionizable fluid (i.e. water) should be present in the region with the sharpest gradients of electric field (i.e. curved electrode). Examining the displacement of interface for the two cases shows that in the first case, the upward movement of interface is observed after 50 $\mu s$ whereas for the second case only a slight distortion is seen at 500 $\mu s$. In Figure 6.4, contours of velocity magnitude and streamlines at different times is presented. In both cases, the vortex starts from the tip of electrode where the highest velocity takes place. In the first case, the vortex is formed near the interface, while for the second cases, it is formed in the organic phase. This is particularity important in reactor design for multi-liquid configuration where a suitable mixing pattern can be achieved by changing interface location.

Figures 6.5 and 6.6 show the distribution of ponderomotive and polarization force at 50 $\mu s$ for two cases. In both cases, ponderomotive force is the dominant force near the electrode and at the interface. The polarization force is only active on the interface, where a gradient of dielectric permittivity is present. Comparing the
Figure 6.2: Electric field vectors and interface location for $h=1$ (top) and $h=-0.5$ (bottom) with a fixed applied voltage ($V=10$ kV)

Magnitudes of ponderomotive and polarization show that even on the interface, the effect of polarization force is negligible compared to ponderomotive. The maximum magnitude of in the two cases are almost identical ($2 \times 10^{11} N/m^3$). However, in the first case ($h=1$), higher force density is seen near the interface which is responsible for the interface displacement. Although polarization force does not have significant effect in hydrodynamics of the system, a higher magnitude of is observed in the first case. (Figure 6.6).

Microsecond pulse was applied to study the effect of pulsing applied voltage on the hydrodynamics of the system. The applied voltage profile is shown in Figure 6.7.
The pulse is generated by Eq. (4.2) with $\tau_1 = 3 \times 10^{-6}$ and $\tau_2 = 7 \times 10^{-6}$. The repetition rate of the pulse was 10 kHz.

In Figures 6.8 to 6.11 the patio-temporal contour plots of velocity magnitude and phase distribution for the cases with $h=1$ and $h=-0.5$ are presented. These simulations are done with repeating pulses and the plots are generated after 1st, 3rd, and 7th pulses. Comparing two cases, displacement of interface is only observed in the first case where the total electric force has stronger vertical component due to the direction of the electric field near the interface. The magnitude of polarization forces is very close in two cases but for the case where $h=1$, the ponderomotive force is an order of magnitude higher than the one with $h=-0.5$. As mentioned earlier, polarization force is only active near the interface and negligibly small magnitude compared to ponderomotive force. Therefore, the hydrodynamics of the system is
Figure 6.4: Velocity magnitude and streamlines for $h=1$ (top) and $h=-0.5$ (bottom) with a fixed applied voltage ($V=10$ kV)

mostly affected by ponderomotive force. Like the simulations with fixed voltage, in the cane with $h=-0.5$, the displacement of interface is not observed. Comparing the velocities in two cases, one can see that higher velocities are observed in the case where interface is located below the anode tip (i.e. $h=-0.5$). In this case, the zone with highest $F_{pon}$ is in the n-heptane phase which has a lower density compared to water. As a result, the fluid body accelerates faster when the electric force is applied. It should be noted that ponderomotive force and hence, hydrodynamics of the system, is a strong function of electrode shape. Regardless of initial interface location, gradient of electric field is mainly a geometric function and sharp gradients happen where the electrode is curved or has sharp corners.
Figure 6.5: Contour plots of ponderomotive force density for $h=1$ (left) and $h=-0.5$ (right) with a fixed applied voltage ($V=10$ kV)

Figure 6.6: Contour plots of polarization force density for $h=1$ (left) and $h=-0.5$ (right) with a fixed applied voltage ($V=10$ kV)

The probability of discharge is studied for five cases where the interface location is varied. Nano-second pulse with the peak voltage of $15$ kV and rise time of $3$ns was applied at the powered electrode. The pulse profile is same as the one used in the other simulation efforts. In Figure 6.12 the initial interface location of these cases is
Figure 6.7: Microsecond pulse applied in pulsing voltage cases

presented. It was found that Zenner tunneling is not active in the range of electric field encountered here. Also, because of extremely short time scales, interface does not undergo any observable displacement within the discharge time. Hamdan and Cha [53] have related the discharge probability (DP) to the magnitude of electric field (Figure 2.4b). They have concluded that when the position of the interface was between the electrodes ($-1.5 < h < 0 \, mm$), the intensity of the electric field at the tip of the anode dropped significantly and becomes insufficient to ignite the discharge. They made an attempt to relate the discharge probability to electric field magnitude. Although the trends of electric field magnitude for some h values match the experimental DP, they have not been able to obtain a generalized relation between electric field and DP.

Figure 6.13a summarizes the peak values of reduced electric field ($|E|/N$) for different interface locations. The maximum $|E|/N$ is observed for the case with h=0, i.e. the interface is at anode tip. At this situation, the phase discontinuity coincides with the sharpest curvature of electrode resulting in highest possible electric field. By increasing h, the phase discontinuity location moves away from the interface and peak electric field intensity decreases. The profile of $|E|/N$ in Figure 6.13a is not
in agreement with experimental observations of Hamdan and Cha (Figure 2.4b). Specifically, the region with negative h values has smaller $|E|/N$ than the positive h zone but in the experiments, higher DP have been reported for this region. The probability of discharge at moderate electric fields is related to the formation of nano-voids. These nano voids are formed due to the presence of the electric forces, notably ponderomotive forces and its interaction with the fluid medium. It has already been shown that other two forces are negligible in the current cases. In Figure 6.13b, maximum ponderomotive force density is plotted against h. At h=-1, a lower $F_{pon,max}$ is seen compared to h=0.5 and h=1. This is due to the fact that the fluid with high dielectric permittivity (i.e. water) should be exposed to the sharp electric field gradient zone to generate sufficient electric force which takes place only for h>0 cases. The trend of $F_{pon,max}$ is in better agreement with the DP data of Hamdan and Cha compared to electric field intensity trends. As a result, discharge probability can be better explained by examining the electric forces rather than field intensity itself.

To study the nucleation rate and cavitation probability, it is required to express the electric forces in terms of electric pressure. The cavitation probability can then be related to total pressure by Eq. (6.2). The procedure for calculating the electric pressure has already been described in section 3.1 (Eq. (3.10)). The contours of cavitation probability ($\Sigma$) are shown in Figure 6.14 for different phase configurations. Based on these simulations, cavitation only happens in cases with h=0.5 and 0.0 and does not happen in the cases where the interface falls below the anode. This is in accordance with the findings of [53]. In the case with only water, cavitation is unlikely. This clearly proves the effectiveness of low dielectric liquid in enhancing cavitation in water. The discharge probability can be directly related to cavitation probability since the water vapor in the nano-voids created by cavitation are ionized by electron impact ionization and initiate the electron avalanche. It should be noted that although at h=0, the highest cavitation is seen, sufficient water might not be
available for cavitation because a part of high electric tension zone remains in the n-heptane phase. At h=1.0 mm, cavitation is not predicted by the simulations while with the same phase configuration, discharge is reported by [53]. This might be because of many factors, notably the shape of electrode and roughness of real electrode surface. Unlike the simulations, real electrode does not have ideally smooth surface and this roughness can generate sharp gradients in electric field which yields localized electric tension and cavitation.
Figure 6.8: Spatio-temporal contour plots of velocity magnitude and phase distribution for the case with interface located at h=1 and pulsing applied voltage (V\text{max} = 10 \text{ kV})
Figure 6.9: Spatio-temporal contour plots of polarization and ponderomotive forces density for the case with interface located at h=1 and pulsing applied voltage (V_{max} = 10 kV)
Figure 6.10: Spatio-temporal contour plots of velocity magnitude and phase distribution for the case with interface located at h=-0.5 and pulsing applied voltage (V_{max} = 10 kV)
Figure 6.11: Spatio-temporal contour plots of polarization and ponderomotive forces density for the case with interface located at $h=-0.5$ and pulsing applied voltage ($V_{\text{max}} = 10 \text{ kV}$)
Figure 6.12: Configuration of two liquids in discharge probability simulations (h is the distance of interface from the anode tip)

Figure 6.13: a) Peak reduced electric field (\(|E|/N\)) and b) peak Ponderomotive force for different interface locations
Figure 6.14: Contours of cavitation probability (Σ) for different liquids configurations at t = 3 ns
6.3 Conclusions

A multi-dimensional multi-phase model considering electric forces and cavitation probability has been developed to study the formation of plasma in the multi-liquid configuration. The simulations were conducted for a needle-plate electrode configuration in water and n-heptane system. Mathematical expressions were developed for electrical forces in multi-phase system and included in the model. Predictions from the model provide insight on the role of interface position relative to the anode tip on the discharge initiation process. It is observed that since the dielectric permittivity is discontinuous at the interface, the electric field is enhanced by a factor that depends on the relative value of the dielectric permittivity of the two liquids. The highest intensity of electric forces was observed in the case with interface exactly located at anode tip. For the cases with interface above the tip, a higher force density was observed whereas for the cases with interface below the tip smaller force density was seen. The magnitude of the electric forces has a direct relation with discharge probability in the liquid phase. Among the three electric forces, electrostrictive ponderomotive force has the dominant effect and others can be safely neglected for the cases studied. The results also showed that the convective effects significantly changes by changing the interface location resulting in a different interface displacement behavior and mixing pattern. It was further found that discharge probability can be related to total pressure using the nucleation relations. The results were in good agreement with the experimental data reported in literature.
Chapter 7

Conclusions and Recommendations for Further Work

7.1 Summary and Main Conclusions

A multi-dimensional multi-physics model was developed to simulate the early stage of plasma initiation in a liquid medium and effect of several parameters on the physico-chemical properties of the plasma was studied. The simulations were conducted for a powered needle-like electrode where the peak voltage and driving voltage profile was varied to assess its impact on the plasma initiation characteristics. The results show that the electrical body forces – electrostatic, polarization and electrostrictive ponderomotive, play a key role in generating strong density variation during the initial stage. Among the three electrical forces electrostrictive ponderomotive force which is directly dependent on the gradient of the electric field has the strongest contribution. It was also found that the fluid medium exposed to these electrical forces can easily reach cavitation threshold condition and forms lower density region near the vicinity of the powered electrode. Parametric study on the driving voltage profiles show that for an exponential voltage rise, the slow response of the fluid results in continuing variation in the fluid phase density and pressure during the voltage decay time. For a linear voltage rise (i.e. slower voltage rise), the resulting fluid velocity is directed towards the powered electrode which undergoes a reversal in direction as the voltage rise time is shortened via an exponential profile. It was further shown by the model that the polarization force only becomes effective when a density variation is estab-
lished and in general have slower response time. However, for a pulsed profile having exponential rise to the peak driving voltage, an earlier onset of strong polarization forces is observed resulting from fast and sharper variation in the fluid density. The major electron formation route was found to be field dependent – Zener tunneling based ionization process even though possible low-density fluid region is formed due to cavitation like conditions. The electric field across the low-density region, due to the small spatial and temporal scales do not reach conditions that allow electron impact ionization to be significant and prominent.

In the second part, the role of kinetics in the liquid phase plasma initiation was investigated. A detailed chemistry modeling approach was implemented to simulate the effect of different field ionization paths. An aqueous chemistry mechanism was included to study the interaction of plasma with water. The results show that tunneling detachment of electrons from OH\(^{-}\) happens at lower electric field strengths, whereas by increasing electric field, electron detachment from water molecules becomes the major ionization route. Due to the limit in the availability of OH\(^{-}\) compared to H\(_2\)O, water ionization generates considerably higher number of electrons. Detachment from OH\(^{-}\) is still ongoing, although not significant, when the field magnitude is sufficient for H\(_2\)O to undergo electron detachment. As electron detachment converts pre-existing hydroxide ions to electrons and hydroxyl radicals, more hydroxide is generated by electron processes. In presence of H\(_2\)O tunneling, more electrons are available for recycling of OH\(^{-}\). It was also found that reaction of e\(_{\text{aq}}\) with water is the major recycling path for hydroxide ions. In presence of H\(_2\)O tunneling, sufficient electrons are produced to sustain the recycling of OH\(^{-}\) and hence OH\(^{-}\) tunneling. The results further show that the electrostatic force plays a key role in higher degrees of ionization. While polarization and electrostrictive ponderomotive forces are dominant in close to neutral situations, their magnitude is not directly affected by net charge of the system but affected indirectly by the perturbation of electric field caused by
alteration of polarity. In presence of both \( \text{H}_2\text{O} \) and \( \text{OH}^- \) field ionization routes, two ionization waves are observed where the first one is caused by electron detachment from water and the second one from hydroxide ion.

Finally, the initial stage of plasma formation was studied in a multi-liquid configuration. A multi-dimensional multi-phase model considering electric forces and cavitation probability has been developed to study the formation of plasma in multi-liquid configuration. The simulations were conducted for a needle-plate electrode configuration in water and n-heptane system. Mathematical expressions were developed for electrical forces in the multi-phase system and included in the model. Predictions from the model provide insight on the role of interface position relative to the anode tip on the discharge initiation process. It was observed that since the dielectric permittivity is discontinuous at the interface, the electric field is enhanced by a factor that depends on the relative value of the dielectric permittivity of the two liquids. The highest intensity of electric forces was observed in the case with interface exactly located at anode tip. For the cases with interface above the tip, a higher force density was observed whereas for the cases with interface below the tip smaller force density was seen. The magnitude of electric forces has a direct relation with discharge probability in the liquid phase. Among the three electric forces, electrostrictive ponderomotive force has the dominant effect and others can be safely neglected for the cases studied. The results also showed that convective effects significantly changes by changing the interface location resulting in a different interface displacement behavior and mixing pattern. It was further found that discharge probability can be related to total pressure using the nucleation relations. The results were in good agreement with the experimental data reported in literature.
7.2 Recommendations for further work

This thesis has been mainly focused on the investigation of the initial stage of plasma formation in liquids. Further improvements to the model as well as several studies using the current model can be done. Here is a few recommendations:

1. Detailed modeling of phase change (i.e. cavitation) during the plasma discharge in water to get a deeper insight into the role of nano-voids in discharge formation.

2. The effect of impurities such as dissolved oxygen on plasma chemistry can give an understanding of the phenomena for more realistic situations.

3. Including a radiation sub-model may be beneficial. Unlike convection and conduction, radiation occurs in the extremely small time scales and might not be negligible in nano-second plasma discharges.

4. An external circuit, similar to the experimental apparatus used for generating discharge, can be included in the model. The information provided by circuit model such as voltage-current data might be useful for designing experiments or plasma devices.
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Appendix A

Academic vitæ
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EDUCATION

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RESEARCH INTERESTS

- Computational fluid dynamics
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MEMBERSHIPS & PROFESSIONAL SERVICES

- American Physical Society (APS) (2014 - present)
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- Conference Travel Grants:
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PRESENTATIONS

Oral presentations:


• A. Charchi Aghdam, T. I. Farouk, “A Volume of Fluid (VOF) Based Approach for Modeling Plasma Discharge in Multi-Fluid Configuration, 72\textsuperscript{nd} APS Annual Gaseous Electronics Conference (GEC), College Station, TX, October 2019.


**Poster presentations:**

• **A. Charchi Aghdam**, E. Viparelli, T. I. Farouk, Implementing a shallow water mathematical modeling approach for simulating plasma interaction in multiphase configurations, 72nd APS Annual Gaseous Electronics Conference (GEC), College Station, TX, October 2019.


• **A. Charchi Aghdam**, H. Gassabzadeh, S. Shafiee, Recovery of Chromium Tanning Liquor from Tannery wastewater, 10th Iranian Chemical Engineering Conference, Zahedan, Iran, November 2005.
Workshops conducted:

- OpenFOAM workshop, University of South Carolina, Columbia, SC, November 2015.
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- Advanced MATLAB workshop, Tabriz University, Tabriz, Iran, 2012.