Chapter 1

Introduction

1.1 Overview

Historically, the study of atmospheric-pressure plasmas (APPS) is indistinguishable from the subject of plasmas as a whole. However, the detail of the measurements and calculations have been limited by the complexity of APPS. The high pressure generally equates to a large number of neutral collisions which can drastically increase the number of possible reactions and the computational difficulty. In many cases, the data to model anything but the simplest reactions does not exist. Likewise, the high number of collisions can significantly complicate data analysis for a great number of plasma diagnostics. In addition, APPS typically feature high electric fields, short time scales, and unpredictable shapes, all of which make even the most basic observations challenging.

In the last several decades, some of this has begun to change. The advent of high-powered computing has produced a number of simulations for APPS with models of previously inaccessible detail. Similarly, advances in plasma diagnostics (particularly those based on optical phenomena) has made precise measurements in these extreme states of matter possible. As a result, the body of knowledge associated with APPS–dominant chemical reactions, degree of gas heating, modes of relaxation, etc.–has increased with tremendous speed. While some of this work is driven solely by scientific curiosity, much of it can be attributed to the broad range of applications for APPS.

Indeed, the applications are almost too numerous to list. One of the first uses of an APP, and plasma general, was to generate ozone for the purification of water. Around the same time, arc lamps (another type of APP) became a popular means for public lighting. To this day, similar arcs are the dominant industrial means for cutting and welding metals. In a sense, APPS have become almost mundane; the polymer skin of almost every potato chip bag is plasma-treated in order to improve the adsorption of ink.

Both of these cases represent relatively low-value transformations. For example, the cost of the plasma-treated polymer used for potato chip bags is on the order of cents. However, researchers have identified a number of opportunities where APP treatment can produce highvalue products. One such example is the use of plasmas as actuators on airfoils. An APP can alter the flow of air over a surface, and significantly increase the flexibility of modern aircraft. A surprisingly similar plasma can be used to sterilize tissue wounds and treat infections. Other work has shown that APPS can improve fuel efficiency in combustion engines.

In each of these cases, the way the plasma is formed, as well as its characteristics, can be immensely different. The original arc discharges were created between graphite rods connected to immense battery banks. Meanwhile, a modern research reactor studying plasma-assisted combustion might use a fast-switching semiconductor circuit. Over the years, several types of APPS have been developed for a number of situations: dielectric-barrier, corona, thermal arc, RF, microwave, pulsed, and more.

Within this array[1], the repetitively-pulsed nanosecond discharge (RPND) is particularly interesting. Generally speaking, a RPND is generated by an electrical pulse on the order of > 1 kV, lasting anywhere from < 1–100 ns. This pulse generates a wave of ionization (and light) which crosses from the powered electrode to the grounded one.

The resulting plasma can fill large volumes (on the order of liters) and can excite many atomic and molecular states with little heating. Changes to the pulse shape and amplitude can be used to enhance

[1] The interested reader is referred to Starikovskaia's review [1] which provides a general overview of APPS in the context of plasma-assisted combustion

specific atomic and/or molecular reactions. This flexibility is highly desirable in plasma processing where the emphasis is on selectivity of the reaction, and control of its rate.

RPNDS have been the extensively studied by several different groups of researchers. However, the body of work is focused on RPNDS in air.

Several research groups have focused on the development of pulsed nanosecond discharges in air. However, the complex chemistry associated with air plasmas obscures some of the more fundamental questions: how is the pulsed nanosecond plasma formed, how are the excited states of the system populated, what significance is there to reactions after the fast ionization wave, the spatial variation of system parameters, what kind of electron energy distribution can be expected? This study will emphasize spectroscopic measurements of a helium pulsed nanosecond discharge.

Such a system retains physical relevance given that helium is a common stabilizing additive to atmospheric pressure plasmas. At the same time, the more simple atomic structure lends itself to a more detailed examination using global models, kinetic simulations, and active spectroscopy. This work will focus its efforts on the description of the spatial variation of the pulsed-nanosecond discharge, an approximation of its electron energy distribution function, and a description of how the neutral atoms are excited.

The remainder of this chapter includes a review of the associated literature, as well as a discussion of basic discharge theory (diagnostic-specific theory will accompany the relevant chapters). Chapter **??** provides the necessary details of the experimental setup as well as some preliminary observations. Next, in chapter **??**, absolute measurements of the helium triplet metastable densities are presented. Chapter **??** covers more general emissions measurements. In order to provide a more clear understanding of the meaning of these measurements, we explore them using a global model and a particle kinetics model. Finally, we conclude in chapter **??** with a discussion of how the collection of models and measurements influences our understanding of the pulsed nanosecond discharge.

1.2 Literature Review

History of Atmospheric-Pressure Discharges

Like most physical phenomena, plasmas are typically only described under ideal circumstances. This means that neutral collisions, and subsequently, atmospheric plasmas, are often ignored. Neutral collisions tend to obscure the electromagnetic effects that distinguish a plasma from a gas. However, the history of observation and study of plasmas is indelibly linked to atmospheric plasmas. Lightning and static sparks are the most prevalent plasmas on earth. Indeed, the among the first artificial plasmas was a constant atmospheric arc gen-

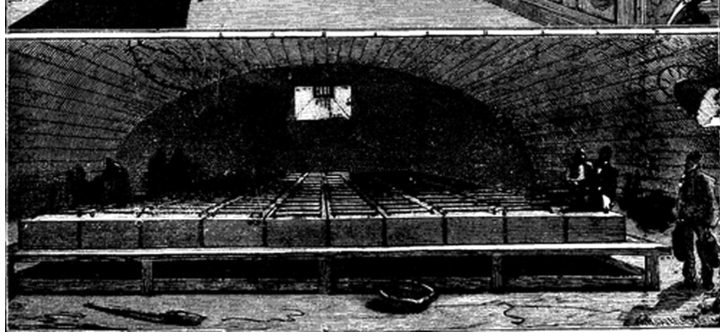

Figure 1.1: This is a test.

erated in 1802, the work of a Russian scientist named Vasilii Petrov [2].

Indeed, at present, there's a relative abundance of different atmospheric pressure discharges: dielectric-barrier, RF, microwave, glow, pulsed, and more. Each has unique range of parameters in which it operates, and a survey of all possible atmospheric discharges would be excessive. Instead, we shall focus on the two most common discharges which, together, illustrate the distinct advantages of the nanosecond-pulsed discharge.

The work of Petrov was the forerunner to what is now referred to as the study of thermal arcs. Such plasmas are common in industrial lighting systems, and for a time were even used as the primary nigh-time illumination of Detroit. Perhaps more common, is the use of thermal arcs for the welding or cutting of metals. This potential was recognized early on. Volta's recent invention of the voltaic pile provided the first source of constant and sufficient electrical energy. Using a series of voltaic cells, Petrov was able to draw the first electrical arc between two sticks of carbon. Its blinding light was recorded in a number of historical prints, such as figure 1.2. Aside from this light, the arcs were characterized by their significant ionization, and high degree of thermal equilibrium. Gas temperatures could reach

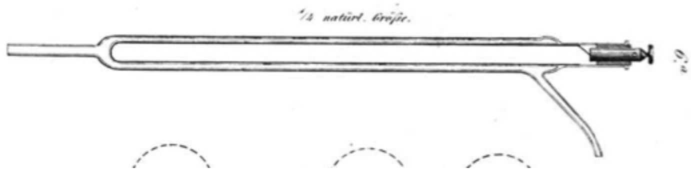

Figure 1.2: Werner von Siemens' silent discharge. Per Rackham requirements, the caption text should be singled-spaced, regardless of the text body. I'm giving this a test right here. Yep. It should stay single-spaced. Pretty please?

thousands of kelvin.

Both the primary advantage and disadvantage of thermal arcs are their high operating temperatures. These high operating temperatures correlate with the ability of the plasma to convert electrical energy to thermal energy; of great values in welding or for continuum light generation. In these plasmas, some of the energy is also converted to excited atoms or molecules. In some cases, these species may be desirable for processing a material. However, contact with these high temperatures will often lead to destruction of the substrate.

In contrast, later work by Werner von Siemens [3], led to the discovery of the so-called "silent discharge," seen in figure 1.2. In recent years, the terminology has changed and this type of discharge is now referred to as a dielectric-barrier discharge, or DBD. The DBD was significantly different from the thermal arc. Visually, it was much dimmer, and appeared to be composed of many thousands of individual filaments. Additionally, the DBD did not significantly heat the air, unlike the thermal arc. Finally, the DBD was used in the first commercial plasma application: ozone generation and water purification. Notably, both the thermal arc and silent discharge predated the 'official' discover of plasma by Sir William Crookes in 1872.

The DBD could be used process materials. Indeed, it has become common to use this type of discharge to treat polymer films, as well as clothes, and medical equipment (sterilization). However, like the thermal arc, there are some limitations. DBDs are not particularly uniform as a result of the large numbers of filaments. Thus, uniform processing will only occur as a result of long processing times–when the relatively random position of these filaments is averaged out–or if the desirable species has a long enough life to diffuse away from where it was created. Another limitation to DBDs is that the filaments characteristics are not a strong function of the applied voltage. This leads to limited flexibility in control of the plasma characteristics.

Nanosecond-Pulsed Plasmas

For a substantial period of time, these two discharges represented the range of atmospheric-pressure plasmas (APP). The thermal arc, though useful, could not be used on delicate substrates. It had the additional problem of having relatively little control over its chemical kinetics. Meanwhile, the DBD was relegated to ozone production and polymer processing (relatively low-value applications). Though the DBD had

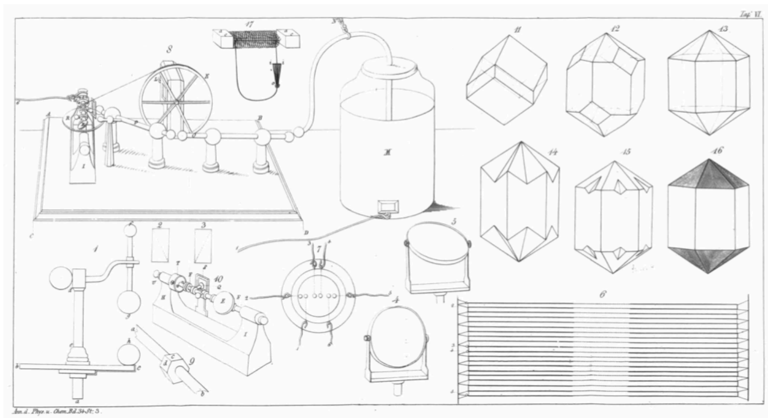

Figure 1.3: Sketches of the discharge apparatus and measurement system used by Wheatstone.

attractive thermal properties, little else was known about how it operated, and how to control its properties. As recently as 2007, the National Academies noted that "the full promise of APPS will be known only if they can be understood and managed based on fundamental scientific principles at two extremes–the nanoscopic kinetic level, where selective chemistry occurs, and the global stability level, likened to aerodynamics." [4]

As with the discovery of the thermal arc and the dielectric barrier discharge, the first pulsed discharges were studied prior to the official discovery of plasma. In 1835, Charles Wheatstone attempted to measure what he called the velocity of electricity in a spark gap, powered by a Leyden jar [5]. In hindsight, the question was poorly phrased; Maxwell's equations had not yet been formalized, and electrons weren't recognized as the carriers of electrical current. Nevertheless, though poorly controlled, the phenomena was essentially the same as modern pulsed nanosecond discharges.

Conceptually, the work of Wheatstone was promising, however the measurements were quite inaccurate. One particularly important outcome of Wheatstone's work was the subsequent observation by von Zahn [6] that the particles emitting the light were not travelling at anywhere near the velocity of the wave of light. J.J. Thomson later repeated the experiment with a 15 m tube, in order to obtain an improved estimate of the wave velocity and its direction [7]. He estimated the velocity of the wave to be approximately one half the speed of light, traveling from the anode to the cathode.

These high velocities caused an moderate amount confusion, particularly because there appeared to be no associated motion of the emitting particles. Subsequent examinations be Beams [8] confirmed the velocity measurements, and more importantly demonstrated that, regardless of the polarity of the applied potential, the luminous wave always travelled from the high potential to the low potential electrode. He additionally noted that the large pulse of current associated with such waves was not detected until after the wave had crossed the length of the tube. This observation led to the astute observation by Beams that the apparent motion of the luminous front was more likely a moving region of ionization.

As observed by Loeb [9] in his unifying description of pulsed nanosecond discharges, aside from the group of people studying the propagation of light in rarefied gas discharges, were a different set of scientists working on the origin of lightning. The endeavor was ambitious, for many of the same reasons that atmospheric discharges have always been difficult to study. Basically, no one was quite sure where to point their cameras, and when to open the shutters. Though out of the scope of this paper, the information gleaned from these studies was both relevant and useful in the development of the theory underlying ionization waves. Interested readers are referred to the review by Gurevich and Zybin [10] for an overview of the models employed in describing natural lightning.

Though studies continued intermittently after a burst of interest in the 1930s, it wasn't until the mid-1960's and 1970s when any significant attention came to the pulsed-nanosecond discharge. Beginning with Loeb's description of the phenomena as "ionizing waves of potential gradient," several more articles appeared exploring the nature of these pulses. Mesyats, Byckhov, and Kremnev [11] developed a theory explaining the breakdown process which is among the first to specifically reference runaway or nonlocal electrons. This theory was continued with a kinetic treatment and several simulations by Kunhardt [12], and Kunhardt and Tzeng [13].

Research Plan

Propose research to fill this gap Specific and cited history of PNDS and related measurements.

1.3 Basic Theory

Basic theory of gaseous breakdown.

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