Cross-correlating discharge physics, excitation mechanisms and plasma chemistry to describe the stability of an RF-excited atmospheric pressure argon plasma jet

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1 Introduction

Cold atmospheric pressure plasmas (CAPs) are characterized by their non-equilibrium properties. While electrons are efficiently heated up to several thousand Kelvin, ions and neutrals remain cold, i.e. the gas temperature is close to room temperature. Consequently, CAPs enable a high temperature complex plasma chemistry with low thermal impact on treated samples. Therefore, CAPs have great potential for various applications such as etching, coating or treatment of biological tissue. Numerous concepts and designs of CAPs are successfully used for bio-medical applications. However, scientific progress is decelerated due to the incomparability of the sources and their parameters. Thus, the challenge is to obtain comparable results. One of the most prominent discharge designs is the micro-scaled Atmospheric Pressure Plasma Jet (µ-APPJ). It has been extensively studied in the past two decades using various diagnostic techniques. Based on this experience, one central idea of this work is to develop and characterize a reproducible and stable discharge design that can serve as a reference source for future bio-medical research. To accomplish this, the focus of this work is on accurately determining the control parameters of the discharge. Subsequently, the benefit from the discharge stability and accurate knowledge of the control parameters is harnessed in investigating the discharge processes of argon, which could hardly be assessed up to now due to unstable discharge designs. The physical mechanisms of instabilities observed in the homogeneous argon discharge are investigated. Using various diagnostic techniques, macroscopic observations are traced back to fundamental, microscopic characteristics and processes. By transferring concepts from the well-investigated helium discharge, differences can be revealed and understood. In the first section of this chapter, a short motivation and introduction of cold atmospheric pressure plasmas is presented. In the second section, the state of the art in this field is discussed and the research focus is derived. At the end, a structural overview of this thesis is given.
1.1 Motivation

Technical plasmas are indispensable and widely used in industry for microelectronic circuitry fabrication and deposition of thin films. They enable tailoring of deposited energy, ions, radiation, heat and radicals. Most of these plasmas are operated at rather low pressure and thus require cost-intensive vacuum-equipment. However, there are many vacuum-incompatible applications such as the treatment of polymers or biomaterials that depend upon the use of atmospheric pressure plasmas. Since according to Paschen’s law, the electrode gap can compensate for the operating pressure of a plasma discharge in terms of ignition voltage, cold atmospheric pressure plasmas can exhibit electrode gaps in the micrometer range. Therefore, they are often referred to as microplasmas. During the last decade, cold atmospheric pressure plasmas have gained high attention due to their technological and biological promises: A number of review papers and topical issues addressing the scientific challenges were published in leading scientific journals [1–3].

However, these sources are prone to instabilities due to the high number of collisions and the high surface-to-volume ratio. Since many of the secondary electron production processes such as stepwise ionization, surface-impact and Penning ionization from metastables are avalanche-like, atmospheric pressure discharges tend to transform from homogeneous to constricted thermal discharges. To avoid this transition, gas heating and build up of current have to be restricted. There are two main concepts to meet these conditions: Either the use of dielectric barrier discharges (DBDs) or high electrical excitation frequencies in the kHz-range and above. Both concepts are adopted in the design of jet-like atmospheric pressure plasma sources working with a continuously flowing gas stream.

Since atmospheric pressure plasma sources, compared to their low pressure counterparts, are inexpensive and straightforward to build, there is a huge variety of different jet sources being used in different groups, especially for biomedical applications [4–7]. Significant effects of plasma on biological materials were observed. Nonetheless, these results suffer from reliability problems: Apart from natural fluctuations relating to the treated biological substrates, the physical effect mechanisms were seldom traced back to plasma processes, which in turn strongly depend on the utilized plasma source. This
1.1 Motivation

makes it difficult to isolate the influence of single plasma parameters, which renders
the obtained results non-transferable. Reproducibility is not a challenge encountered
by plasma physicists only. Instead, it is a demanding challenge faced by science in gen-
eral, especially in medical sciences [8], and has recently been addressed by numerous
editorials and articles in high ranking journals such as Nature [9, 10].

This issue is also well-known to the low pressure plasma community as researchers
in this field encountered the exact same problems 30 years ago. The response to
this challenge was the GEC RF Reference Cell [11]. The design for this reference
discharge chamber was developed at the Gaseous Electronics Conference (GEC) in
1988 to provide a platform for comparing experimental data from different setups
amongst each other as well as to theoretical models. A large number of different
experimental measurements using various diagnostics were performed providing an
extensive fundamental database towards a fully characterized discharge for validation
of theoretical models. The GEC RF Reference Cell was a valuable tool to achieve an
in-depth understanding of RF discharges.

Applying this successful concept to atmospheric pressure plasmas, a similar reference
source would prospectively facilitate comparability of results and accelerate scientific
progress as well. However, transferring this concept to atmospheric pressure plasmas
presents some challenges. For example, according to its name, atmospheric pressure
plasmas are often operated in the ambient atmosphere. This facilitates the penetration
of impurities into the discharge. Another complicating factor is the challenge of
measuring control parameters. Since the volume of atmospheric pressure plasmas is
often in the sub-mm$^3$ range, the currents and powers to be measured are also small.
Therefore, the relative error of the measurement is large. Many commercially available
systems actually are not specified for such a small measuring range.

As stated above, one of the most extensively studied homogeneous atmospheric pressure
plasma sources is the so-called micro-scaled Atmospheric Pressure Plasma Jet (µ-APPJ).
This makes it a suitable candidate as a basis for an atmospheric pressure reference
source. It was developed by Schulz-von der Gathen and co-workers [12] and is a
well-investigated jet source that allows to operate a homogeneous glow discharge in
helium. It facilitates optical access to the bulk discharge and is thus an ideal design
concept for fundamental studies of plasma processes. Detailed characterization of the
device operated in helium both experimentally, and through simulations and models, has been carried out.

However, the $\mu$-APPJ has an important restriction. Until now, processes have been investigated almost exclusively in helium. This process gas is a valuable resource and therefore very costly. The more affordable argon is also frequently used for atmospheric pressure discharges. A numerical study even shows, that operation in argon should offer a wider operation range compared to helium [13]. However, surprisingly, preliminary measurements have so far hardly been able to produce a stable, homogeneous discharge in this device. Although helium and argon have a very similar atomic structure, observations show that the argon discharge is unstable and prone to filamentation [14]. Therefore, it has hardly been possible to investigate the discharge processes in argon. It is still unclear which processes lead to this filamentation and how this compares to the helium discharge. Many fundamental questions on the plasma physics of an argon discharge at atomic pressure remain unanswered to this day. The physics of the homogeneous argon discharge is hidden in its irreproducibility. Here, stable discharge conditions would make an investigation of the main discharge processes in argon possible in the first place.

Nevertheless, in the following section, a short review of studies is presented that qualify the $\mu$-APPJ as a reference source candidate.

### 1.2 State of the art

To predict the behavior of the plasma discharge and tailor its properties to the requirements of an application, it is necessary to understand the underlying processes. Therefore, it is not sufficient to vary the control parameters of a given plasma device, but crucial to understand the interaction of these parameters and their influence on the intrinsic plasma parameters. The three main control parameters for atmospheric pressure plasmas are the confining structure, the electrical excitation and the gas mixture, as illustrated in figure 1.1. In the following, an overview of the recent developments in terms of these main control parameters that are most relevant to this thesis is given.
1.2 State of the art

The **confining structure** is defined by the design of the discharge geometry and has a strong influence on plasma processes. In case of the µ-APPJ, its principal characteristics always remained the same, but a few design-changes were made over the past decades: Originally inspired by the Atmospheric Pressure Plasma Jet [15], the first publication concerning the µ-APPJ by the group of Schulz-von der Gathen appeared in 2007 [16]. At that time, the device consisted of two plane-parallel stainless steel electrodes enclosed by two glass panes. Since then, the discharge-geometry was slightly adjusted as needed for specific measurements. The length of the electrodes varied from 30 mm [17, 18] to 40 mm [19, 20], and the mounting of the electrodes was realized using various concepts ranging from a glass cuvette [16, 21, 22], to clamping by a PTFE (Teflon) or POM housing [23, 24], up to glueing [25, 26]. The electrode gap varied from 0.25 mm [20] to 2.0 mm [27] up to 2.7 mm [28]. The electrode width also differed from 1 mm to 11 mm [29, 30]. As for all atmospheric pressure plasmas [31], impurities were a serious issue for all of these geometries. There are studies that claim a back flow of ambient air into the discharge channel [20] and others that point out the importance of stainless steel tubing [32, 33]. Up to now, it was never questioned how prone to impurities the device design itself was.

The **electrical excitation** determines heating mechanisms in the plasma discharge. In case of the µ-APPJ, the electrical supply is a commercial 13.56 MHz generator coupled to the powered electrode via an impedance matching network [23, 30]. To denote the applied electrical parameters in publications, usually, the generator power was given [34, 35] and sometimes, the ignition and arcing point were provided [23]. This

---

**Figure 1.1:** Sketch of the three control parameters relevant for atmospheric pressure plasmas.
denotation was used even though for both, low and atmospheric pressure discharges, the generator power is not a representative, meaningful parameter [36], since it depends on the electrical circuit. Consequently, these parameters do not allow to transfer the results from one setup to another. An alternative parameter is the applied voltage across the discharge gap [18], which is closely connected to the reduced electrical field in the discharge. In principle, this control parameter is transferable. However, it does not capture the whole relevant physical information, especially when working with different chemical gas compositions. From electron particle and energy balance, it is found that the characteristic size of the confining structure, power density and pressure are a suitable set to define external experimental control parameters [37]. Since the geometry and thus the characteristic size of the discharge is fixed, only pressure and power density have to be determined when comparing results of the COST-Jet. Hence, it is desirable to measure the power that is dissipated in the discharge to calculate the power density.

The third parameter is the gas mixture. For jet-like atmospheric pressure sources, this includes the gas flow rate, which determines the particles' residence time in the plasma discharge. The gas flow rate typically is in the range of 0.5 slm to 5 slm. Usually, helium was used as a carrier gas with various molecular admixtures such as oxygen [38], nitrogen [30], water [39], hexamethyldisiloxane (HMDSO) [40] or atomic gases such as argon [23]. Even if argon is one of the most commonly used operation gases in low temperature plasmas, it proved to be challenging to produce a stable argon discharge in a capacitively coupled discharge geometry. Experimental studies have shown that jet-like sources driven at MHz frequencies are homogeneous when operated in helium [41, 42], but tend to form streamers when operated in argon in the exact same discharge geometry [43, 44]. Up to now, there is little literature available on atmospheric pressure argon processes. Only when using larger electrode surface areas or higher excitation frequencies, the use of argon as a feed gas in a capacitively coupled geometry basically similar to the μ-APPJ is reported [45, 46].
1.3 Research focus

Based on the above mentioned existing research and literature on atmospheric pressure discharges, the current thesis focuses on the following aspects:

- With respect to the various different discharge designs, a consistent and functional design is necessary. Therefore, the development of the COST-Jet - a stable, reproducible and comparable plasma device - is a fundamental aspect of this thesis. The design should concentrate on simplicity and stability of the geometry and reduction of impurities. Additionally, construction plans for interested researchers should be provided to make a step towards comparable discharge conditions and experimental results.

- Past studies show that it is challenging to transfer experimental results from one setup to another. Especially when comparing different gas compositions, the applied voltage is not an appropriate parameter. To tackle this problem of transferable control parameters, the development and characterization of miniaturized electrical probes is another key part of this thesis. Using these probes, the power dissipated in the plasma discharge will be deduced. To further simplify the experimental setup, a substitute for the commercial matchbox and generator combination will be developed.

- Using the developed COST-Jet design, these stable conditions allow for measurements using argon as a feed gas. The main discharge processes will be identified by linking different plasma diagnostics. This allows the observed phenomena to be decoupled and their influence on the discharge to be identified. To point out differences to the well-known helium discharge, results in argon will be compared to results from literature and new experiments in helium. To simplify the complexity of the system, the free parameters are reduced and controlled: Most of the experiments will be conducted in a discharge chamber using stainless steel gas supply and a cold trap to minimize impurities and control the pressure.

In working on these current impediments of atmospheric pressure plasma research, this thesis assesses the following questions:
1. How transferable are experimental results obtained using different COST-Jet devices?

2. Can the implemented electrical probes be used to determine the dissipated power and what is the accuracy of this measurement?

3. Why does the discharge behave so differently depending on the used feed gas, even if the atomic structure of argon and helium is rather similar?

4. Which physical mechanisms limit the stable operation of the argon discharge?

5. What are the fundamental plasma parameters in the argon discharge and how do they compare to the helium discharge?

6. Which processes play a key role in the sustainment of the argon discharge?

The answers to these questions will contribute to a better fundamental understanding of existing and future plasma processes. In the longterm, this thesis can make a new carrier gas and thus a new plasma chemistry available for applications and predict its behavior.

Summarized in one paragraph, the focus of this thesis is to unravel the microscopic processes that cause the observed macroscopic differences between argon and helium discharges in the \( \mu\text{-APPJ} \) configuration: For this purpose, various diagnostic techniques are combined to separate the intertwined discharge processes. The basis for this investigation is the development of a stable device.

### 1.4 Thesis outline

This thesis is structured in six chapters:

- Following the introduction, chapter 2 reviews the fundamentals of atmospheric pressure plasmas with a special focus on capacitively coupled plasmas. The findings for the \( \mu\text{-APPJ} \) operated in helium are summarized. A discussion on differences between helium and argon and existing studies comparing plasma discharges follows.
1.4 Thesis outline

- In chapter 3, the device developed within this thesis, the COST Reference Microplasma Jet, is presented in detail. The experimental setup for operating the discharge and the used diagnostics are briefly explained.

- Chapter 4 deals with the reproducibility, stability and comparability of the COST-Jet. An error analysis of the power measurements and comparison between different devices is given.

- Finally, chapter 5 presents the findings of the investigations of this developed device operated with argon as carrier gas. It is characterized and compared to the helium findings. Electrical measurements are used to deduce information on fundamental plasma parameters, such as electron density and energy. Subsequently, discharge species are analyzed using optical emission spectroscopy in the visible and ultra violet range. Electron kinetics are investigated using phase-resolved optical emission spectroscopy.

- The last chapter summarizes the findings of this work, draws conclusions and provides a brief outlook for future investigations based on open questions resulting from this thesis.
2 Fundamentals

The first part of this chapter presents general properties of cold atmospheric pressure plasmas. Capacitively coupled plasma jets excited at radio-frequency are emphasized. Their excitation mechanisms, operation modes and instabilities are discussed. As a reference for chapters 4 and 5, the most important findings on the micro-scaled atmospheric pressure plasma jet operated in helium are presented in the second section. The third part of this chapter deals with the principles of electrical modeling. On this basis, an equivalent electrical circuit for an atmospheric pressure plasma is developed.

2.1 Characteristics of cold atmospheric pressure discharges

In 1928, Langmuir introduced the term "plasma" for the quasi-neutral part of a gas discharge showing collective behavior [47]. These two properties, expressed in mathematical criteria, and their validity for atmospheric pressure plasmas will be briefly discussed in the following section [48]. The following parameters are well known to experts in the field, yet they are presented here in due brevity to classify the plasma discharge investigated in this thesis into the wide parameter space of plasma discharges.

In a plasma, the typical length scale for quasi-neutrality is the Debye length

$$\lambda_D = \sqrt{\frac{\varepsilon_0 k_B T_e}{n_e e^2}},$$

(2.1)
where $\varepsilon_0$, $k_B$ and $e$ represent the common physical constants vacuum permittivity, Boltzmann constant and elementary charge, and $n_e$ and $T_e$ are the electron density and temperature, respectively. It describes the length scale, for which the potential of a local potential disturbance in front of a static ion background has dropped to $1/e$ of its initial value. To be considered as a plasma, the electron density of an ionized gas has to be high enough to fulfill

$$\lambda_D \ll L,$$  \hspace{1cm} (2.2)

where $L$ is a typical discharge dimension. The derivation of the Debye shielding is only accurate if the concept is statistically valid, which implies that the Debye sphere contains a sufficient amount of particles for shielding

$$N_D = n_e \frac{4}{3} \pi \lambda_D^3 \gg 1.$$  \hspace{1cm} (2.3)

A second basic plasma parameter is the so-called plasma frequency defined as

$$\omega_p = \omega_{pe} = \sqrt{\frac{n_e e^2}{\varepsilon_0 m_e}},$$  \hspace{1cm} (2.4)

where $m_e$ is the electron mass. The plasma frequency describes the time-scale of oscillations of disturbed particles in the plasma. It may be defined for both electrons and ions equivalently by inserting the respective density and mass.

The third condition for an ionized gas to be called a plasma is that electromagnetic forces rather than collisions dominate the motion of charged particles with a collision time $\tau$. Therefore, we require

$$\omega_p \tau > 1.$$  \hspace{1cm} (2.5)

To check the validity of these three conditions, we use plasma parameters from literature for plasma discharges that are comparable to the plasma discharge used in this work. Using typical parameters in the order of $n_e \approx 7 \times 10^{16} \text{ m}^{-3}$ [27] and $T_e \approx 2.5 \text{ eV}$ [49]
2.1 Characteristics of cold atmospheric pressure discharges

for a helium plasma discharge, \( p \approx 1 \times 10^5 \) Pa and \( T_{\text{gas}} \approx 350 \) K, we obtain

\[
\lambda_D = 4.44 \times 10^{-5} \text{ m} \ll L \quad (2.6)
\]
\[
N_D = 2.57 \times 10^4 \text{ particles} \gg 1 \quad (2.7)
\]
\[
\omega_p \tau = 1.49 \times 10^{10} \text{ s}^{-1} \cdot 3.88 \times 10^{-15} \text{ s} = 5.44 \times 10^{-5} \leq 1. \quad (2.8)
\]

The given plasma obviously fulfills the conditions for quasi-neutrality and collective behavior, whereas the third condition is not satisfied. Therefore, the given plasma is not a plasma in the strict sense, but also referred to as collisional. A collisional plasma is defined by the electron-neutral collision-frequency being greater than the plasma frequency [50]. For atmospheric pressure plasmas, the collision frequency of electrons with neutral background gas is found to be of the order of \( 1.52 \times 10^{12} \) Hz [51] or higher, i.e. two orders of magnitude higher than the plasma frequency. In this case, gas kinetic effects dominate over the long ranged electrostatic Coulomb interactions. The dominance of the gas kinetic effects is also underlined by the low ionization degree of

\[
\frac{n_i}{n_i + n_G} \approx \frac{n_i}{n_G} = 3 \times 10^{-9} = 0.003 \text{ ppm}. \quad (2.9)
\]

Atmospheric pressure plasmas are traditionally more commonly found in high-temperature applications such as plasma welding, cutting or cauteterization. In recent years, however, concepts have also been developed to operate so-called cold atmospheric pressure discharges. In this context, cold means that the neutral gas temperature is close to or slightly above room temperature. One of these concepts are capacitively coupled plasmas (CCPs) using an alternating current. This type of plasma and its characteristics will be briefly discussed in the following.

2.1.1 Capacitively coupled radio-frequency plasmas

The excitation frequency plays a decisive role for the plasma processes in alternating current driven plasmas. The ratio of plasma frequency \( \omega_p \) to driving frequency \( \omega_{\text{rf}} \) defines the individual energy transfer to the respective species. If the driving voltage is chosen in such a way that \( \omega_{pi} < \omega_{\text{rf}} < \omega_{pe} \), this implies the electrons being heated by the external electric field, resulting in a high electron temperature. Meanwhile,
the ions cannot follow the electric field due to their much higher mass. Additionally, electrons cannot transfer their energy to ions due to their mass ratio. Therefore, the ions remain cold, resulting in a low ion temperature. These plasmas are referred to as non-equilibrium plasmas. Since only the ions can effectively transfer energy to neutral atoms due to the kinematic factor being close to one, the temperature of neutrals also remains cold. Notably, the equation for preferential electron heating is not a harsh condition. Instead, the transitions are smooth. For a typical electron density at atmospheric pressure in the order of $n_e \approx 10^{16} \text{ m}^{-3}$ \cite{27}, the plasma frequency for electrons and ions is $\omega_{pe} \approx 6 \times 10^9 \text{ s}^{-1}$ and $\omega_{pi} \approx 7 \times 10^7 \text{ s}^{-1}$, respectively. Consequently, frequencies in the MHz regime are often used to operate these plasmas.

In radio-frequency (RF) excited discharges, electrons gain energy due to their interaction with the external electric field. Due to their low mass, they transmit the energy from the electric field to all the plasma species via collisions. From low pressure discharges, two main heating mechanisms are known. Both mechanisms are based on the destruction of a phase-coherent electron motion. Thus, the directional energy of the electrons can be converted to isotropic energy. First, Ohmic heating in the bulk is realized by collisions with electrons (elastic) and other particles (elastic and inelastic) that cause isotropization, excitation, ionization and dissociation. Second, stochastic heating (or plasma series resonance heating) is caused by interaction of the electrons with the oscillating sheath. However, this second effect is most prominent only in discharges with asymmetric electrode surfaces. For higher pressures, not only Ohmic heating in the bulk but also Ohmic heating in the sheath at high voltages due to collisions of the oscillating electrons with the neutral gas can be an important contributor \cite{52}.

RF-excited capacitive discharges operating at atmospheric pressures have not been studied as thoroughly as low- and moderate-pressure discharges. Nevertheless, many concepts and mechanisms are transferred to the high pressure regime. In addition, it may also be appropriate to describe the breakdown mechanism based on low pressure DC discharges, as explained in the following paragraph.

For a low pressure DC discharge, Paschen’s law adequately describes the ignition criterion. It is based on the electron production mechanisms in the volume ($\alpha$) and on the surface ($\gamma$). Assuming the breakdown criterion is met if a secondary electron from the cathode can ionize at least one atom on its way to the anode, the breakdown
2.1 Characteristics of cold atmospheric pressure discharges

![Breakdown curve in hydrogen at a gap distance of 20 mm, data from Lisovskiy et al. [53].](image)

**Figure 2.1**: Breakdown curve in hydrogen at a gap distance of 20 mm, data from Lisovskiy et al. [53].

The ignition processes in a radio-frequency discharges differ from those in low pressure DC discharges. In RF discharges, a displacement current sustains the discharge. Since ions cannot follow an alternating electric RF field, breakdown processes are governed by electrons. To ignite an RF plasma, the electron production processes have to outweigh the electron loss processes.

RF discharge breakdown curves exhibit three branches [54]: Figure 2.1 shows a characteristic RF breakdown curve in hydrogen exhibiting a turning point (at pressure $p = p_t$ and RF voltage $U_{tr} = U_t$), a minimum point at $(p_{min}, U_{min})$ and an inflection.

The resulting shape of the Paschen curve shows a minimum at a certain value of the product $p \cdot d$ around some 1 cm Torr.

The voltage was empirically observed to be

$$V_{bd} = \frac{Bpd}{\ln(Apd) - \ln[\ln(1 + \gamma^{-1})]}$$

with $A$ and $B$ denoting parameters depending on the gas and defining the ionization coefficient $\alpha$ and $\gamma$ being defined by the work function of the electrode material [51].
point at \((p_{\text{inf}}, U_{\text{inf}})\). On the right-hand side of the inflection point \(p_{\text{inf}}\), at high pressures, secondary electron emission from electrode surfaces plays a minor role in the breakdown mechanisms. Therefore, this region is called emission-free branch. When the pressure is decreased, electron collisions with other particles become less frequent. Thus, less energy is lost for excitation of atoms and molecules. Therefore, the electrons can gain the energy necessary for ionization in weaker electric fields, which results in a lower breakdown voltage. When the pressure is decreased below the inflection point \(p_{\text{inf}}\), a fraction of electrons can reach the electrodes and induce secondary electron emission. This secondary electron emission is an additional source of electrons. Therefore, the decrease of breakdown voltage is faster with decreasing pressure than in the emission-free branch. The pressure range between the inflection point \(p_{\text{inf}}\) and the turning point \(p_{\text{t}}\) is the so-called diffusion-drift branch. The shape of this branch strongly depends on the discharge geometry. When the pressure is further decreased, even more electrons reach the electrodes and are lost. This results in an increase in breakdown voltage. When the amplitude of electron oscillation is equal to half of the discharge gap, the breakdown curve passes through the turning point \(p_{\text{t}}\). At this point, an incremental increase of the voltage is not sufficient to cause breakdown, because most of the electrons are lost to the electrodes. Instead, a much higher voltage has to be applied to enable a high energy gain of the electrons and thus ionization at these low pressures. This behavior causes the multi-valued breakdown voltage. At very large electric fields, when the amplitude of the electron oscillation is larger than the electrode gap, the RF breakdown is similar to the DC breakdown. Correspondingly, this branch is called Paschen branch.

Since the homogeneous argon discharge in the COST-Jet has to be ignited using a high voltage spark gun (see chapter 5), examining the breakdown curve was not possible. Instead, the extinction curves were studied in this work. Lisovskiy et al. report that at low pressure, extinction curves exhibit the same form as breakdown curves. They are just shifted to lower pressures and RF voltages \([53]\).

When interpreting breakdown and extinction curves, another difference between low and atmospheric pressure has to be taken into account: Especially at low pressure (of the order of 100 Pa), the impact of secondary electrons and loss due to diffusion is not negligible. These effects are observable in the dependence of the breakdown and extinction curves at low pressures on the discharge gas and reactor design \([53]\).
2.1 Characteristics of cold atmospheric pressure discharges

In contrast, at atmospheric pressure, the electron-neutral collision frequency is larger than the plasma frequency. Consequently, elastic electron collisions dominate and production of secondary electrons is less important. In this regime, not only the electric field amplitude but also the phase of the electron motion with respect to the external electric field is determining the power coupling. Hence, the breakdown voltage is mainly proportional to the pressure.

Another important aspect at atmospheric pressure is the charge density multiplication. So far, it was assumed that the charge carriers do not affect the external electrical field. However, due to the high neutral gas density at atmospheric pressure, electron avalanches can produce such high numbers of electrons that the local electrical field in the vicinity of this avalanche is comparable to the external field. Thus, the avalanche itself can trigger the ignition. This effect is called the streamer mechanism [55, 56]. When the streamer mechanism occurs, the influence of electrode surface on the ignition disappears. As a result, ignition is much faster than at low pressure, since streamer propagation does not depend on the drift velocity of ions or even electrons. Instead, photo ionization supports the propagation. In principle, there are two types of streamers: Positive and negative streamers differ in their direction of propagation. The Meek-criterion determines the occurrence of streamers to a minimum number of $10^8$ electrons at the streamer head. Due to their complexity and multi-scale processes, streamers are still the subject of current research [57].

Chapter 5 discusses the above mentioned mechanisms on an atomic scale. To understand these mechanisms, the next section presents the most important population processes in RF-excited atmospheric pressure plasmas.

2.1.2 Population processes

Due to their low mass and high mobility, electrons in an RF discharge can follow the external electric field. Therefore, electrons dominate the energy transfer into the plasma. Their kinetic energy is transferred to other species by inelastic collisions causing excitation, ionization, dissociation and secondary processes. For an inelastic collision process, the energy of the impacting electron has to exceed a certain threshold value. Therefore, the collision rate and thus the energy transfer strongly depend on the
number density and energy of the electrons. This is described by the electron energy distribution function (EEDF). The electron energy distribution function denotes the number of electrons (or the probability) having a certain energy. The shape of the EEDF depends on the external driving electric field, the gas composition of the discharge and thus the resulting discharge processes. If the plasma is in (local) thermodynamic equilibrium, the EEDF has the shape of a Maxwell-Boltzmann distribution function, so that the electron energy can be described by one single parameter, i.e. the electron temperature \( T_e \) [48]. Even if the EEDF is not Maxwellian, the electron temperature is often used as a measure of the average thermal energy of the particle ensemble [58, 59] defined as \( E_{\text{av}} = k_B T_e \).

Atmospheric pressure discharges are commonly operated in noble gases because of their favorable properties. Due to the high ionization energy threshold of noble gases, the discharge is dominated by the high energetic part of the EEDF. Processes such as stepwise ionization from excited states play an important role in such plasmas. The effectiveness of these processes strongly depends on the number density of excited states. In atmospheric pressure plasmas, these excited states can be represented by atoms in metastable states. However, in contrast to low pressure plasmas, these states can be effectively depopulated by the generation of excited dimers. Due to the high number of collisions, the probability for generation of metastable excited dimers and ion dimers via three-body reactions is higher than in low pressure discharges. Thus, the balance of these processes plays a key role in the sustainment of the discharge. At atmospheric pressure, also super-elastic collisions play a crucial role where the sum of kinetic energy is increased by the de-excitation of an excited state.

As chapter 5 discusses these processes frequently, the reaction schemes of the dominating discharge processes are explained in the following section. Figure 2.2 illustrates the most relevant processes schematically, using argon as an example.

**Electron impact excitation**

The most basic reaction in a plasma discharge is electron impact excitation. If an electron collides with a particle in ground state, the electron can transfer its kinetic
2.1 Characteristics of cold atmospheric pressure discharges

Figure 2.2: Partial energy diagram that illustrates the most relevant states in atmospheric pressure noble gas plasmas and the corresponding transition processes using argon as an example. The nitrogen molecule represents possible energy transfer processes to potential impurities in the feed gas.

Energy to the particle and excite it to a higher level. The reaction scheme is

\[ e^- + X \rightarrow X^* + e^- , \]  

(2.11)

where \( e^- \) is the electron and \( X \) and \( X^* \) are the ground state and the excited state of the particle, respectively. To realize this reaction, the kinetic energy of the electron has to exceed the excitation energy threshold. This means that the cross section for this reaction is zero below the excitation threshold. This implies that only the electrons in the high energetic tail of the EEDF can participate in such a process. The excited state \( X^* \) can also be a long-living metastable state \( X_m \) that is quantum-mechanically not allowed to de-excite by electric dipole radiation. If the kinetic energy exceeds the ionization threshold, this process can lead to direct ionization of an atom. As already mentioned above, direct ionization has a high energy threshold. Hence, stepwise ionization is an alternative pathway to generate ions.
**Stepwise ionization**

The ionization by collision of an electron with an already excited particle is called stepwise ionization:

\[
e^- + X^* \rightarrow X^+ + 2e^-.
\]  

(2.12)

Due to the high pressure, the mean free path is short. This results in a high inelastic collision rate of electrons with particles in the ground state. These inelastic collisions notably deplete the high energetic part of the EEDF above the lowest excitation threshold. Hence, stepwise ionization becomes more probable than ionization from the ground state. In fact, stepwise ionization is the dominant ionization process.

**Transfer of excitation**

Another important process leading to ionization in atmospheric pressure plasmas does not directly involve electrons. When a gas phase particle \( M \) reacts with a particle in an excited state \( X^* \), an ion can be formed. This process is called transfer of excitation and the reaction can be expressed as follows [60]

\[
X^* + M \rightarrow X + e^- + M^+.
\]  

(2.13)

where \( X^* \) represents an excited feed gas atom. \( M \) can represent any other particle, e.g. from impurities or admixtures, but it can also represent an excited state of the feed gas atom. Depending on the products, these reactions are also called Pooling reactions or chemoionization. If the excited atom is in a metastable state, this process is known as Penning ionization. If the internal energy of the excited-state particle \( X_m^* \) is higher than the ionization potential of a target molecule \( M_2 \) (or atom) in the ground state, ionization can occur.

These excitation processes are very important in atmospheric pressure plasmas, especially when working with admixtures such as molecular oxygen or nitrogen. Since the potential energy of most noble gas metastable states suffices to dissociate or even ionize
2.1 Characteristics of cold atmospheric pressure discharges

molecules such as nitrogen, hydrogen, oxygen, water, carbon dioxide or methane, these processes strongly affect the plasma chemistry.

Formation of excited dimers

At atmospheric pressure, the formation of excited rare gas dimers is an important process that contributes to the energy transport within the discharge [61]. Especially at low gas temperatures and low electron densities, the absolute number density of molecular rare gas ions is comparable or even higher than the atomic ion density, so that they can offer a fast volume recombination channel. Since three-body collisions form rare gas dimers, the high number of collisions of the discharge promotes the generation. The excited dimer molecule $X_2^*$ formation is realized via metastable states $X_m$ by two common reaction pathways [62]: First, electron impact excitation of metastable atoms can directly generate them

$$e^- + X \rightarrow X_m + e^-,$$  \hspace{1cm} (2.14)

$$X_m + 2X \rightarrow X_2^* + X,$$  \hspace{1cm} (2.15)

or second, electron-impact ionization via molecular ions $X^+_2$:

$$e^- + X \rightarrow X^+ + 2e^-,$$  \hspace{1cm} (2.16)

$$X^+ + 2X \rightarrow X_2^+ + X,$$  \hspace{1cm} (2.17)

$$e^- + X_2^+ \rightarrow X_m + X,$$  \hspace{1cm} (2.18)

$$X_m + 2X \rightarrow X_2^* + X.$$  \hspace{1cm} (2.19)

In either case, the last reaction is identical and involves a metastable atom. Hence, two things are required [62] to generate excited dimers efficiently: First, several electrons with a kinetic energy above the excitation (or ionization) threshold that is high enough to generate a high number of metastable states. Second, a pressure that enables the particles to collide in three-body reactions frequently.
Secondary electrons

Unlike in DC discharges, electrons emitted from the electrode surface, i.e. secondary electrons, are unnecessary for the sustainment of an RF plasma. However, secondary electrons increase the power dissipation. Especially at high pressure, they have an impact on the discharge, since their energy is captured by the plasma due to the high number of collisions impeding diffusion. The energy of the impacting ions determines the number density of secondary electrons. At ion energies below 1 keV, secondary electrons are produced by Auger ejection [63, 64]. The energy of the secondary electrons depends on the work function of the electrode material. Not only ions but also impacting atoms with high kinetic or high potential energy, e.g. in metastable states, are responsible for secondary electron emission. At low reduced fields, UV radiation from resonant states or excited dimers can additionally contribute to secondary electron production [65].

Additionally, at atmospheric pressure, pooling reactions among metastable atoms and metastable dimers generate electrons in the sheaths. These electrons can also be accelerated and seed avalanches similar to those initiated by secondary electrons. Thus, these electrons can also contribute to the heating of the discharge inside the sheath region, even in the absence of true secondary electron emission [66].

The high electric field of the sheath accelerates secondary electrons, which in turn heat the discharge by elastic and inelastic collisions. This contribution is a criterion to distinct different discharge modes that are described in the following section.

2.1.3 Discharge modes

At low pressure, glow discharges are usually classified into different operating modes according to optical appearance, current-voltage characteristics or dominant heating mechanism.

In low pressure capacitively coupled glow discharges, two main discharge modes are defined by the location of the dominant ionization zones [67]: (i) The α-mode is characterized by ionization in the plasma bulk. The name is derived from the first
2.1 Characteristics of cold atmospheric pressure discharges

Townsend-coefficient characterizing charge multiplication in the plasma volume. (ii) The \( \gamma \)-mode is typically reached at higher applied powers and is characterized by the generation of secondary electrons by ion impact on the electrode surface. Accordingly, the name comes from the Townsend-coefficient.

At atmospheric pressure, this terminology is often adopted even if due to the high number of collisions and consequently small mean free path of electrons and ions, this mode classification is considered being misleading by some authors [27, 66]. Probably due to this reason, the terminology is not used unambiguously in the literature. In the case of the capacitively coupled homogeneous helium glow discharge, some papers speak of a pure \( \alpha \)-discharge [68–70] while other papers also report \( \gamma \)-like or diffused \( \gamma \)-discharges [66, 71].

In this work, the different heating mechanisms in homogeneous mode will be referred to as \( \alpha \)-mode and \( \gamma \)-like mode. This choice of words will be explained in more detail in the scope of the findings presented in chapter 5.

The classification according to current-voltage characteristics adapted from DC glow discharges distinguishes between normal mode, abnormal mode and arcing mode or constricted mode [72]. The normal mode is characterized by a plasma volume that expands over the electrode surface as the discharge current increases. If the plasma has covered the electrode surfaces to the maximum extent, the plasma changes into the abnormal mode and the discharge voltage increases with increasing current. If the power is even further increased, an instantaneous transition to a constricted discharge is observed. In the literature, this mode is sometimes also referred to as ‘arcing mode’ [18, 19, 70, 73]. This constriction is thought to be caused by one of the instabilities described in the following section.

2.1.4 Instabilities

Atmospheric pressure discharges are highly susceptible to instabilities. This is because according to one of the scaling laws, the current density is proportional to the square of the pressure for a normal glow discharge [51]. An instability occurs if the charge source terms cannot be compensated by charge loss terms. These instabilities induce physical
changes in the discharge and thus often lead to a spontaneous, rapid constriction or filamentation of the homogeneous glow discharge. There are two types of instabilities leading to a constriction of the homogeneous glow discharge. They can be categorized as electronic and thermal instabilities, according to the participating processes [50].

The thermal instability (or ionization overheating instability) as described in the literature [51, 74] is one of the two common pathways for the development of a constricted discharge at atmospheric pressure [70] and is well understood. It evolves as a positive feedback loop between an increase in current and gas heating. A sketch of the process chain leading to a thermal instability is illustrated in figure 2.3. A local increase of electron density $n_e$ is accompanied by high conduction current density and hence an increase in power dissipation $j_eE$. Since the pressure is constant, this leads to an increase of neutral gas temperature $T_{\text{gas}}$ and thus to a decrease of the neutral gas number density $n_0$. Hence, the reduced electric field $E/n_0$ is increased, which causes an increase in electron temperature $T_e$. The elevated electron temperature increases the ionization rate and thus results in an even higher electron density $n_e$. The process chain described above only plays a role at elevated pressures since the increase of electron density and power dissipation has to induce an increase in the neutral gas temperature. The time constant of this instability is determined by the slowest process, i.e. the temperature increase.
2.1 Characteristics of cold atmospheric pressure discharges

The **α-γ-transition instability** is named according to the discharge modes described above in section 2.1.3. The α-γ-transition instability can be induced when the electric field in the sheath reaches a certain threshold value and sheath breakdown occurs [51]. After the breakdown of the gap-sheath boundary, an ionization wave can travel to the electrode, thus creating a plasma channel and reducing the initial sheath thickness to a value corresponding to optimal conditions for charge multiplication by secondary emission. At high pressure, this sheath breakdown leads to an abrupt mode change. The threshold value of the critical electrical field can be calculated from the Townsend condition [67].

These two discharge instabilities differ largely in their transition time constants, since the growth rate depends on the slowest step: Thermal instabilities are dominated by gas heating (~1 ms [75]), whereas in contrast, the α-γ-transition instability is defined by the drift of positive ions (~10 µs).

To avoid the build-up of instabilities, there are several counter-measures that help to reduce the probability of their occurrence. Reducing the size of the electrodes limits the total current and thus the risk for constriction. Additionally, continuously exchanging the gas in the discharge, i.e. establishing a gas flow, reduces the residence time of the particles in the discharge and thus the heating of the gas. Due to its high thermal conductivity, using helium as discharge gas is favorable for reducing heat peaks in the gas, especially in combination with the use of so-called Penning mixtures. A Penning mixture consists of an inert gas with a small admixture of a second gas, that has lower ionization voltage than the inert gas. Consequently, numerous cold atmospheric pressure plasmas belong to the group of jet-like sources and are operated in helium.

The next section describes the aforementioned characteristics using the prominent example of the micro-scaled Atmospheric Pressure Plasma Jet operated in helium, thus completing the cold atmospheric pressure plasma chapter.
2.1.5 The micro-scaled Atmospheric Pressure Plasma Jet operated in helium

Capacitively coupled plasmas are a frequently used and well-investigated group of low temperature non-equilibrium discharges at atmospheric pressure. They stand out due to their simple geometry and consequently their convenient technical realization. Additionally, the complex knowledge already gained in the last decades in the low and medium pressure regime for this type of discharges is advantageous. Consequently, various models, geometries and individual designs have been developed in the past.

In general, there are two geometries to realize capacitively coupled discharges at atmospheric pressure: (i) coaxial and (ii) coplanar arrangement of the electrodes. In both designs, the electric field is perpendicular to the gas flow, so that there is no electric field and hence no electrical heating outside the jet configuration. Consequently, only reactive species reach a treated surface. Design (i) allows easy modification of various device components such as dielectrics and capillaries. Design (ii) is similar to conventional low pressure CCP discharges. The setup of design (ii) is simplistic, which facilitates numerical modeling and optical access.

The original 'Atmospheric Pressure Plasma Jet' (APPJ) concept was developed and patented (Patent No.: US 6,262,523 B1) by Selwyn et al. [15] to produce a uniform discharge at low temperature and atmospheric pressure to be used in materials processing applications. The discharge was constructed like design (i) and consisted of two concentric electrodes one of which was powered with an RF voltage and one of which was grounded. Several publications presented its applicability for etching [76], deposition of silicon dioxide [77] and decontamination of chemical and biological warfare [78].

To improve access to the discharge volume and reduce the gas flow required for operation of the APPJ, Schulz-von der Gathen et al. elaborated the design of the micro-scaled atmospheric pressure plasma jet (µ-APPJ) [29]. The gap distance and the volumetric flow rate were kept constant, but the setup was changed to co-planar electrodes (design (ii)) enclosed by two quartz windows at each side. Thus, a discharge channel of 1 mm × 1 mm × 30 mm is formed. As mentioned in chapter 1, the µ-APPJ can be operated in pure helium or in helium with small admixtures of molecular gases such
2.1 Characteristics of cold atmospheric pressure discharges

![Image](image.png)

**Figure 2.4:** Photograph of one of the early designs of the $\mu$-APPJ consisting of two steel electrodes in a glas cuvette [29].

as oxygen or nitrogen. A photograph of one of the early designs is shown in figure 2.4. The $\mu$-APPJ has been frequently used and is still actively investigated by several research groups. Up to today, more than 50 articles on experimental measurements as well as numerical simulations of the $\mu$-APPJ have been published. In the following, the characteristics of the $\mu$-APPJ being operated in helium are summarized as these data are frequently being referenced and compared to the argon discharge in chapter 5.

The most important intrinsic parameters describing a plasma are the electron density and electron temperature. Based on these parameters, Debye length, plasma frequency, ionization degree and many other parameters of a plasma discharge can be deduced (see section 2.1). Since these quantities at the moment can hardly be directly measured in a cold atmospheric pressure discharge, typical values are often taken from simulations. Using a PIC simulation, Hemke et al. modeled the electron density to be of the order of $n_e \approx 7 \times 10^{16} \text{ m}^{-3}$ [27] in pure helium. In a fluid simulation by O’Neill et al., the electron temperature was determined to be of the order of $T_e \approx 2.5 \text{ eV}$ in the bulk region [49].

Since at atmospheric pressure, the electrons determine the heating of the discharge, their behavior is particularly important to understand discharge processes. Therefore, the electron excitation in the electrode gap was investigated using one-dimensional fluid models and phase-resolved optical emission spectroscopy by Schaper et al. [79]. They show two distinct heating mechanisms as described in section 2.1.3 with a pronounced
γ-like mode at high dissipated power.

As the admixture of molecular gases leads to the production of highly reactive species such as atomic oxygen, many studies were conducted using a small admixture of oxygen of the order of 0.5%.

Bibinov et al. used optical emission spectroscopy combined with a chemical model for a helium discharge with small nitrogen admixtures to confirm the electron density to be \( n_e = 5 \times 10^{16} \text{ m}^{-3} \) [35]. This corresponds well to the density from the simulation cited above. Additionally, the averaged electric field was estimated to be of the order of 300 V/mm, which corresponds to a reduced electric field of 12.5 Td at atmospheric pressure.

Since the rate constant for many chemical reactions in the gas phase depends on the neutral gas temperature, this temperature plays an important role for the composition of the plasma discharge. Fluid modeling and measurements of the gas and heat dynamics confirmed that the gas temperature is of the order of 315 K to 355 K, but varies with applied power and gas flow [80]. However, the gas flow is always laminar up to gas flow rates of 2000 sccm.

As already described in section 2.1.2, atoms in metastable states play a key role in atmospheric pressure plasmas. Hence, they were investigated in detail by different groups. Niemi et al. measured the number density of the \( ^2S_1 \) metastable states of helium in the μ-APPJ using tunable diode laser absorption spectroscopy. In pure helium, they measured an absolute density of \( 2 \times 10^{16} \text{ m}^{-3} \) [17], decreasing with increasing oxygen admixture. Notably, this density is comparable to the overall electron density which underlines the important character of metastables as energy storage. Also, the number density increases slightly more than linearly with increasing power. Niermann et al. measured the highest density in the vicinity of the sheaths [23, 28].

Highly reactive species generated in the plasma discharge are of high interest for surface applications. The reactions on the surface are dependent of the flux of reactive species onto the surface. This flux is determined by the reactive species density in the discharge. One possible candidate for the built-up of reactive oxygen species is atomic oxygen. Consequently, Knake et al. determined its number density using two-photon absorption laser induced fluorescence (TALIF) to be of the order of \( 3 \times 10^{15} \text{ cm}^{-3} \). The
2.1 Characteristics of cold atmospheric pressure discharges

measurement was conducted in a helium discharge with an admixture of 0.6% of oxygen, where the atomic oxygen number density shows a maximum [19, 34, 81]. The number density increases linearly with the applied power [38]. Direct comparison of measurements and models by Waskoenig et al. revealed good agreement of measured and simulated data [22, 82]. However, not only oxygen, but also nitrogen [30], water [39] or mixtures of the aforementioned species were admixed. Typical admixtures are in the range up to a few percent.

Not only reactive species, but also high energetic radiation plays an important role for the treatment of targets. Optical emission spectroscopy in the vacuum ultraviolet range showed that photons with an energy above 10 eV, generated in the plasma discharge by atomic line and excimer emission, are transported through the helium atmosphere of the plasma effluent over distances of several centimeters [83, 84]. This underlines the importance of molecular dimers in the discharge.

Impurities in the discharge strongly influence the discharge chemistry. This was confirmed by numerical models, but also by empirical measurements [20, 32, 33]. In numerical models, humid air impurities in the plasma discharge considerably increase electronegativity, but decrease the densities of reactive oxygen species [85]. Instead, other potentially important reactive hydrogen and nitrogen species such as atomic hydrogen, hydroxide, hydrogen peroxide or nitrogen oxide are generated [86]. Große-Kreul et al. used mass spectrometry to prove that without purification of the feed gas, water cluster ions dominate the mass spectrum [33]. Consequently, appropriate counter-measures have to be taken to reduce impurities if a pure discharge is desired (see section 3.2).

For the sake of completeness, the following paragraph also briefly describes investigations of the effluent and applications: The gas phase chemistry in the effluent was investigated using mass spectrometry [18, 33, 87–91], numerical modeling [86], infrared optical emission spectroscopy [92] and TALIF in front of a target [24]. There were also biological experiments carried out showing the effect of plasma treatment on biological species such as DNA [93] or bacteria [25, 26, 94, 95]. Additionally, the µ-APPJ was used for the investigation of surface reactions during deposition of silicon oxide films [40, 96–98].
Chapter 2 Fundamentals

2.2 Characteristic properties of argon and helium

Both argon and helium are noble gases (also called rare gases), which means that they possess a full valence electron shell. They are chemically inert and a good basis to investigate fundamental physical mechanisms in plasmas without interference of chemical processes. They are both standard gases for plasma generation and investigation. Noble gases have a small atomic volume and a high ionization energy.

In the ground state, argon has the electron configuration $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$. A schematic Grotrian diagram of excited argon has already been shown in section 2.1.2 (figure 2.2). Energy levels are sorted by their multiplet state of the electron configuration ($3s^23p^5ns$, $3s^23p^5np$, $3s^23p^5nd$). Different energy levels result from different coupling of core electrons and spin and angular momentum conditions of the outermost electron.

For heavy rare gases, $LS$ notation is not appropriate to designate levels. There are two common alternatives: Racah's notation (based on $jK$ coupling scheme [99]) and Paschen's notation (based on empirical findings), the latter being adopted in this thesis. For a conversion between the two notations and an overview of the respective quantum numbers, see table C.1 in appendix C.

Among the most extensively studied energy levels are the 1s and 2p levels of excited argon (Ar I) [100]. Spectral lines in the visible and UV region originating from transitions involving these levels are frequently present in various discharges. Argon has two metastable states ($1s_3^1$, $1s_5^1$) at approximately 11.6 eV that are marked in red in the Grotrian diagram in figure 2.2. As stated in section 2.1.2, the transition (dipole radiation) from these states to the ground state is quantum-mechanically forbidden. The remaining two 1s levels ($1s_2^2$, $1s_4^2$) are resonant states, i.e. they can directly de-excite to the ground state by emitting a photon in the UV range.

Table 2.1 summarizes the most important physical constants of helium and argon, respectively. The molecular mass of argon is ten times higher than that of helium which is also reflected by the mass density. Therefore, in contrast to argon, helium ions in an RF discharge with a frequency of 13.56 MHz cannot in general assumed to be at rest. Additionally, the energy transfer via electron collisions is much more efficient.
2.2 Characteristic properties of argon and helium

Table 2.1: Comparison of physical constants of argon and helium at 0 °C, 1013 mbar, data from Haynes et al. [101] and Raizer [51].

<table>
<thead>
<tr>
<th>characteristic property</th>
<th>argon</th>
<th>helium</th>
</tr>
</thead>
<tbody>
<tr>
<td>molecular mass</td>
<td>40 u</td>
<td>4 u</td>
</tr>
<tr>
<td>density</td>
<td>1.7837 kg m$^{-3}$</td>
<td>0.1785 kg m$^{-3}$</td>
</tr>
<tr>
<td>ground state configuration</td>
<td>[Ne] 3s$^2$ 3p$^6$</td>
<td>1s$^2$</td>
</tr>
<tr>
<td>ionization energy</td>
<td>15.7596 eV</td>
<td>24.5874 eV</td>
</tr>
<tr>
<td>boiling point</td>
<td>−185.848 °C</td>
<td>−268.928 °C</td>
</tr>
<tr>
<td>thermal conductivity</td>
<td>17.7 mW m$^{-1}$ K$^{-1}$</td>
<td>155.7 mW m$^{-1}$ K$^{-1}$</td>
</tr>
<tr>
<td>specific heat capacity at 25 °C</td>
<td>0.520 J g$^{-1}$ K$^{-1}$</td>
<td>5.193 J g$^{-1}$ K$^{-1}$</td>
</tr>
<tr>
<td>Townsend ionization coefficient A</td>
<td>12 cm$^{-1}$ Torr$^{-1}$</td>
<td>3 cm$^{-1}$ Torr$^{-1}$</td>
</tr>
<tr>
<td>Townsend ionization coefficient B</td>
<td>180 V cm$^{-1}$ Torr$^{-1}$</td>
<td>34 V cm$^{-1}$ Torr$^{-1}$</td>
</tr>
</tbody>
</table>

for helium, because the mass ratio of neutrals to electrons is lower for helium than for argon. Hence, the electron density required to sustain a helium plasma is usually low [102].

Another important difference between argon and helium is the lowest excitation level: The lowest excited helium state has an energy of 19.8 eV, which is approximately 70% higher than the lowest excited argon state with 11.55 eV. Hence, for direct electron impact excitation of helium, much higher electron energies are required. This can influence the electron energy distribution function, as in argon, the high energy tail is more likely to be depleted than in helium.

The boiling point of helium is considerably lower than that of argon. This is important for technical purposes, such as an implementation of a cold trap for minimizing humidity in the feed gas.

Due to its low mass, the thermal conductivity of helium is approximately ten times higher than that of argon. Additionally, the specific heat capacity is ten times higher for helium than for argon. This can have an impact on the development of instabilities as is further discussed in chapter 5.

In plasma discharges, the population processes described in section 2.1.2 are determined by their particular cross sections. Figure 2.5 exemplary shows cross sections versus electron energy for elastic momentum transfer, excitation and ionization of both,
helium and argon. The graph shows that significant differences between the cross sections exist. For elastic collisions between electrons and neutrals, the momentum transfer (black lines) cross section is relevant. Here, the argon cross section is a strongly varying function of electron energy and shows a distinct minimum for low electron energies of 0.25 eV. This is the so-called Ramsauer-Townsend minimum, that is caused by quantum-mechanical interference effects. At certain energies, electrons can pass the gas atoms if their wavelength is in the same order as the size of the atoms [104]. In helium, this Ramsauer minimum is missing since its force field is too weak [105] and the momentum transfer cross section is almost constant for low electron energies. For high electron energies (> 5 eV), the momentum transfer cross section is higher for argon than for helium. Both, excitation and ionization thresholds are lower for argon than for helium. Additionally, the absolute values of these cross sections are higher for argon than for helium, thus facilitating these processes. These differences play a role for the dominating excitation mechanisms in both discharges and thus for the macroscopic behavior and the continuous operation of the discharge and are further discussed in chapter 5.
Comparing argon and helium plasmas empirically, it has been found that at high $p \cdot d$ values above 10 Torr cm, the breakdown voltage is higher for argon than for helium both for DC and RF electric fields [106, 107]. Moravec et al. measured RF breakdown curves that show breakdown voltages five times higher for argon than for helium discharges [108]. Additionally, the Townsend first ionization coefficient $\alpha/n_g$ (DC case) for argon is smaller than for helium at reduced electric field strengths below 100 Td ([52]) as can be calculated from the Townsend ionization coefficients in table 2.1. The typical electric field in the $\mu$-APPJ configuration is of the order of 15 Td (see section 2.1.5) and hence, the volumetric ionization rate will be smaller for argon than for helium. This plays a decisive role in the ignition of the discharge as will be shown in chapter 5. In the past two decades, numerous studies have found that it is easier to generate a homogeneous discharge at atmospheric pressure in helium than in argon [31, 109, 110]. Homogeneous argon plasmas are often ignited with the help of helium admixtures [109, 111], as the homogeneous ignition has proven to be difficult. However, this is only one possible method to realize a homogeneous argon discharge. Section 3.2 describes, how this problem is solved in this study.

Besides empirical comparisons of discharges in different operating gases, there are also respective models of these plasma discharges. Jonkers et al. compared argon and helium discharges at atmospheric pressure [37]: They found that for a plasma being operated at the same external conditions, an argon plasma has a lower electron temperature and a higher electron density than a helium plasma. A smaller ion mass favors the diffusion of charged particles of the plasma and thus decreases the residence time. Hence, a higher power density is necessary in helium plasmas to obtain the same electron density as in argon plasmas. Additionally, a helium plasma is further from equilibrium than an equi-operational argon plasma.

Thus, both empirical findings and models predict different behavior of homogeneous argon and helium discharges. Yet, a discharge geometry that allows to compare both discharges at atmospheric pressure under sufficiently stable and reproducible conditions was not available until now.
2.3 Electrical modeling

To compare plasma discharges operated in different gas mixtures, plasma parameters have to be determined in dependence of equi-operational control parameters. This is done in chapter 5 using electrical measurements in combination with a global electrical model. This model is based on the homogeneous model by Lieberman et al., that is briefly described in this section based on standard literature [52, 112].

To determine the plasma electrodynamics, fluid equations can be used when describing plasma from the viewpoint of dielectrics or conductors. At low frequencies, the electric field causes motion of the charged particles, that can be interpreted as currents. This current, in turn, may be expressed as a corresponding conductivity. At high frequencies, the displacement of charged particles, can lead to a polarization that corresponds to a permittivity. The choice of approach depends on the frequency domain.

In a uniform, unmagnetized bulk plasma with infinite ion mass that is driven by a small amplitude time-varying electric field, a one-dimensional electrostatic solution of Maxwell’s equation can be used to determine the fields. The complex total current amplitude $\tilde{J}_{Tx}$ depends on the complex outer electrical field $\tilde{E}_x$ via

$$\tilde{J}_{Tx} = i \omega \varepsilon_0 \varepsilon_p(\omega) \tilde{E}_x,$$  \hspace{1cm} (2.20)

where $\varepsilon_0$ is the vacuum permittivity. Taking into account the displacement current caused by the time-varying field and the conduction current caused by the electron motion, the complex plasma permittivity is given by

$$\varepsilon_p(\omega) = 1 - \frac{\omega_p^2}{\omega(\omega - i \nu_m)} = 1 - \frac{\omega_p^2}{\omega^2 + \nu_m^2} - i \frac{\nu_m}{\omega} \frac{\omega_p^2}{\omega^2 + \nu_m^2},$$ \hspace{1cm} (2.21)

where $\omega_p$ is the plasma frequency, $\omega$ the RF angular driving frequency, $\nu_m$ the electron-neutral collision frequency, $n_e$ the electron density, $m_e$ the electron mass and $e$ the elementary charge.

On the right-hand side, the '1' comes from the displacement current, whereas all other contributions relate to the local particle motion ([112]). The real part of the permittivity
2.3 Electrical modeling

is related to the stored energy within the medium, whereas the imaginary part of the permittivity is related to the dissipation (or loss) of energy within the medium.

Making use of equation 2.21, the RF impedance $Z_p$ of a bulk plasma slab is therefore

$$
\frac{1}{Z_p} = i \omega \frac{\varepsilon_0 \varepsilon_p A}{d} = i \omega \frac{\varepsilon_0}{\varepsilon_p} \left( 1 - \frac{\omega_p^2}{\omega (\omega - i \nu_m)} \right) \frac{A}{d}, \quad (2.22)
$$

with $A$ being the cross-sectional area and $d$ the thickness of the plasma bulk. Since $Z_p$ is supposed to be a global quantity, this expression should be based on spatially averaged quantities for $\omega_p$ and $\nu_m$ [112] ('homogeneous model').

Equation 2.22 can be recast into

$$
\frac{1}{Z_p} = i \omega C_b + \frac{1}{i \omega L_p + R_p}, \quad (2.23)
$$

where $C_b = \frac{\varepsilon_0 A}{d}$ is the vacuum capacitance of the slab geometry, $L_p = \frac{d}{\omega_p^2 \varepsilon_p A} = \frac{m_e e^2 d}{n_e A}$ is the inductance that results from the electron inertia and $R_p = \nu_m L_p = \frac{m_e \nu_m e^2 d}{n_e A}$ is the resistance that results from the elastic electron-neutral collisions. Note that the inductance and resistance are non-linear components, since they depend on the plasma density and thus are functions of the amplitude of the power (or current, or voltage) in the system.

In the sheath, the current is almost entirely displacement current, since the conduction current is mainly carried by electrons, and the electron density is assumed to be approximately zero in the sheath, whereas the ion density is assumed to be uniform across the discharge gap.

The sheath voltage is a non-linear function of the applied current and can be calculated by integrating Poisson's equation and then deriving the displacement current and the sheath boundary. Although each sheath is non-linear, the combined effect of both sheaths is linear in this simplified model. Taking into account the conduction current, the average sheath thickness can be determined and we obtain this simple relation between applied current $I_{rf}$ and combined sheath voltage $V_s$

$$
I_{rf} = C_s \frac{dV_s}{dt}, \quad (2.24)
$$
Chapter 2 Fundamentals

Figure 2.6: The plasma equivalent circuit a) for the simplified homogeneous discharge model a) is composed of a capacitance ($C_b$) in parallel with a resistance ($R_b$) and an inductance ($L_b$) in series for the bulk plasma and a capacitance ($C_s$) in series representing the combined sheath capacitance.

with $C_s = \frac{\varepsilon_0 A}{2s_0}$ being a linear capacitance, where $s_0$ is the average sheath width.

Based on equations 2.23 and 2.24, the equivalent electrical circuit of the plasma consists of the RLC network shown in Figure 2.6. In this simple model, further sheath effects such as an equivalent sheath resistance due to stochastic heating or current sources due to ion heating in series with capacitances have been neglected.

For collisional plasmas ($\nu_m \gg \omega$), equation 2.21 reduces to

$$\varepsilon_p(\omega) = 1 - i \frac{\omega^2 p}{\omega \nu_m}, \quad (2.25)$$

and thus the inductance in Figure 2.6 b) can be omitted [113]. This equation will be used in section 5.2 to deduce fundamental plasma parameters such as the electron density.
3 Experiment and diagnostics

In this study, a microscaled atmospheric pressure plasma jet device was developed to obtain a stable, comparable cold atmospheric pressure plasma where the control parameters can be accurately measured. The following chapter is dedicated to the experimental setup used in this work and is structured in three sections: The first section gives a detailed description of the COST Reference Microplasma Jet device, where a focus is put on the electrical characterization of the discharge. The second section deals with the peripheral equipment necessary to operate a stable and reproducible discharge. In the third section, the diagnostics used for the investigation of plasma processes are introduced. For each diagnostic, a brief introduction into the physics and a description of the experimental implementation is given.

Parts of this chapter have already been published [Golda2016].

3.1 Design of the COST Reference Microplasma Jet

The COST Reference Microplasma Jet (COST-Jet or COST-RMJ, see figure 3.1) represents the successor of the original µ-APPJ concept. Its design is based on a huge number of experiments and simulations, and on years of experience in the working group. Inspired by the GEC reference cell, it is supposed to serve as a reference for atmospheric pressure plasma applications. The device comprises two main components: (i) The 'head' consists of the electrode stack with quartz panes and the gas tubing which is attached by the gas connector. (ii) The housing clamps down the head, includes the electrical connections, and miniaturized voltage and current probes. These two constituents will be described in detail below. The technical drawings are available via the website www.cost-jet.eu.
Figure 3.1: The ignited COST Reference Microplasma Jet (COST-Jet): The discharge is generated between the two symmetric, plane-parallel electrodes which are held by the housing [Golda2016].

3.1.1 Head

The main component of the head (see figure 3.2) is the electrode assembly. This assembly is a stack of a quartz pane, two metal electrodes and another quartz pane. The stack is glued by a two-component adhesive suitable for high-vacuum applications (TorrSeal®), thus forming the discharge channel. This assembly is secured into a ceramic gas connector which joins the ¼ inch stainless steel gas tubing to the electrode assembly.

3.1.1.1 Electrode assembly

The two symmetric metal electrodes are separated by a gap of 1 mm width. To fulfill quality requirements for biological applications, they are made of medical stainless steel (SS 316) with a thickness of 1 mm. The quartz panes (Corning 7980) serve as windows
3.1 Design of the COST Reference Microplasma Jet

Figure 3.2: Detailed sketch of the head including the two symmetric stainless steel electrodes with connection wings. The quartz panes are covering the electrodes from both sides. The blue line at the circumference indicates the TorrSeal® adhesive inside the groove formed between the panes and the electrodes. The gas connector attaches the gas tubing to the head [Golda2016].

for direct optical broadband observation of the discharge. They allow wavelength transmission down to 200 nm. Their thickness is 1.5 mm and they cover the electrodes over a length of 50 mm thus forming the discharge channel. Since the quartz panes are slightly larger than the electrode configuration, a 1 mm groove is formed at the outer edge, which is used to glue the entire stack with the two-component adhesive (TorrSeal®) without any contact between the feed gas or the plasma and the adhesive. This is important to minimize interaction between the glue and the plasma discharge. To avoid any space between electrodes and pane, the stack is pressed together in a vice during assembly. Thus, any air intrusion during operation is minimized. As indicated by the blue circumference in figure 3.2, the adhesive reaches from the electrode wing up to the flat exit which is formed by the decreasing width of the quartz panes 5 mm over a length of 3.5 mm. This wedge shape is well-suited for biological applications, e.g. for the insertion of the tip into the cavities of a 24 well titer plate to treat samples.

The gas channel features three different zones: (i) The premix zone is a region of 11.5 mm length and is partly covered by the gas connector. Here, the electrodes are
widely spaced, which prevents the discharge from igniting in this area. In this region, the gas from the supply is allowed to redistribute before entering the main discharge volume. The height of this zone is 5 mm.

(ii) The discharge channel is the subsequent downstream part to the premix zone and extends over a length of 30 mm. This length was chosen based on previous measurements, which demonstrated a saturation state for chemical reactions at this point. The electrodes are closely spaced, thus defining the 1 mm high discharge channel. Here, the discharge is supposed to ignite and form a homogeneous discharge. For typical gas flow rates, the flow is laminar in this region (see appendix B).

(iii) The safety gap is formed by the quartz panes extending beyond the electrode tips and has a length of 1 mm. This safety gap serves two main purposes: Firstly, any electrical contact between the powered electrodes and a user or a target is prevented and secondly, when coming in contact with a surface, the gas flow is not blocked immediately, thus allowing regular operation of the device.

To describe different positions in the plasma discharge, an uniform coordinate system is used throughout this thesis. The tip of the electrodes at the COST-Jet exit represents the origin of this coordinate system. Since investigations often cover both the discharge region and the effluent, positive ‘+’ coordinates point into the effluent and negative ‘-’ values into the discharge region, with zero defined at the electrode edge. As the COST-Jet discharge is often defined as a two-dimensional system, the perpendicular direction is defined by the distance to the powered electrode.

3.1.1.2 Gas configuration

The gas connector is a cube of machinable ceramic (Macor®), that provides an electrically isolated connection to the gas line. The electrode assembly and a 1/4 inch stainless steel tube are inserted into a slot and a drilled hole on opposite sites of the cube and tightly glued (see figure 3.2). The feed gas is supplied from the steel tube through a drilling in the gas connector with 1 mm diameter into the electrode assembly. This construction and the selected materials ensure that only stainless steel, alumina ceramic and quartz as inert materials come in contact with the gas and the plasma. Depending on the requirements, the length of the feed gas tube can be varied. A typical length
3.1 Design of the COST Reference Microplasma Jet

Figure 3.3: Sketch of the complete assembly consisting of head, housing and gas tubing. In the housing, the guidance and fastening of the head, the electrical power connections with coil and variable capacitor, and internal current and voltage probes are illustrated [Golda2016].

used throughout this study is 60 mm. A flexible connection to standard gas fittings is realized via an O-ring fitting adapter (right of figure 3.3). Thus, the complete head can be removed from the housing. This might be necessary if any components such as the electrodes are damaged during operation. The housing is described in the next section.

3.1.2 Housing

The housing (see figure 3.3) is built into a rigid aluminum casing (Fischer Elektronik, AKG412450ME) with a size of 41 mm × 24 mm × 50 mm. Its outer surfaces are anodized, which makes them electrically insulating. Therefore, any incidental electrical contact of the user is prevented. The complete head can be inserted into the housing and mounted by fastening a metal clamp around the gas tubing. Thus, excellent grounding of the device and stable support are ensured. Electrical contact between the power supply and the electrodes is provided by screwing threads through the electrode
wings into a flat copper conductor. The bottom of the housing also provides an M5 thread to mount the jet on optical posts which facilitates investigations.

The front cover includes a slot for the head and a thread to mount an electrode shielding for the grounded electrode. The shielding is necessary for current measurements, for more details see section 3.1.3. The electrical connectors are positioned at the back cover of the housing, including the power connector (SMA), two probe connectors (SMC), and the adjustable tuning capacitor. To reduce the risk of confusion, different connectors for probes and power supply were selected.

A low loss coax cable (H-155 PE Low Loss) with a damping of 0.46 dB/m at 2 GHz connects the COST-Jet to the power supply.

An internal resonance coupling circuitry replaces external tuning networks (matchbox) which are usually required and widely used. The configuration is based on the work by Marinov and Braithwaite [114] (see figure 3.4). It consists of an LC circuit with an inductor ($L = 9.6 \mu H$, Amidon T68-2 core, 41 windings) and a tunable capacitor (Sprague Goodman $C_t = 0.8 \text{ pF} \text{ to } 8 \text{ pF}$). The latter can be used to tune the circuit into resonance at a frequency of 13.56 MHz. The inductor and capacitor are installed in
series and in parallel to the electrode stack, respectively, forming an LC circuit with a Q-factor of about 30, which corresponds to a thirty-fold increase of the applied voltage. This enables the use of small power supplies capable of delivering 7V and 10W to ignite the discharge.

3.1.3 Miniaturized, integrated current and voltage probe

To control operation parameters, a miniaturized current and voltage probe was developed and integrated into the housing of the COST-Jet. The advantages of the probes being integrated into the head of the COST-Jet are constant availability and reproducibility of the measurements. Additionally, the voltage probe reduces loading of the source, as described in detail in the following paragraph.

Often, commercial probes are used to measure current and voltage. But physically attaching a probe to the test point establishes an electrical connection between the electrode and the oscilloscope. For reliable measurement results, this connection must have minimum effect on the circuit operation and the signal transmitted through the probe to the oscilloscope. One unwanted effect is signal source loading, because an external device, such as a probe, appears as an additional load to the signal source. It draws a signal current from the circuit and thus changes the signal seen at the test point. An ideal probe draws zero current, that corresponds to an infinite impedance, which cannot be achieved in practice. However, the amount of loading should be minimized. For alternating currents, the capacitance of the probe tip defines the reactance of the probe. Especially for high frequencies, this reactance becomes important. Thus, reducing the amount of loading implies reducing the capacitance of the probe tip.

There are commercial voltage probes on the market that are able to resolve the high frequency of 13.56 MHz and withstand the high voltages. Unfortunately, these probes have a capacity of typical 8.0 pF. This is not much, but compared to the small capacity of the COST-Jet with $C_{\text{Jet}} = 0.293$ pF, they exceed its capacity by a factor of 27. Thus, these probes presumably cause signal source loading. To avoid or at least minimize this influence, we developed our own miniaturized probes that are described hereafter.
The voltage across the discharge channel is measured via a pick-up voltage probe, which consists of a copper pin with a length of 5 mm located 4 mm below the flat copper conductor leading to the powered electrode. The location was chosen to maximize the distance between voltage and current probe. Thus, cross-talk is minimized. The voltage probe is capacitively coupled to the electrode and thus the measured signal is proportional to the voltage across the discharge. The capacity of the pick-up antenna can be estimated using the formula for a wire parallel to a wall \( C = \frac{2\pi \epsilon l}{\text{arcosh}(d/R)} = 2 \times 10^{-13} \text{F} \), with \( \epsilon \) being the permittivity, \( l \) the length of the probe, \( d \) the distance between probe and copper conductor and \( R \) the radius of the probe. After calibration with an external voltage probe, the voltage between the electrodes can be obtained using an oscilloscope. The calibration procedure is described in more detail in chapter 3.3.1.1.

The current probe consists of a resistive current measurement. The voltage drop over a resistor \( (R_m = 4.7 \Omega \pm 1 \%) \) which is in series with the ground-side electrode and ground is measured. This voltage drop is proportional to the discharge current via Ohm’s law. To avoid distortion of the measured signal by electrical cross-talk, a surface-mountable thick film resistor was chosen. It has low parasitic properties and small dimensions. Additionally, it was mounted on a small printed circuit board to avoid an antenna loop. The measured signal is delivered using a semi-rigid coaxial cable. Thus, the position of the cable is fixed inside the housing keeping any parasitic coupling effects constant. Using SMC bulkhead connectors and soldering as close as possible to the resistor eliminates another potential source of interference. Around the ground-side of the electrode assembly, a grounded shielding is secured (see figures 3.1 and 3.3). It nearly completely covers the grounded electrode except for the surface directly facing the discharge. Thus, it makes the parasitic stray capacity a fixed value. Additionally, it also reduced the reactive current passing through the current sense resistor enabling a better accuracy of the measurement. For more details on the electrode shielding, see the publication by Beijer et al. [115].

### 3.1.4 Power supply

Since the internal LC circuit of the COST-Jet enables the use of low-power supplies, a simple, tailored, miniaturized power supply for 13.56 MHz was developed. It is
3.2 Discharge chamber and gas supply

capable to deliver the required voltage to safely operate the COST-Jet in helium with a 0.5% admixture of oxygen. The maximum output power of the amplifier is 12 W. This power supply is not mandatory. Instead, the COST-Jet can be operated by any power generator capable of delivering this voltage and power range, when the required matching to the LC circuitry can be achieved.

3.2 Discharge chamber and gas supply

For reproducible experimental conditions, all measurements were performed in a vacuum discharge chamber. To ensure a controlled ambient atmosphere, the chamber was evacuated prior to any measurements and then refilled with the feed gas. The chamber consists of a cylindrical stainless steel housing of 32 cm inner diameter that is uprightly mounted onto an experiment table, which can be used as a base for optical setups. The top cover plate is removable and sealed with two viton gaskets. The lateral surface is equipped with several flanges of different sizes. Four flanges with quartz windows allow easy optical access down to 200 nm. The remaining flanges are used for pressure monitoring, as well as electrical, optical and gas feedthroughs for the gas supply system.

The pumping system (see figure 3.5) is connected to the chamber via a bottom flange. It comprises two independent systems: (i) A two-stage-system consisting of rotary vane pump (Brook Crompton BS2208) and a turbomolecular pump (Edwards EXT 200/100 CF), which allows to evacuate the discharge chamber to a final pressure of $1 \times 10^{-4}$ mbar. A rotary valve can be used to separate the chamber from the pumping system. (ii) To prevent any contamination by oil, a diaphragm vacuum pump (Pfeiffer Vacumm, MVP 015-2) with a fine tuning rotary valve allows to stabilize the gas pressure in the discharge chamber during plasma operation. To establish an accurate measurement of pressure in the discharge chamber over a wide range, two pressure gauges are used for monitoring: One for low pressures (Balzers PKR 250) down to $1 \times 10^{-9}$ mbar and one for elevated pressures around atmospheric pressure (Pfeiffer Vacuum, CMR 371). To avoid overpressure in the discharge chamber, a pressure relief valve is installed for safety reasons. If the pressure is above 1300 mbar, it opens and enables the release of the gas from the discharge chamber.
As already discussed in section 2.1.5, control of impurities is essential for reproducible results and thus is a major issue in atmospheric pressure plasmas [31]. Water attached to the gas tubing was identified to be one of the main sources for impurities [32, 33]. Hence, if not stated otherwise, the discharge chamber described above is used in all experiments to provide a controlled atmosphere. The gas supply system (see figure 3.5) is attached to the discharge chamber via a feedthrough flange close to the top cover plate. The gas supply consists of stainless steel tubing with a diameter of 1/4 inch and the accompanying fitting components (swagelok).

For purification of the feed gas, a cold trap is installed in between the gas supply system and the discharge chamber. Since mostly argon is used as feed gas, liquid nitrogen cannot be used for the cooling as the temperature of liquid nitrogen is below the boiling point of argon (see section 2.2). Instead, a cooling bath consisting of a mixture of ethanol and dry ice (CO₂) is used. Since the sublimation point of dry ice is 194.6 K [101] and and ethanol freezes below this temperature, the mixture maintains a temperature of −78 °C. Even though this temperature is higher than that of liquid
3.2 Discharge chamber and gas supply

nitrogen, it is sufficient to remove most of the water impurities by freezing them out. However, nitrogen impurities from the gas cylinders remain in the gas.

To allow reproducible mixing ratios of the feed gases, the gas flow rate is controlled via mass flow controllers (Analyt-MTC series 358) with different maximum gas flow rates (2 slpm for the carrier gas and 1 sccm, 10 sccm, 50 sccm for the admixed gases). To facilitate change of the feed gases, an additional by-pass is installed for quick evacuation of the gas supply system. To ensure a minimum of impurities from the feed gas source, the gas used in this thesis has a purity of 99.999% and is provided by gas cylinders.

Mixing two gases with considerably different flow rates requires an appropriate gas mixing setup. Especially if a fast response of the gas composition is desired, e.g. for admixture variations, a counter-flow mixing unit is the preferable option [116]. Therefore, the gas with the high flow rate was counter-directed onto the mass flow controller of the low flow rate gas so that immediate mixing takes place. To ensure that the mass flow controller was not disturbed by the counter-flow, a test measurement with a mass flow meter was conducted. The mass flow meter was installed in front of the mass flow controller and the gas flow rate was checked to be displayed correctly even with the counter flow directed onto the controller. The test measurement confirmed that the set point of the mass flow controller was not disturbed.

For reproducible variations of the position, the COST-Jet is mounted onto a high precision relative positioning system inside the discharge chamber. It consists of a
translational two-orthogonal-axis positioner (Thorlabs DT25/M). A second, homemade
two-axis translational stage is installed at the floor of the discharge chamber. This
stage allows vertical and horizontal positioning of additional probes such as optical
fibers for optical emission spectroscopy to investigate the discharge. The two stages
can be controlled electronically via a customized software.

For ignition of a homogeneous argon discharge in the COST-Jet, an initial high voltage
spark is needed. This high voltage spark is generated using a high voltage spark gun
outside the discharge chamber. To deliver a trigger spark to the tip of the COST-Jet, a
coaxial cable with a thin wire tip is used via an electrical feedthrough.

For precise voltage adjustment, the driving voltage in this thesis was provided by an
RF generator (coaxialpower RF 150) and delivered via a manual impedance matching
network (coaxialpower MMN150) to the COST-Jet. The probes are connected to
an oscilloscope (Agilent Technologies DSO7104B) with a bandwidth of 1 GHz and
a resolution of 4 GSa/s. A high temporal resolution is necessary for an accurate
measurement of the phase difference between voltage and current.

An optical fiber feed-through flange is installed to enable OES fiber optic measurements
inside the discharge chamber. These measurements, besides other plasma diagnostic
methods, are described in the next chapter.

3.3 Plasma diagnostics

In order to comprehensively investigate the plasma discharge in the COST-Jet, a wide
variety of plasma diagnostics were used, which are briefly described below.

3.3.1 Electrical measurements

Because gas discharges can be considered as electrical systems, the most straightforward
but integral method to evaluate the behavior of a plasma is measuring electrical
properties such as current, voltage and the phase difference between them [117]. As
secondary parameters, the actual dissipated power and impedance can be derived. The
3.3 Plasma diagnostics

Figure 3.7: Amplitude of a commercial probe (Tektronix P5100A) signal as a function of internal probe signal. A calibration factor for the internal voltage probe can be deduced from the linear regression curve. Due to small manufacturing differences, this calibration has to be performed for each individual COST-Jet device. The used oscilloscope is indicated in the legend. (For improved visibility, only one value out of twenty measured values is shown, represented as the square symbols.) [Golda2016]

procedure to calibrate the voltage probe and to calculate the power from the measured waveforms is briefly described in the following sections.

3.3.1.1 Voltage probe calibration

Since the used voltage probe is a pick-up probe, the voltage drop measured by the oscilloscope is only proportional to the voltage drop across the electrodes. Hence, to calculate the actual voltage, a conversion factor is needed. Thus, prior to any measurements, the probe has to be calibrated. For this calibration, a commercial voltage probe (Tektronix P5100A) was connected to the electrodes of the COST-Jet. The commercial voltage probe will be used for calibration only. In this case, the disturbance of the electrical circuit by the commercial voltage probe is not critical,
Chapter 3 Experiment and diagnostics

since during the calibration, only the amplitudes of both measured voltage signals are relatively compared. Even if the voltage across the discharge gap might be reduced due to capacitive loading, both voltage amplitudes, that are measured by the commercial and by the internal voltage probe, will reflect this distortion in the same way. The compensation network of the probe was properly adjusted to the oscilloscope’s input impedance to ensure high fidelity in the 13.56 MHz region. An uncompensated probe can lead to various measurement errors such as distorted waveforms and incorrect measurement values due to high or low pass properties of the uncompensated probe. This is especially relevant for high attenuation probes.

When directly connecting the internal voltage and current probes to the oscilloscope, the measured signal depends on the cable length and the exact input impedance of the used oscilloscope. This is due to the fact that cable and input impedance are part of the divider network and hence determine the signal attenuation. To avoid this effect, a 50 Ω termination was used. The termination defines a known impedance and thus a unity voltage standing wave ratio is obtained, which minimizes the signal reflection. To assess the effectiveness of this measure, the internal voltage and current probes were connected to two different oscilloscopes (LeCroy WavePro 735Zi (40 GS/s, 3.5 GHz) and Tektronix DPO 2024 (1 GS/s, 200 MHz)) with different input impedances of 16 pF and 14 pF, respectively. During the voltage calibration, no difference was observed between the measurements using these oscilloscopes.

To calculate a calibration factor for the internal probe, the absolute amplitude values of the voltage signals measured with the internal and the commercial voltage probe were compared. They exhibit a linear correlation (see figure 3.7) and hence a single calibration factor was calculated by linear regression. The calibration factor from internal to commercial probe voltage was 2630 ± 50 for this individual device with a relative error of 2%. The error in calibration factors can most likely be attributed to the error of the voltage probe (± 1.75%) and an imprecise compensation of the commercial voltage probe, which cannot be entirely avoided. A detailed analysis of the error and a comparison of several devices will be given in section 4.1.

Notably, this calibration factor has to be re-measured for each COST-Jet device due to slight variations of probe positioning inside the housing.
3.3 Plasma diagnostics

To calculate the discharge current, the voltage measured by the internal current probe can be used. The current can be calculated via Ohm’s law, since the internal current probe simply measures the voltage drop \( U_i \) over the resistor \( R_m \). Taking into account the termination of \( R_t = 50 \Omega \) at the connection to the oscilloscope, the current can be calculated using

\[
I = U_i \frac{R_m + R_t}{R_m R_t}.
\]

### 3.3.1.2 Power measurement

The power \( P \) dissipated in a plasma can be deduced from time-resolved voltage and current measurements:

\[
P = \frac{1}{T} \int (U(t) \cdot I(t)) dt,
\]

with \( T = 74 \text{ ns} \) being the period of the 13.56 MHz RF cycle. If both voltage and current signal forms are sinusoidal, this formula simplifies to

\[
P = U_{\text{rms}} \cdot I_{\text{rms}} \cdot \cos(\Delta \phi)
\]

and the power can be calculated by multiplying the respective effective amplitudes and the cosine of the phase difference \( \Delta \phi \) between voltage and current. To check whether this prerequisite is fulfilled in our case, a Fourier transform analysis was performed. As the analysis revealed a ratio of the amplitudes of first harmonic to fundamental frequency of the order of 1.2\%, this prerequisite is considered to be fulfilled.

Measuring phase differences at high frequencies is a challenging task, since the wavelength is in the order of the system length e.g. cables. As a result, the phase difference detected at the oscilloscope might be different from the actual phase difference between the signals at the electrodes. Additionally, the expected phase difference for the plasma produced by the COST-Jet is of the order of only a few degrees because the dissipated power is supposed to be small. Hence, it is necessary to perform a calibration and define a reference phase difference \( \Delta \phi_{\text{ref}} \). This is performed with the discharge switched off, so that the COST-Jet electrodes basically represent a capacitor. This implies that no
power is consumed and the phase difference between current and voltage is assumed to be $-90^\circ$, since the electrodes of the COST-Jet represent a capacitor. When the plasma is switched on, the phase deviation from the reference phase can be used to calculate the dissipated power using equation 3.3. The dissipated power is calculated using a customized software. This software collects the signal waveforms from the oscilloscope, fits a sine waveform to both signals, and calculates the dissipated power taking into account the respective calibration factor and reference phase shift. The calibration factor and reference phase shift can be determined and saved using the software and are automatically included throughout the subsequent measurements. Thus, this system allows real-time measurements of the actual dissipated power in the discharge.

### 3.3.2 Optical emission spectroscopy

Using optical emission spectroscopy (OES), the fluorescence light emitted by excited heavy particles such as neutrals, ions or molecules in the plasma discharge can be evaluated. It is a non-invasive diagnostic technique which allows identification of species and thus gives insight into the chemical composition. Additionally, it provides indirect access to fundamental plasma parameters such as electron temperature or density. The technical implementation is simple, however, the deduction of absolute population densities and determination of plasma parameters relies on theoretical models. These models strongly depend on the knowledge of processes in the plasma such as excitation, competing de-excitation mechanisms and optical thickness.

A source of information about plasma parameters is the line profile. Depending on the broadening mechanisms, the shape of the line profile (e.g. lorentzian, gaussian) can reveal plasma parameters such as electron density (Stark broadening), neutral gas temperature (Doppler broadening) or gas density (resonance broadening). However, for cold atmospheric pressure plasma discharges, the line profile is usually determined by pressure broadening, so that it is not possible to deduce important intrinsic plasma parameters, such as the electron temperature.

Nonetheless, also the emission intensity of atomic line radiation contains information about the plasma discharge. The emission intensity $I_{ki}$ per area and solid angle at a
frequency $\nu_{ki}$ depends on the excited state density $n_k$ via [118]

$$I_{ki} = \frac{h \nu_{ki}}{4\pi} n_k A_{ki},$$

(3.4)

where $h$ is Planck’s constant and $A_{ki}$ is the Einstein coefficient for spontaneous emission. Therefore, absolute intensity measurements can reveal the population density of the upper state of the transition. However, absolute intensity calibration of spectrometers is challenging. Because no PTB-approved standard source was available, a relative calibration was used in this thesis.

Then, to deduce plasma parameters from emission lines, population models are required, which take into account populating and depopulating processes for each individual energy level of the considered species. One of the simplest approaches is the corona model [118]. It assumes excitation by direct electron impact collisions and de-excitation by spontaneous emission. Thus, the population of an excited state satisfies the equation

$$n_e n_1 X_{1k}^{\text{exc}}(T_e) = n_k \sum_{i<k} A_{ki},$$

(3.5)

where $X_{1k}^{\text{exc}}$ is the excitation rate coefficient. Equation 3.5 balances electron impact excitation rate from the ground state and decay by spontaneous emission to the optically allowed levels $i$. The excitation rate coefficient in turn depends on the excitation cross section $\sigma$ and the electron energy distribution function $f(E)$ via

$$X_{1k}^{\text{exc}}(T_e) = \int_{E_{\text{thr}}}^{\infty} \sigma(E)(2/m_e)^{1/2} \sqrt{E} f(E) dE.$$

(3.6)

So in this simplified model, a change in emission line intensity can be due to a change in ground state density, electron density or electron temperature. This assumption is used when discussing the development of emission lines in chapter 4 and 5.

To identify species composition in the discharge, overview spectra were taken using a commercial spectrometer (Ocean Optics HR4000) with a spectral range of 200 nm to 1100 nm and a resolution of 0.5 nm. The light was collected through the quartz panes using an optical fiber (Ocean Optics QP 600-2-UV-BX) positioned perpendicular
to the discharge channel. The spectra are used for a basic characterization of the argon discharge and the degree of impurities as presented in section 5.3.

### 3.3.3 Phase-resolved optical emission spectroscopy

Phase-resolved optical emission spectroscopy (PROES), which is used in section 5.4, gives insight into the kinetics of a discharge [Kulsreshath2014b]. It enables the observation of transient excitation processes and hence space- and time-resolved electron dynamics during one RF cycle. The challenge of low fluorescence yields due to the small integration period (1 ns) can be overcome by integration over several RF periods. Hence, a prerequisite for this diagnostic technique is a repetitive and stable discharge. Additionally, the effective temporal resolution is limited by the lifetime of the observed species, which is mainly determined by quenching.

Using PROES, the electron impact excitation from the ground state $E_{i,0}$ can be calculated from the measured spatio-temporal emission via [119]

$$E_{i,0} = \frac{1}{A_{ik} n_0} \left( \frac{d\dot{n}_{ph,i}(t)}{dt} + A_i \dot{n}_{ph,i} \right), \quad (3.7)$$

with the ground state population density $n_0$, the transition probability $A_{ik}$ of spontaneous emission from level $i$ to level $k$, the effective decay rate $A_i$ taking into account re-absorption and quenching and the measured number of photons per unit volume and time $\dot{n}_{ph,i}(t) = A_{ik} n_i(t)$. At atmospheric pressure, the effective decay rate $A_i$ is difficult to determine. However, due to the high number of collisions and thus quenching processes, $A_i$ is dominant. Consequently, at atmospheric pressure, the emission is proportional to the excitation rate from the ground state.

The maximum lifetime of excited resonant argon 2p states can be estimated via

$$\tau = \left( \sum_k A_{ik} + k_q n_{Ar} \right)^{-1}, \quad (3.8)$$

with the spontaneous emission probabilities $A_{ik}$, the quenching rate constant $k_q$ [120] and the argon ground state density $n_{Ar}$, to be shorter than 10 ns. Impurities in the feed
gas can cause additional quenching terms in equation 3.8 and thus a further reduction of the lifetime. However, they are often omitted as their density is low.

The setup used for these measurements is illustrated in figure 3.6. The emission of the discharge in the COST-Jet is imaged onto the intensified charge-coupled device (ICCD) chip of a camera (PicoStar HR 16). To obtain good spatial resolution for both axes, an anamorphic lens system is used consisting of two cylinder lenses (focal length $f = 80$ mm and $110$ mm for horizontal and vertical imaging, respectively). This lens system changes the aspect ratio of the discharge from 1:30 to 4:11 to better fit the dimensions of the CCD chip. With the camera chip being a conventional CCD chip (512x512 pixel, pixel size $25 \mu m \times 25 \mu m$), this results in a spatial resolution of $5.5 \mu m$ across the discharge channel and $72 \mu m$ along the discharge channel. The CCD chip is combined with a microchannel plate (MCP), which serves as a fast gated intensifier. The CCD chip integrates over several seconds, whereas the MCP is synchronized to the RF excitation cycle, using a customized trigger box and delay generator. The MCP gatewidth usually is $1$ ns and the delay is $0.72$ ns. Thus, one RF cycle is scanned and divided into 103 images which represent the whole cycle. The CCD integration time is usually $1$ s to $4$ s depending on the emission intensity of the respective transition. To select a specific transition, optical filters are inserted into the optical path. Table 3.1 lists the optical filters with their full width at half maximum (FWHM) used during PROES measurements and the respective observed emission lines. Optical emission spectroscopy measurements of the argon discharge (not shown here) reveal that only the listed lines are observed in the PROES setup and no significant background was measured.

### 3.3.4 Vacuum ultraviolet spectroscopy

Vacuum ultraviolet (VUV) spectra offer an insight into highly energetic radiation. Important mechanisms of the plasma discharge can be observed in this spectral region, such as the de-excitation of $\text{Ar}_2^*$ in the range of $100 \text{ nm}$ to $150 \text{ nm}$. Not only plasma processes but also biological applications are influenced by this wavelength range due to the influence on inactivation of microorganisms, because proteins and DNA absorb these photons.
Table 3.1: Optical filters and respective transmission lines used during PROES measurements.

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<thead>
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<th>Filter</th>
<th>FWHM</th>
<th>Species</th>
<th>Transition</th>
<th>Emission line</th>
<th>λ / nm</th>
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<tbody>
<tr>
<td>λc / nm</td>
<td>λf / nm</td>
<td>Ar I</td>
<td>2p₁ → 1s₂ and 2p₅ → 1s₄</td>
<td>750.39 and 751.47</td>
<td></td>
</tr>
<tr>
<td>750</td>
<td>10</td>
<td>Ar I</td>
<td>2p₇ → 1s₄ and 2p₉ → 1s₅</td>
<td>810.37 and 811.53</td>
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<tr>
<td>810</td>
<td>10</td>
<td>O I</td>
<td>(3p)⁵P₁,₂,₃ → (3s)⁵S₂</td>
<td>777</td>
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<tr>
<td>780</td>
<td>10</td>
<td>N₂</td>
<td>C³Πᵤ(v' = 0) → B³Π₅(u'' = 0)</td>
<td>337.1</td>
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<tr>
<td>337</td>
<td>10</td>
<td>N₂⁺</td>
<td>B²Σ⁺ₘ(v' = 0) → X²Σ⁺ₘ(v'' = 0)</td>
<td>391.4</td>
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</tr>
<tr>
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<td>10</td>
<td>N₂⁺</td>
<td>B²Σ⁺ₘ(v' = 0) → X²Σ⁺ₘ(v'' = 0)</td>
<td>391.4</td>
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In this study, spectra were taken using a windowless Seya-Namioka design monochromator with a platinum coated concave corrected grating (McPherson) having a focal length of 0.2 m and 2400 G/mm. To enable measurements of the spectrum below the cutting edge of MgF₂, the monochromator was used in windowless operation mode. For this purpose, the monochromator was completely filled with helium and continuously purged.

The detector consists of a sodium salicylate coated window in combination with a photomultiplier (Hamamatsu, type R928). Sodium salicylate is a fluorescent material with a nearly stable quantum efficiency between 200 Å to 1000 Å ([121]). Thus, the measurable spectral range is 50 nm to 300 nm.

The COST-Jet was oriented parallel to the optical axis inside the monochromator so that all measurements are integrated over the length of the discharge channel. To prevent any heavy particles from entering the monochromator and thus increasing absorption of VUV photons, an additional perpendicular helium flow in front of the entrance slit was realized. All measurements using the VUV monochromator were performed in ambient air atmosphere.

3.3.5 Laser schlieren deflectometry

Measuring temperatures in atmospheric pressure plasmas is challenging due to their small spatial dimensions, which impede the insertion of probes. A new optical method...
3.3 Plasma diagnostics

called laser schlieren deflectometry (LSD) was developed by Schäfer et al. [122, 123], allowing non-invasive measurements of the neutral gas temperature. The technique relies on the change of refractive index of a gas due to temperature changes.

The experimental setup is described in detail elsewhere [122–124]. A helium-neon laser is led through the effluent of the COST-Jet discharge onto a high speed camera with high spatial resolution. The Jet is mounted on a stepper motor, which moves the effluent through the laser beam. When the effluent hits the laser beam, it is deflected by a small angle due to the different refractive index of the surrounding gas. The deflection angle $\delta$ is recorded and can be correlated to a temperature change $T_0$ via

$$T = T_0 \frac{1}{1 - \frac{\delta}{\delta_0}},$$

where $T_0$ is the temperature of the surrounding gas and $\delta_0$ is a calibration constant. The calibration constant strongly depends on the diameter of the laser beam and the shape of the temperature profile. Using a numerical model by Schäfer et al. [122, 123], the calibration constant and thus the temperature can be determined. For the temperatures presented in this work, a Gaussian temperature profile was assumed resulting in a calibration constant of $\delta_0 = 0.48 \text{ mrad}$.

3.3.6 Tunable diode laser absorption spectroscopy

Tunable diode laser absorption spectroscopy (TDLAS) is a non-invasive technique, which can be used to determine the density of the metastable $1s_5$ state of argon. The setup was described in detail by Niermann et al. [23]. It consists of a tunable diode laser with a wavelength of 811.531 nm, which corresponds to the energy for excitation of the $1s_5$ to the $2p_9$ state.

Using this setup, the absorption profiles can be measured by scanning the laser wavelength. Measuring the laser transmittance of the absorbing medium, absolute number densities of the argon metastable state can be deduced. In cold atmospheric pressure plasma discharges, the line profile is dominated by collisional broadening [125]. Consequently, the line profile can be approximated by a Lorentzian profile. The absolute
density of the absorbing species can be determined via [126]

\[ n_{Ar,m} = \frac{4\varepsilon_0 m_e c}{e^2 f_{ik} l} S = \frac{4\varepsilon_0 m_e c}{e^2 f_{ik} l} \int_0^\infty \ln \left( \frac{I_0(\nu)}{I(\nu)} \right) d\nu, \]

with the speed of light \( c \), the oscillator strength of the absorption line \( f_{ik} \), the absorption length \( l \), the integrated logarithm of the transmittance, i.e. the area under the absorption profile \( S \), \( I_0 \) and \( I \) the intensities with and without absorption, respectively.

The laser radiation was generated using a tuneable laser diode (Toptica photonics DL 100 L) with a power of a several mW, an emission wavelength at 811.5 nm and a mode hop free tuning range of 25 GHz. The laser is guided through two beam splitters and the discharge and is then measured by a photo diode. The wavelength of the laser is calibrated using a Fabry-Pérot with a free spectral range of 1 GHz and a low pressure reference lamp as it is scanned. The intensity of the laser beam is reduced using a neutral glas filter to 90 \( \mu \)W in order to avoid saturation effects. An optical filter at a wavelength of 811.5 nm in front of the diode minimizes the plasma emission. By moving the COST-Jet inside the laser beam, a map of the whole plasma volume can be recorded.
4 Stability and reproducibility of plasma in the COST-Jet device

The main idea and purpose for the development of the COST jet were to enable the transferability of research results in order to increase and accelerate scientific progress. However, the idea of comparing research results is only within reach if the plasma produced in the COST-Jet is stable from day to day as well as comparable from device to device. Therefore, a reproducible control parameter, stable operation and comparability of the devices are required.

The dissipated power was chosen as an external control parameter, since it is a very basic and physically meaningful parameter (section 4.1). A detailed error analysis of the power measurement is carried out to estimate the statistical significance and reproducibility of measurements. The stability is investigated conducting day-to-day measurements with respect to temperature and the dissipated power (section 4.2).

The comparability is assessed by comparing five different COST-Jet devices (section 4.3). Furthermore, the impact of the impurity reduction method by using a cold trap as introduced in section 3.2 is investigated by optical emission spectroscopy (section 4.3.1). Lastly, the influence of the outer electrical circuit on the discharge performance is studied (section 4.3.2).

To explore the full range of operation, most of the measurements presented in this section are conducted with helium as the carrier gas.

Parts of this chapter have already been published [Kelly2015].
4.1 Reproducibility of power measurement

Following Jonkers et al. [37] (see chapter 1), the measurement of the dissipated power as an external control parameter was developed to facilitate comparison of plasma discharges operating at different experimental conditions. To compare measurements and interpret the significance of results, an error analysis of the power measurement is essential. In the following section, a detailed error analysis is performed to classify the significance of subsequent measurements.

To perform an error analysis for the power measurement using the miniaturized probes developed in this study, all variables that are relevant for the calculation of the power have to be analyzed. As already described in detail in section 3.3.1, the dissipated power is calculated via

\[
P = U_{\text{rms}} \cdot I_{\text{rms}} \cdot \cos \left( -\frac{\pi}{2} + \Delta \phi - \Delta \phi_{\text{ref}} \right)
= \frac{1}{2} \cdot c \cdot U_{U,0_{\text{int}}} \cdot R_m + R_t \cdot U_{I,0_{\text{int}}} \cdot \cos \left( -\frac{\pi}{2} + \left( \varphi_U - \varphi_{U_{\text{ref}}} \right) - \left( \varphi_I - \varphi_{I_{\text{ref}}} \right) \right), \tag{4.1}
\]

where \( c \) is the calibration factor, \( R_m \) is the measuring resistor and \( R_t \) the termination resistor. \( U_{U,0_{\text{int}}} \) and \( U_{I,0_{\text{int}}} \) are the amplitudes of the sine fitted to the voltage waveform measured by the internal voltage probe and current probe, respectively. \( \varphi_U \) and \( \varphi_I \) are the phases of the measured voltage and current signal, respectively, and \( \Delta \phi_{\text{ref}} = \varphi_{U_{\text{ref}}} - \varphi_{I_{\text{ref}}} \) is the reference phase difference. \( U_{U,0_{\text{int}}}, U_{I,0_{\text{int}}}, \varphi_U \) and \( \varphi_I \) are measured quantities, whereas the remaining variables are calibration variables. All of these variables may contain errors and result in significant deviations in the determination of the dissipated power.

There are two types of errors associated with an experimental result: statistical (precision) and systematic (accuracy) errors [127]. The total error is composed of these two types of errors. It is calculated by summation over the absolute values of statistical and systematic error.

Statistical errors are due to statistical variations of an experimental result and vary in amplitude and sign. Accordingly, individual statistical errors can be added up using Gaussian error propagation. For the power measurements conducted in this study, these
4.1 Reproducibility of power measurement

errors are caused by fluctuations of the measured waveforms, for example by electronic noise of the 8-bit analog-to-digital converter of the oscilloscope, its sample rate and jitter of the measured data. Since due to the size of the plasma discharge, the power dissipated in the discharge is expected to be small, the measured phase differences are also expected to be small. Hence, especially the error of the phase has a strong influence on the overall error of the power measurement. To reduce these errors, the signal waveforms are averaged over 2048 measurements. For an appropriate temporal resolution within the RF period, the oscilloscope has a rather high sampling rate of 4 GSa/s to reduce digitizing jitters of the phase. The voltage scale is chosen according to the signal to exploit the full 8-bit analog-to-digital converter but at the same time to avoid the necessity of changing the scale during the measurement. These errors and their effects on the power calculations were estimated by repeating the power measurement at the same experimental conditions 10 times using the same discharge voltage and number of averages. The total statistical error was calculated using Gaussian error propagation taking into account the statistical error of the amplitudes and the phase position of the signal measured by the voltage probe and the current probe. For all measurements, the statistical error was 1 % or smaller. This is also in the range of commercially available systems for power measurements such as the RF power sensor 'Octiv' from Impedans [128].

Systematic errors have a different origin than statistical errors. When repeated, they tend to shift the experimental result always in the same manner so the mean value of the experimental result is displaced. Such errors can be due to an incorrect calibration of instruments or failure to account for physical effects properly. Hence, the total systematic error is the sum of the absolute values of each individual error.

For the power measurements conducted in this study, the considered systematic errors are caused by uncertainties associated with the three calibration variables:

(i) The calibration factor $c$ is sensitive to errors during the calibration measurement of the internal voltage probe as described in section 3.3.1.1. First, the calibration factor can be influenced by the compensation of the commercial voltage probe. Since this procedure strongly depends on the experimentalist, the calibration factor can vary. To minimize this error, the probe was always connected to the same channel of the oscilloscope. This avoids influences of the differences between the channels and thus
avoid the necessity of repeated compensation. Second, attaching the probe to the electrical circuit changes stray capacitances and thus change the coupling during the calibration procedure. Thirdly, the measured voltage strongly depends on the position of the pick-up antenna for the internal voltage probe (compare figure 3.3). If this position is changed, e.g. by an accidental displacement during handling, the measured voltage changes. This change can be estimated with the help of a first approximation. Using the formula for an electric field around a wire \( \vec{E} = \frac{\lambda}{(2\pi \varepsilon_0 \varepsilon_r) \cdot \vec{e}_r} \), it becomes obvious that the electric field strength and thus the induced measured voltage depends anti-proportionally on the radial distance \( r \) between pick-up antenna and copper conductor. Hence, a displacement of 0.05 mm from the original position at a distance of 2 mm from the conductor would result in a change of the measured voltage of 2.5 \%. This translates to an absolute calibration factor error of approximately \( \delta c = 50 \) (compare section 3.3.1.1) with \( c \) being in the range 1900 to 2700 (compare section 4.3).

(ii) The manufacturers of the resistances \( R_m \) and \( R_t \), that are needed to calculate the current, guarantee an error smaller than \( \delta R_m = 1 \% \) and \( \delta R_t = 2 \% \).

(iii) The reference phase errors are firstly influenced by the jitter of the signal during the determination measurement. Secondly, systematic errors of the reference phase difference \( \Delta \phi_{\text{ref}} \) are physical changes of the reference phase difference during measurement. These changes can be caused by changes of the electrode surfaces, parasitic capacitances or excessive heating of the coil, which introduces a considerable amount of resistive impedance into the electrical circuit. Therefore, this error is accounted for with an error of \( \delta \phi_{\text{ref}} = 0.002 \text{ rad} \), where the reference phase difference is typically of the order of \( \Delta \phi_{\text{ref}} = 0.07 \text{ rad} \). This value was derived from a day-to-day analysis presented in section 4.2.

Additionally, there are a few more general error sources that could have an influence on the measurement. However, they are assumed to have a negligible effect on the power calculation because of the precautionary measures that were taken. A deviation of the measured waveforms from the assumed sine introduces an error, but was estimated in section 3.3.1.2 to be negligible. Reflected signals at the entrance of the oscilloscope can impose standing wave effects in the measurement cables, but should be minimized by the 50 \( \Omega \) termination. Other effects such as bad contacts (e.g. solder joints) can also
4.1 Reproducibility of power measurement

![Graph showing power and error bars](image)

**Figure 4.1:** Calculated power with respective error bars and relative error for a discharge operated with a typical gas flow rate of 1000 sccm helium and 5 sccm oxygen.

cause wave reflection and thus change the measured signal. Ground loops can cause wrong reference potentials for voltage measurements. Therefore, connections are kept as short as possible. Parasitic capacitances change the power coupling into the plasma discharge. During the calibration procedure, the housing of the COST-Jet was closed to shield the LC resonance circuit and only a small borehole for the probe is used to keep stray capacities constant. Additionally, the position of the electrode shielding has an influence on the current measurement: If the position is changed, the measured current is overestimated. Therefore, the shielding position was always checked prior to any measurements. Lastly, an important challenge when working with RF excitation is cross-talk between electric lines, e.g. for probes. This cross-talk is avoided by careful shielding of the cables also inside the housing.

To illustrate the impact of these errors as a whole, the results for a typical measurement of the dissipated power are discussed below. Figure 4.1 shows the dissipated power in a plasma discharge operated with a typical gas flow rate of 1000 sccm helium and 5 sccm oxygen. The dissipated power (black squares) and the absolute error of the
power (see error bars) increase with increasing voltage. In contrast, the relative error (red circles) decreases with increasing voltage. The maximum relative error is 9.3% and the average relative error is 7.5% over the whole voltage range. Notably, the error of the measured voltage seems to be greater than that of the power, but this is due to the scaling and the aspect ratio of the axes.

Comparing these values to the aforementioned commercial system 'Octiv', the error appears to be large. However, the error of this commercial system also increases for increasing phase angle of the load impedance. This implies that for the phase angle of the impedance of the plasma in the COST-Jet (around $-80^\circ$, see chapter 5) the error of the power measurement is above 10%. Additionally, the system is not specified for measuring powers below 200 mW.

In order to analyze the origin of the errors, figure 4.2 illustrates the composition of the two components of the total error: a) The statistical and b) the systematic error. The statistical error is mostly due to the error of the phase measurement. For higher voltages, voltage and current error increase over-proportionally since the reference phase error is constant once the reference phase shift was determined and is not proportional to the signal amplitude. The large phase error at highest measured voltage is due to the discharge being close to the constricted mode. Therefore, phase instabilities are not
4.1 Reproducibility of power measurement

unlikely. For all data points, the statistical error is below 6% of the total error and thus negligible.

The systematic error is composed of the calibration error, the resistance errors and the reference phase shift error. At low voltages, the largest part of the error is due to the reference phase shift error, followed by the calibration error and the resistance error. With increasing voltage, this ratio changes. While the resistance error percentages stay approximately constant, the share of the calibration error increases in concert with a decrease of the reference phase error. This behavior is due to the fact that the impact of the reference phase error decreases non-linearly but with a tangent function on the increasing power (compare derivative of equation 4.1).

To illustrate the relevance of the total error when estimating the significance of a measurement, three different scenarios are considered: How comparable are measurements using

1. the same COST-Jet device in the same laboratory?

2. different COST-Jet devices in the same laboratory?

3. different COST-Jet devices in different laboratories?

Scenario 1 applies to situations where the dissipated power is measured using one single COST-Jet device in the same laboratory (i.e. the same oscilloscope, commercial voltage probe etc.). If the calibration is performed once and then used thereafter, only the reference phase error and the statistical error are relevant for comparison of measurements. This leads to an effective reduction of the error for the power to $\delta P/P = \pm 4.6\%$ at most. This scenario is valid for most of the data presented in this thesis.

Scenario 2 applies to situations where the dissipated power is measured using different COST-Jet devices in the same laboratory. If the calibration is performed once per COST-Jet device, the total relative error as calculated in the previous section is applicable and in the range of $\delta P/P = 9.3\%$. This scenario is important for comparing results of different setups.
Scenario 3 applies to situations where the dissipated power is measured using different COST-Jet devices in different laboratories. This includes the usage of different equipment, e.g. voltage probe for the calibration of the internal voltage probe. This leads to an even larger estimated error of the calibration of 18%, thus producing a total error of approximately 24%. This scenario applies when researchers from different laboratories compare their results of experiments with different COST-Jet devices. These exemplary values were obtained by comparison of calibration measurements performed at the York Plasma Institute by Frederik Riedel. The resulting error may sound rather inaccurate at first. However, this problem is due to the commercially available voltage probes and cannot be solved easily, so that other scientists are faced with the exact same problem. Nevertheless, this value is more accurate than many other commonly used plasma diagnostic techniques.

In summary, the power measurement is an adequate control parameter when it comes to comparing atmospheric pressure plasmas operated using different feed gases. In spite of the challenges that arise due to the capacitive character and small dimensions of the plasma, an operando power measurement can be realized by carefully selecting the probe design and evaluating the current and voltage forms. The detailed error estimation allows the assessment of the significance and transferability of research results. Overall, the power measurement can be considered to be reproducible within the determined error limits. The errors of the three presented scenarios have to be kept in mind when comparing the significance of results. Thanks to the special design of the COST-Jet, comparative measurements are meaningful even if performed in different laboratories. In this thesis, the error bars are usually in the same range as discussed in scenario 1 in this section. Hence, they are not shown in graphs for better readability.

To demonstrate the validity of the error analysis of the power measurement, two of the aforementioned scenarios are tested and described in the following sections.

4.2 Stability

In order to investigate the stability of the discharge in the COST-Jet from day to day, a test measurement was carried out. An appropriate indicator of the discharge stability
4.2 Stability

for this purpose is the gas temperature. For biomedical applications of atmospheric pressure plasmas, the neutral gas temperature is a critical parameter. The biological function of most mammalian proteins is optimized around 37°C. Temperatures above 41°C will denature most proteins over time. To avoid the denaturation of proteins, the temperature at the treated sample may only temporarily exceed 37°C [129, 130]. Additionally, from a plasma physical point of view, the neutral gas temperature is one of the determining factors for the transition to the constricted mode. Hence, the gas temperature has to be reliably stable.

To check whether this is the case, the gas temperature, as well as the temperature of the coil of the resonance coupling circuit and the gas supply line, were measured on four subsequent days. During these four days of measurement, the whole setup was not changed to guarantee reproducible measurements and the generator power was kept constant. The entire procedure represents scenario 1 from the above-mentioned possibilities and is therefore also used to check the theoretical error estimation from section 4.1.

To measure the temperature, thermocouple sensors were used. One of them was attached to the gas supply line (steel tube) inside the housing, another one was attached to the coil and the third thermocouple was positioned in a distance of +3 mm from the electrodes inside the effluent of the COST-Jet. An additional thermocouple sensor was used to measure the room temperature. For this experiment, the home-made power generator without any matchbox was used to demonstrate the stability of the complete, simplified setup. The measurements were conducted at a power of 0.4 W and a gas flow rate of 1000 sccm helium with an admixture of 5 sccm oxygen. Notably, repeating the measurements on four subsequent days is not sufficient for a representative sample as the sample size is too small, but it gives an exemplary picture of the stability.

The results are shown in figure 4.3. On the left-hand side (figure 4.3 a)), the measured temperature is shown in dependence of the time span after the generator was switched on. Except from the room temperature sensor, all other temperature sensors show an exponential saturation until the temperature is stable after about 15 minutes. At this power and gas flow rate, the temperature of the effluent was measured to be below 37°C. Hence, treated biological targets should not be affected by this neutral
gas temperature as it is below the critical value of denaturation. There are only small deviations of ±2 °C observed. At closer inspection, the observed deviations result primarily from deviation in the ambient temperature of the setup. Since there is no climate control in the laboratory, room temperature fluctuates depending on the weather (outdoor temperature, solar radiation etc.). These fluctuations directly influence the measured temperature of the effluent. The right-hand side of figure 4.3 shows that the corresponding temperature increases with the room temperature subtracted. Obviously, the deviations visible in figure 4.3 are reduced even further. This has to be kept in mind when interpreting any published temperature values. Ideally, a temperature difference relative to room temperature is given for physical interpretation as shown in figure 4.3 b). Of course, for biological applications the absolute temperature is an important parameter.

The temperature measurements have shown that the discharge conditions are stable for four subsequent days. Since the setup corresponds to scenario 1 of the error analysis in section 4.1, the measured values of the dissipated power are a good basis for empirical
4.2 Stability

Figure 4.4: Development of applied discharge voltage and the dissipated power in the first 30 minutes after discharge ignition, measured at 0.4 W, 1000 sccm helium, 5 sccm oxygen.

validation of the error analysis. Figure 4.4 shows the development of the applied discharge voltage measured using the internal probe and the calculated dissipated power in the first 30 minutes after discharge ignition. The applied voltage as well as the dissipated power decrease exponentially with time until they reach a steady state after 15 minutes. This behavior is due to the heating of the setup. As already shown in figure 4.3, the coil, that is part of the resonance coupling circuitry, heats up. Thus, the inductance and resistance of the coil are slightly changed which affects the Q-factor of the LC resonance circuit. Commercial matching systems have exactly the same problems except that due to the larger components this warm-up time is infinitely long. After the temperature of the system reached a steady state, the voltage is constant. Comparing the steady-state absolute values of the measured dissipated power, the maximum difference is 7.8% which corresponds well with the error analysis in section 4.1.
In summary, the day-to-day analysis revealed that the temperature of the effluent of the plasma in the COST-Jet is stable and only depends on the actual room temperature if the setup is not changed. The same holds for applied voltage and current. This is an indicator that the COST-Jet design and the discharge remain stable over a long period of time. This measurement also enabled an empirical estimate of the reproducibility of the power measurement. The resulting maximum power difference corresponds well to scenario 1 thus confirming the error calculation above. Using the room temperature as an example, the measurements presented in this section show that the properties of the plasma depend more on external influences than on variations within the plasma. This is a clear indication that the control of these external parameters is crucial and a prerequisite for reproducible scientific results.

Examples for these external parameters are the discharge reactor geometry, the feed gas and the electrical circuit. Their influence on the discharge performance is assessed in the following section.

4.3 Comparability

One prerequisite for comparable scientific results in different working groups is the comparability of the discharge reactor. In this section, dissipated power measurements as well as temperature and optical emission measurements are used to compare five identically manufactured COST-Jet devices and their operation. These measurements correspond to scenario 2 presented in section 4.1.

In addition, the effects of impurity reduction (section 4.3.1) as well as of the matching (section 4.3.2) are assessed. These aspects are relevant to both scenario 2 and 3.

Prior to any measurements, a voltage calibration was performed for all of the devices. This is necessary, because the position of the pick-up antenna inside the housing may easily vary from device to device by several tenths of millimeters. Figure 4.5a) demonstrates the necessity of this calibration: The graph on the left hand side shows the voltage measured by the commercial probe $U_{com}$ as a function of the internal probe voltage $U_{int}$. Each straight line and its respective calibration factor ($U_{com} = c \cdot U_{int}$, see legend) corresponds to a specific COST-Jet device. These calibration factors
4.3 Comparability

**Figure 4.5:** a) Voltage calibration curves and b) power measurements for five different COST-Jet devices at a gas flow rate of 1000 sccm helium and an admixture of 5 sccm oxygen at ambient atmosphere.

differ by about 40% which corresponds to a difference in the position of the pick-up antenna smaller than 0.7 mm. If the calibration was not performed for each COST-Jet device individually, this huge deviation would directly increase the error of the power measurement.

In figure 4.5 b), the dissipated power in the plasma discharge is shown as a function of the applied voltage. The plasma was operated with a typical gas flow rate of 1000 sccm helium and an admixture of 5 sccm oxygen. All of the five curves show a similar behavior: Below 175 V, there is no plasma discharge yet, so that the dissipated power is zero. Above this voltage, the plasma discharge ignites and the dissipated power increases linearly with increasing voltage until an exponential increase starts. The shape of the curve will be discussed in detail in section 5.1. Strictly speaking, these curves should be identical if the devices and thus the plasma discharge produced therein were identical, too. This includes, for example, the electrode distance accuracy or the air tightness of the devices.

However, the power curves differ from each other, especially for applied voltages larger than 300 V. Yet, this difference cannot directly be attributed to deviations...
between the individual COST-Jet devices. Due to the error analysis discussed in section 4.1, it is known that the error is approximately 7.5% when comparing the dissipated power in different COST-Jet devices. Hence, the observed differences cannot uniquely be attributed to physical changes of the plasma discharge but are most probably due to measurement errors. This implies that the five COST-Jet devices, that are compared above, generate well-reproducible plasmas within the limits of the measurement uncertainties.

To get an insight into physical discharge processes, two additional measurements were conducted. For a first order energy balance, the temperature of the effluent in a distance of +3 mm was measured using a thermocouple. Furthermore, optical emission spectroscopy was used to investigate the excitation processes in the plasma discharge. The emission spectrum was measured with an optical fiber oriented perpendicular to the COST-Jet device and mounted at approximately −15 mm. The atomic emission line of helium at 706 nm was traced.

Figure 4.6 shows the results: On the left-hand side, the temperature difference $\Delta T$ between room temperature and effluent temperature is plotted as a function of the
dissipated power. The temperature rises linearly with increasing dissipated power. This behavior suggests that a constant fraction of the dissipated power is directly transferred into heat. Using

\[ P = \frac{Q}{t} = c \cdot \frac{m}{t} \cdot \Delta T = c \cdot \rho \cdot \Gamma \cdot \Delta T, \] (4.2)

where \( Q \) is thermal energy, \( c \) the heat capacity of helium, \( m \) is the mass, \( \rho \) the density, \( \Gamma \) the volumetric gas flow rate and \( \Delta T \) the temperature difference of the helium feed gas caused by the plasma discharge, the heat output was calculated from the temperature difference. In figure 4.6, the left ordinate represents the measured temperature difference whereas the right ordinate represents the corresponding heat output calculated using equation 4.2. The black solid line represents the case where all of the dissipated electrical power is transferred into heat. Consequently, no data point should lie above the solid line due to energy conservation. If only a fraction of the dissipated electrical power was transformed into heat, the measured data points should lie below the black solid line. Interestingly, all of the experimental data points are scattered around this straight line. Notably, this graph hence demonstrates that, within the limits of the measurement uncertainty, apparently nearly 100% of the dissipated power is eventually transferred into heating the discharge gas. Only a small fraction is transferred to emission, chemical reactions or other processes such as heating of the device components. This is an important physical result that could only be achieved by the new, accurate power measurements using the miniaturized electrical probes. It shows that the measured dissipated power is a realistic value. This finding is additionally corroborated by numerical simulations: the power calculated from fluid simulations using COMSOL multiphysics \[80, 82\] confirms these results.

In figure 4.6 b), the intensity of the 706 nm emission line is shown. This atomic emission line is one of the most prominent lines of the helium spectrum. The overall behavior is the same for all of the devices. Interestingly, in contrast to the temperature, the intensity rises exponentially with increasing dissipated power. This behavior might be due to the high excitation energy (20.96 eV) of the upper state of this transition. Since only fast electrons can excite this state, the excitation rate strongly depends on the high energy tail of the electron energy distribution function. This high energy tail is more pronounced when processes in the plasma discharge tend to produce high
energy electrons. This is the case for a γ-like mode and will be discussed in detail in section 5.1. The deviations in the overall intensity of the emission line originate from imprecise fiber positioning.

**In summary**, all of the five COST-Jet devices show the same distinct behavior with regard to the dissipated power, the effluent temperature and various atomic emission lines (only one of them was shown here). The observed deviations are well within the error bars of the measurements. Thus, the COST-Jet enables the comparability of experimental results. The temperature measurements also provide an insight into the opportunities offered by the developed *operando* power measurement. Using this measurement, it is possible to investigate in detail how the dissipated power is distributed and transferred to the plasma system.

### 4.3.1 Impurity reduction

As already discussed in the introduction of the thesis, the feed gas is one of the three main control parameters for an atmospheric pressure plasma jet. A cold trap was installed to reduce impurities in the feed gas as much as possible. A small section of the feed gas line (~40 cm) is cooled by passing it through a dewar vessel filled with the cooling bath. Usually, liquid nitrogen is used for this purpose in cold traps \[33\]. However, as already mentioned in section 3.2, the boiling point of argon is above the boiling point of nitrogen, so that the feed gas would liquefy inside the gas tube. For this reason, a mixture of ethanol and dry ice (CO\(_2\), −78 °C) is used as a cooling bath. To qualitatively demonstrate its effect on plasma chemistry, optical emission spectroscopy was used.

For this qualitative analysis, the measurement was carried out at ambient atmosphere and not in the controlled environment inside the discharge chamber. Since the sensitivity of the spectrometer has not been calibrated, a direct comparison of the absolute emission intensity of different lines is not possible. To demonstrate the effect of feed gas purifying on the argon discharge, argon was used as feed gas with a gas flow rate of 1000 sccm and at a power of 600 mW. The emission of the plasma discharge was collected using an optical fiber oriented perpendicular to the discharge channel and attached at the position −15 mm.
4.3 Comparability

Using a thermocouple sensor in the effluent of the COST-Jet, it was confirmed that the feed gas reaches room temperature after passing the cold trap and before entering the electrode region. Hence, all changes observed in the measurement shown above are solely due to purification of the feed gas and not due to cooling of the feed gas.

The effect of gas purification on the plasma chemistry is illustrated as a time-resolved measurement in figure 4.7. The graph shows the peak intensity development of selected emission lines originating from the argon discharge. While the peak intensity of selected emission lines originating from the argon discharge is continuously monitored, the cold trap is switched on. The initial conditions prior to switching on the cold trap correspond to a stable operation of the COST-Jet in ambient atmosphere after 20 minutes of operation time.

At $t = 0\ s$, the cold trap is switched on, i.e. dry ice is poured into the cold trap already filled with ethanol at room temperature. After a short time period, most of the signals show a considerable response to the gas purification. The signals of oxygen
containing species such as atomic oxygen (777 nm) and hydroxide (308 nm) show a
distinct decrease by more than a factor of two. In the case of nitrogen (337 nm), no
visible change is observed and the signal is more or less constant. The argon emission
lines show individual behavior: The strong argon emission lines (762 nm, 772 nm,
774 nm) increase by ~ 10% at most. At the same time, the emission line at 750 nm
remains nearly constant (2%).

The delay of the signal showing a response to the cold trap (100 s) is due to the
whole system consisting of ethanol, dewar vessel and gas line. These all need to be
cooled down prior to any effect on the feed gas temperature. The reduction of the
oxygen containing signals (OH 56%, O 38%) can be explained by condensation and
freezing of water humidity on the inner walls of the gas tube. Since atomic oxygen
and hydroxide are both products from water molecule dissociation, their decrease
indicates a decrease of the humidity in the feed gas. However, these emission lines do
not decrease to zero. This behavior can be explained by the fact that the oxygen signal
can also originate from gaseous oxygen from air impurities in the feed gas. Since the
boiling temperature of liquid oxygen is 90 K, which is well below the temperature of
the cooling bath, gaseous oxygen impurities will not be removed from the feed gas.
The boiling temperature of liquid nitrogen is 77 K, which is below the temperature of
the cooling bath as well. Hence, the nitrogen density in the feed gas is not affected by
the cold trap and the signal is constant.

To explain the behavior of the argon emission lines, it is necessary to have a closer
look on the excitation mechanisms of the upper levels of the particular transitions.
The intensity of an emission line depends on the density of the upper level. This
density is determined by all the processes populating and de-populating this level
(see section 2.1.2). In the Corona model (see section 3.3.2), the population process
is dominated by excitation by electron impact collisions from the ground state. This
implies that the line intensity depends on the ground state density of atoms, the
electron density and the overlap of the excitation cross sections with the electron
energy distribution function (see section 3.3.2). Hence, an increase in emission intensity
can imply an increase of the ground state density (as is the case with impurities), a
change in electron density or of the shape of the electron energy distribution function.
Since the argon ground state density is constant, an increase of the argon emission
lines represents an increase in electron density or average electron temperature. A
4.3 Comparability

decreasing number density of impurities in the feed gas can lead to an increased average electron temperature. Since many of these impurities are molecules, they can absorb a considerable amount of energy in their vibrational and rotational energy states. If this energy storage is removed, i.e. molecules are absent in pure noble gas plasmas, less electron energy is lost to this excitation. Thus, the electrons can be further accelerated in the plasma discharge and increase the electron temperature. This in turn can lead to an increased electron density due to higher ionization frequencies. This hypothesis is supported by the observation of the temporal behavior of the emission lines. The 750 nm emission line originates from the $2p_1$ state, which is predominantly excited by direct electron impact from the ground state. However, the remaining observed argon lines can also be occupied by stepwise excitation from the metastable state and therefore require less excitation energy. Therefore, these emission lines react more strongly to a change in the mean electron energy compared to the 750 nm line, which only slightly increases.

In summary, the composition of the feed gas is a crucial external control parameter. Only small amounts of impurities such as nitrogen or humidity notably change the discharge processes. A cold trap using a cooling bath of dry ice and ethanol effectively reduces the amount of humidity and other impurities in the discharge. This enables reproducible measurements and the transfer of scientific results. Only with these measures, the discharge processes in pure noble gas discharges can be investigated. Such investigations provide valuable results for benchmarking of numerical models for atmospheric pressure glow discharges.

4.3.2 Influence of matching circuitry

Different publications show that the external matching circuit parameters had a significant effect on the discharge characteristics of capacitively coupled atmospheric pressure discharges [68, 131]. Depending on the matching circuit parameters, the discharge operated in $\alpha$- or $\gamma$-mode. If the COST-Jet is used in different laboratories to compare results (scenario 3), the operation of the discharge has to be independent of the power supply and the outer electrical circuit that is used to sustain the plasma discharge.
To make sure that the plasma discharge created in the COST-Jet and its physical properties are independent of the outer electrical circuit, voltage, current and the dissipated power in the discharge were measured for different matchbox settings and hence different complex impedances of the circuitry. If the plasma is independent of the outer electrical circuitry, the exact same voltage-current (V-I) characteristics are expected for different matchbox settings. The matchbox consists of an 'L' type matching circuit, i.e. a loading capacitor in parallel, and an inductor and a tuning capacitor in series to the power supply. Its purpose is to match the impedance of the plasma discharge to the RF power supply. During the measurement, the capacity of the loading capacitor \( C_L \) was varied, thus changing the outer electrical circuit impedance. A capacitance of 60% \( C_T \) and 50% \( C_L \) represents optimal matching to the homogeneous plasma discharge, i.e. low reflected power and thus the lowest possible voltage set-point on the generator.

Figure 4.8 shows the V-I characteristic of the plasma discharge in argon at a pressure of 990 mbar and a gas flow rate of 400 sccm. Correspondingly, figure 4.9 shows photographs of the COST-Jet operated in the different modes. The shape of the V-I curve and the different zones are discussed in detail in section 5.1. Apparently, in
4.3 Comparability

**Figure 4.9:** Photograph of the COST-Jet operated in argon in a) homogeneous glow mode at low voltages, b) homogeneous glow mode at moderate voltages and c) constricted mode.

In certain regions, the V-I curves are identical whereas in other regions, they differ from each other depending on the matchbox settings. One of these points is marked by the letter A. This point represents the extinction of the plasma discharge. For lower voltages, the plasma discharge is not ignited and the curves are identical. For higher voltages, from point A to point B, the plasma is in the homogeneous glow mode and the V-I characteristics are identical (figures 4.9 a) and b)). Then, a sudden transition from point B to point C represents the transition from homogeneous glow to constricted discharge (figure 4.9 c)). The position of point C after the transition strongly depends on the loading capacitance and is labeled as C, C', C'' in the graph. When the generator power is reduced, the current decreases while the voltage stays constant until the discharge turns back from constricted to homogeneous mode at point D.

The most remarkable difference between the V-I curves is point C after the transition to constricted mode. Here, the transition is either accompanied by an increase or decrease in the current. This difference strongly depends on the loading capacitance and was also observed in other studies [68]. This behavior is also reflected in the dissipated power. In the constricted mode, the dissipated power is slightly increased compared to the homogeneous mode (see figure 5.5). However, the power density locally increases enormously due to the constriction of the discharge. Hence, the device and its electrodes might be damaged during constricted discharge operation.
Chapter 4  Stability and reproducibility of plasma in the COST-Jet device

The dependence of the power or current on the matching parameters in the constricted mode can be explained by a simple analogy from DC plasma discharges: most electrical circuits (also AC circuits) can be reduced to an equivalent voltage source with an internal complex impedance and an impedance load in series (see figure 4.10 a)). In the used setup, the voltage supply with the internal impedance represents the generator including all the impedances from matchbox, cables and all the components of the outer electrical circuit. The load is represented by the plasma discharge. To find the operating point of this circuit, a simple V-I graph can be used. Figure 4.10 b) demonstrates this principle. The dashed straight line represents the characteristic V-I curve of the voltage source whose slope only depends on the internal resistance, e.g. $R_1$ represents a higher internal resistance than $R_2$. The V-I characteristic of a DC discharge is also shown as a solid line. The operating point, that defines stable operation of the electrical system, is determined by the intersection of the dashed straight line (voltage source) and the V-I characteristic (plasma discharge, solid line). In most regions of the V-I characteristic, this point of intersection is a stable operating point (e.g. point 1 in the normal glow discharge). However, there are regions where the operating point is not stable. This is

Figure 4.10: a) Equivalent voltage source with plasma load and b) construction of operating point of the electrical circuit (Figure adopted from D.B. Graves [132]).
4.4 Summary

the case if the condition $\frac{dV}{dI} + R > 0$ is fulfilled [51], where $R$ represents the internal resistance of the equivalent voltage source and $\frac{dV}{dI}$ represents the slope of the V-I characteristic of the plasma load. This implies, for example, that point 2 will transit to point 3. This is usually the case if the discharge goes into arcing regime.

Notably, operating point 3, which corresponds to the constricted mode, strongly depends on the internal resistance $R$ of the voltage source since it is determined by the slope of the straight line. The higher the internal resistance, the higher the voltage $V_0$ needed to sustain the plasma in homogeneous mode (see figure 4.10 b)). Therefore, a high internal impedance (high absolute steepness of the straight) results in a higher power in arcing mode. For RF networks, the interrelationships are a little more complex and therefore only qualitatively transferable, since reflected power and control loops in the RF generator also play a role.

In summary, the electrical circuit is another external parameter that can influence discharge processes. However, the dissipated power in the homogeneous glow mode is independent from matchbox settings. This is an absolutely necessary prerequisite when comparing results in this regime using different power supplies. In contrast, the maximum dissipated power in the constricted mode strongly depends on matchbox settings. This has to be kept in mind when operating in this regime, for example using the self-pulsing $\mu$-APPJ [133]. This device is similar to the COST-Jet except for the fact that the electrode gap increases from the entrance to the exit by a factor of three. It operates in a self-pulsing constricted mode. In this case, it is not sufficient to use the discharge voltage as the only control parameter but to measure the discharge current and the dissipated power as well. As the above measurements have shown, it is extremely important to record the conditions of the outer electrical circuit when operating in this regime. Otherwise, the experimental conditions cannot be reproduced.

4.4 Summary

In this chapter, the COST-Jet and the power measurement using the internal electrical probes were thoroughly studied with regard to reproducibility, stability and comparability.
Three different measurement scenarios were considered to assess the power measurement as a reproducible control parameter. For measurements with a single device in the same laboratory but on different days, an error of less than 5% was predicted and confirmed by measurements. For different devices, an error of less than 10% was predicted and also confirmed. This value is even better than that of commercially available systems. For different COST-Jet devices and different laboratories, the error was predicted to be less than 25%. Overall, the power measurement can be considered to be reproducible within the determined error limits.

With the help of temperature measurements in the effluent, the day-to-day stability of the discharge in the COST-Jet was demonstrated. Using the room temperature as an example, the measurements presented in this section show that the properties of the plasma depend more on external factors than on variations within the plasma. This is a clear indication that the control of these external parameters is crucial and a prerequisite for reproducible scientific results.

Therefore, the influence of three external parameters was assessed: the discharge geometry, the feed gas composition and the external matching circuit.

The comparability of five different COST-Jet devices was presented in terms of power, temperature and optical emission measurements. These measurements revealed that the measured dissipated power in a helium plasma is almost completely transferred into the heating of the discharge gas. This finding provides an insight into the opportunities offered by the developed *operando* power measurement. Using the power measurement, it is possible to investigate in detail how the dissipated power is distributed and transferred to the plasma system.

In addition, it was shown that the control of impurities in the feed gas by a cold trap has a crucial influence on the operation of the discharge. Only with these measures, the discharge processes in pure noble gas discharges can be investigated. Such investigations will provide valuable results for benchmarking of numerical models for atmospheric pressure glow discharges.

Furthermore, it was demonstrated that the external matching circuit has no influence on the discharge parameters in the homogeneous mode. However in constricted mode, these parameters have to be considered. Therefore, it is extremely important to record...
4.4 Summary

the conditions of the outer electrical circuit when operating in this regime. Otherwise, the experimental conditions cannot be reproduced.

In conclusion, the development of the COST-Jet, the miniaturized probes and the corresponding calculation of the dissipated power provides a new platform for reproducible, stable, and comparable measurements and thus the basis for transferability of scientific results.
5 Physical properties of an argon discharge in the COST-Jet

As already described in the introduction, the predecessor of the COST-Jet, the µ-APPJ, was usually operated using helium. Exploratory measurements revealed fundamental differences in the operation of the helium and argon discharge even if the atomic structure of the two elements is similar (compare section 2.2).

In preliminary experiments studying the ignition of an argon discharge in the µ-APPJ, it was observed that the argon discharge changes to a constricted mode immediately after spontaneous breakdown. Only by clever variation of the gas flow and the discharge voltage, the constricted mode could be transferred into a homogeneous glow mode [14]. This is done by producing a constricted discharge at high gas flow rates and subsequently lowering the gas flow rate until a homogeneous discharge spreads along the discharge channel. This homogeneous discharge is seeded by the constricted mode. After a while, the homogeneous mode is extinguished and the step has to be repeated. This process can take up to half an hour. During this time, the plasma is always partly operated in constricted mode. This contrasts with investigations in helium, in which the discharge is in homogeneous glow mode directly after breakdown. Since this argon transfer process is very time-consuming and wearing out the device due to the heat load, an alternative ignition method was developed in this thesis. A voltage is applied to the jet’s electrodes for this purpose. A high voltage spark gun is then used to pre-ionize the argon in the discharge channel and thus enables a homogeneous discharge.

Apart from the ignition, there is another difference to the helium discharge: Experiments have shown that in contrast to helium [134], the stability of the argon discharge strongly depends on the gas flow rate. The higher the gas flow, the more difficult it is to maintain a homogeneous operation mode.
A second decisive factor for homogeneous operation of the argon discharge is the amount of impurities in the feed gas. Even admixtures in the ppm range can lead to a discharge constriction. As already demonstrated in chapter 4, a cold trap reduces the amount of impurities, which favors the stable operation of a homogeneous discharge. In contrast, the helium discharge is rather insensitive and molecular gas admixtures in the range of a few percent are possible.

After the stability and reproducibility of the COST-Jet was demonstrated in chapter 4, this chapter deals with the physical properties of an argon discharge in the COST-Jet. Specifying the more general research questions from the introduction, the following chapter will address the following questions:

1. Why is the argon discharge more susceptible to instabilities leading to a constricted mode compared to the helium discharge?
2. Why does the size of the stable regime of the argon discharge depend on the gas flow rate?
3. Why can even a small amount of impurities prevent a homogeneous argon discharge?
4. Why does the argon discharge directly transfer into the constricted mode after spontaneous breakdown and why does the ignition via a high voltage spark gun avoid this problem?

To answer these questions, the microscopic differences between the helium and the argon discharge mechanisms leading to the observed differences in macroscopic behavior have to be studied. Hence, the experimental conditions have to be really stable and well reproducible in order to operate and study a homogeneous argon discharge in the device. The preceding chapter demonstrated that the outstanding stability of the COST-Jet device enables the operation of a homogeneous argon discharge. Thus, the COST-Jet allows the investigation of the physical processes that were inaccessible up to now due to the lack of reproducibility.

For this purpose, a global overview is obtained by investigating the electrical characteristics of the discharge first (section 5.1). Power, pressure and gas flow variations are conducted to study the discharge modes, the operational range and stability criterion.
5.1 Electrical characterization and operational range

Based on a simple electrical model, the measured impedance of the discharge is used to deduce internal plasma parameters such as the electron density and temperature (section 5.2). To complete the microscopic picture, the discharge composition is analyzed by optical emission spectroscopy in the visible and ultraviolet range (section 5.3). For a temporal resolution of the discharge species, the discharge kinetics are visualized by phase-resolved optical emission spectroscopy and the electrical heating mechanisms are analyzed (section 5.4). The findings for the argon discharge are compared to results obtained with helium as feed gas. All of the results will be cross-linked. Therefore, this chapter will often make use of references.

Discharge current and voltage are global parameters that can be measured with a considerable effort. These electrical measurements can help to understand space averaged, steady processes and control the discharge. The relation between current and voltage of an electrical system provides information about its operating properties such as differential resistance, hysteresis and operation modes. Using the current and voltage probes integrated into the COST-Jet housing that were developed in this thesis, detailed measurements of these parameters are possible in order to obtain an estimation of the plasma properties.

A typical voltage-current characteristic of an argon discharge in the COST-Jet measured at a pressure of 990 mbar and a gas flow rate of 400 sccm is shown in figure 5.1. The data were acquired by varying the applied generator power. The V-I characteristic shows distinct transitions that are attributed to three modes in the following paragraphs. Because of the similarity to the behavior of the V-I characteristics of classical low pressure DC discharges [52], these modes are named correspondingly in this thesis. The chronological sequence of the measurement is marked by grey arrows in figure 5.1.

In contrast to the operation in helium, a homogeneous argon discharge in the COST-Jet cannot be ignited by simply applying a voltage to the electrodes, because the discharge then transforms into a constricted discharge immediately after ignition. In this thesis, a homogeneous operation mode is initiated instead by an additional high voltage
Figure 5.1: V-I characteristic of an argon discharge: The discharge shows distinct modes exhibiting different behavior. The direction of the curve is marked by grey arrows (pressure 990 mbar, gas flow rate 400 sccm).

pulse from a spark gun. Hence, the argon discharge was ignited manually prior to the measurement. For this purpose, the applied voltage was set to a medium value (approximately 170 V) and the high voltage gun was used to ignite a homogeneous argon plasma. The point of ignition and its corresponding voltage and current signal are indicated by a black arrow in figure 5.1. When the discharge is ignited this way, its appearance is homogeneous and it fills the complete discharge channel.

Subsequently, the generator power was increased. In this mode (indicated by black squares), the discharge current increases linearly with increasing voltage. Since this behavior corresponds to the behavior of an abnormal mode of low pressure plasmas, this mode is accordingly called abnormal mode.

At a certain threshold voltage (≈ 250 V, marked by a black arrow in the graph), current and voltage drop abruptly. Hereinafter, this point is called constriction, since this discontinuity corresponds to transformation of the discharge into a constricted mode. It is indicated by red circles in the graph. In the constricted mode, the discharge
contracts at the very tip of the electrodes and has an arc-like, filamentary appearance. Due to the reduced discharge area, the current density increases dramatically. Therefore, gas temperature as well as discharge emission are considerably higher than in abnormal mode (not shown here). As already explained in section 4.3.2, in this mode, the V-I characteristic strongly depends on the matching circuitry. The generator power was then reduced until the re-transition to the homogeneous abnormal mode occurred at 220 V. At this threshold, the I-V characteristic jumps back into the original, linear shape and the discharge is homogeneous (blue triangles).

When the generator power was even further reduced, another threshold was reached at 145 V (marked by a black arrow). The discharge begins to extinguish slowly from the gas inlet and the discharge channel is only partly filled. Hereinafter, this point is called extinction. In this mode, the discharge shows behavior of a normal mode discharge (pink triangles). In normal mode, the current remains constant when the discharge voltage is varied since the increase in voltage is compensated by a larger discharge surface. At even lower generator powers, the plasma eventually extinguished completely (green diamonds). In this range, the V-I characteristics only consists of displacement current and voltage and is therefore linear.

As the discharge in the COST-Jet is capacitively coupled and therefore driven using an AC voltage, the measurement of the current and voltage amplitudes does not contain complete information about the electrical state variables. As a third variable, the variation of the phase angle difference between voltage and current with voltage caused by the discharge is shown in figure 5.2. It is obtained using the method and software described in chapter 3.3.1. Without a plasma discharge, the phase angle between current and voltage is -90°, which corresponds to a purely capacitive electrical element. When the discharge is ignited, the phase angle difference drops to approximately -86°. In the abnormal mode, it is nearly constant and only slightly decreases with increasing voltage. When the discharge transforms into constricted mode, the phase angle increases notably, indicating the discharge moving to a strongly resistive mode. When the generator power is lowered, the discharge jumps back to homogeneous mode and the phase angle difference increases with decreasing voltage. The normal mode (pink triangles) is clearly visible in the phase behavior represented by the decreasing phase angle, while the voltage is nearly constant. In this mode, the discharge channel is only partly filled and the phase angle results from two parallel capacitors filled with
In summary, current and voltage measurements allow the classification into different operating modes: the argon discharge exhibits a normal, an abnormal and a constricted mode. The measurements of the phase show that in abnormal mode in argon, the phase decreases with increasing dissipated power. In contrast, in helium, the phase increases with increasing dissipated power. This difference might be caused by different...
5.1 Electrical characterization and operational range

**Figure 5.3:** Phase angle of a helium discharge depending on voltage (pressure 990 mbar, gas flow rate 1000 sccm).

discharge processes in argon compared to helium, which will be analyzed further in the following section.

**5.1.1 In-situ actual dissipated power measurements**

From voltage, current and phase difference, a variety of different intrinsic plasma parameters can be estimated. The dissipated power calculated using these electrical parameters was demonstrated in section 4.3 to deliver realistic results using the example of a helium discharge. The advantage of the technique developed in this thesis is the *operando* character. Using this diagnostic technique, real-time measurements of the deduced variables are possible, allowing for a continuous monitoring of the plasma parameters. Thus, the discharge, physical processes and the plasma chemistry can be adjusted to the needs of applications in real-time, for example during the treatment of a biological substrate.
The power dissipated in an argon discharge at a pressure of 990 mbar and a gas flow rate of 400 sccm is shown in figure 5.4. When the discharge is ignited, the power dissipated in the abnormal mode is around 0.3 W. With increasing voltage, the dissipated power increases linearly until the threshold voltage of 252 V is reached. During the abrupt transition to constricted mode, the dissipated power is nearly doubled from 0.64 W to 1.5 W, even if the voltage drops by 20 %. This is due to the different physical processes in constricted mode. As explained in section 5.1, the plasma is closer to thermal equilibrium than in abnormal mode, the gas temperature is higher and also secondary electron emission plays an enhanced role in the discharge physics. Even if the current drops (see figure 5.1), the current density is higher since the discharge area is considerably reduced. As shown in section 4.3.2, the maximum power in constricted mode is affected by the matchbox settings. Since the current is limited, the constricted mode is prevented from transforming into a fully developed arc discharge. This is also manifested in the non-sinusoidal current and voltage form observed on the oscilloscope that show a considerable amount of conduction current at the time of maximum current amplitude. In this mode, the calculated dissipated power has to be interpreted with
5.1 Electrical characterization and operational range

Figure 5.5: Power dissipated in the helium plasma depending on discharge voltage (pressure 990 mbar, gas flow rate 1000 sccm). The black dashed line is the linear part of the power curve as described in the text.

cautions, because the current and voltage waveforms deviate from their sinusoidal form. Thus, the fitted waveforms used for the power calculation do not exactly represent the physical data but the dissipated power is most probably underestimated. When the generator power is reduced, the discharge jumps back into abnormal mode. As the discharge eventually transforms to normal mode, the power is reduced whereas the voltage stays approximately constant. Once the plasma is extinguished, the power equals 0 W, even if the voltage is increased above ignition voltage.

The power density in the abnormal plasma discharge is of the order of $1.52 \times 10^7$ W m$^{-3}$ (corresponds to 1.52 W cm$^{-2}$). This is comparable to typical low pressure discharges, such as an ICP argon discharge (2 W cm$^{-2}$) [135] or a PECVD discharge (1 W cm$^{-2}$) [136]. For comparison, the power density in constricted mode is about $1.5 \times 10^9$ W m$^{-3}$ when a discharge volume of 1 mm$^3$ is assumed (compare photograph 5.6). This is two orders of magnitude higher than in homogeneous mode.

As a comparison to argon, figure 5.5 shows the dissipated power in a pure helium
plasma discharge as a function of the discharge voltage at a gas flow rate of 1000 sccm. The overall shape is similar to the argon power curve, but there are major differences. First, the helium discharge is self-igniting, which means that no additional high voltage spark is necessary for the ignition of a homogeneous plasma discharge. Consequently, the power curve starts with plasma off and breakdown occurs spontaneously as the generator power is increased at a voltage of approximately 150 V (marked by an arrow) and the discharge is ignited. A stable operation in abnormal mode was possible in a voltage range of 155 V to 260 V. This corresponds to an active power of 0.13 W to 1.24 W. Model calculations by Waskoenig et al. confirmed this power range in a helium discharge with oxygen admixture [82].

Second, the shape of the power-voltage curve in abnormal mode changes at approximately 185 V and 0.28 W. Below this voltage, the power rises linearly with increasing voltage. For higher voltages, an additional exponential trend is observed, which is absent in argon. Using a fit function consisting of a linear and an exponential summand, those two parts can be separated. The fit reveals that at 185 V the exponential part causes 5% of the overall dissipated power. This value is marked by a vertical dotted line. To guide the eye, the linear summand of the fit function is also plotted in figure 5.5 as a dashed line. The shape of the power curve confirms measurements by Marinov and Braithwaite [114]. They measured the dissipated power in the \( \mu \)-APPJ using a commercial power probe (OctIV) and also found an exponential increase with increasing voltage. Even though their measurements reveal the same power range, the measured discharge voltages were higher compared to the measurement shown in figure 5.5. This might be due to molecular impurities in the feed gas.

The difference in shape between the power curves of helium and argon discharges could be an indicator for the two discharges being dominated by different heating mechanisms. Whereas the dissipated power in the argon discharge is almost linear over the entire voltage range, a second heating mechanism appears to play a role in the helium discharge, providing an additional exponential component in the dissipated power rise for high operating voltages. This is also evident in simple photographs: Figure 5.6 shows photographs of the COST-Jet operated in helium at different voltages. At low voltages, the emission is dominated by bulk emission (see figure 5.6 a)), whereas for higher voltages, the emission is more pronounced in the sheath regions (see figure 5.6 b)). As the transition to the \( \gamma \)-like mode is smooth and not characterized
5.1 Electrical characterization and operational range

Figure 5.6: Photograph of the COST-Jet operated in helium in a) \(\alpha\)-like mode at low voltages, b) \(\gamma\)-like mode at higher voltages and c) constricted mode.

by sharp distinct point, these to different, it will be called \(\gamma\)-like mode throughout this thesis. In constricted mode (see figure 5.6 c)), the homogeneous discharge transforms into a constricted plasma filament visible at the very tip of the electrodes. The images show the complexity of the different heating mechanisms that coexist in the discharge. Comparing to figure 4.9 b) in chapter 4 confirms that the \(\gamma\)-like mode is, if visible at all, less pronounced in the argon discharge compared to helium. This hypothesis of different dominant heating mechanisms will be taken up and deepened in the course of this chapter.

In summary, in this section, the dissipated power in the argon and helium discharge was measured. For both gases, the power is in the range of 0.5 W which corresponds to a power density of \(1.5 \times 10^7\) W m\(^{-3}\). However, for argon, the power linearly depends on the applied voltage, whereas for helium, the power dependence exhibits an additional exponential term. This difference might be explained by different dominating electron heating mechanisms as will be assessed in section 5.4.

Apart from the differences in dissipated power observed in the abnormal mode, there is also the difference in the transition points in the power curve (ignition, extinction and constriction). Since for the argon discharge, the ignition has to be triggered manually, this point cannot be compared to the behavior in helium. Also, the transformation of the homogeneous into constricted discharge (constriction) in helium appears to occur at higher dissipated power values than in argon. Furthermore, the behavior of
the discharge extinction differs: While the argon plasma exhibits a normal mode, this mode was not observed in the helium discharge at all. However, this was probably due to unfavorable matching circuitry settings. For applications, the abnormal mode is especially important. Therefore, we will have a closer look on the limitations, i.e. constriction and extinction of the discharge. To investigate the underlying mechanisms of constriction and extinction in the argon discharge, two parameter studies were conducted.

5.1.2 Influence of gas flow rate

An external parameter which influences the discharge on time scales of milliseconds is the feed gas flow rate. The gas flow rate does not affect fast plasma processes on the nanosecond scale but is known to affect plasma chemistry, e.g. when oxygen is admixed to a helium plasma [19]. The flow rate was varied while the pressure was kept constant at 990 mbar to determine the effect of species' residence times in the plasma on the stability of the discharge. Intuitively, there is no change in the discharge processes expected, since only argon is present in the discharge channel and no chemical processes should be involved.

Figure 5.7 shows the regime of the abnormal mode for several gas flow rates in a power curve. As expected, the shape of the power curves is linear and identical for all gas flow rates. This was expected, since the discharge power and the gas density is kept constant. Yet surprisingly, the operation range of the discharge is affected. This is in contrast to the helium discharge. There, breakdown voltage, current-voltage curves and spectroscopic results are usually more or less the same for various helium flow rates [134]. However, in the argon discharge, the point of transition from abnormal to constricted mode (constriction, right end of each curve) as well as from abnormal to normal mode (extinction, left end of each curve) vary with gas flow rate.

Figure 5.8 is an alternative representation of figure 5.7 showing the limits of the abnormal mode as a function of the gas flow. Since the dissipated power is approximately linear to the applied voltage in the argon discharge (see figure 5.4 and 5.7), the voltage is also displayed on the right ordinate. Each data point in the graph is the mean value of at least two measurements, wherein the error bars represent the
5.1 Electrical characterization and operational range

![Graph showing dissipated power as a function of voltage for an argon discharge at various gas flow rates (pressure 990 mbar).](image)

**Figure 5.7:** Dissipated power as a function of voltage for an argon discharge at various gas flow rates (pressure 990 mbar).

maximum deviation. The applied voltage at the moment of constriction (extinction) is the constriction (extinction) voltage. In figure 5.8, the voltages are presented as a constriction (extinction) curve.

Both curves show a linear increase of transition power density and voltage with increasing gas flow rate. The constriction voltage rises slightly with increasing gas flow rate from $249 \text{ V}$ at a flow rate of $100 \text{ sccm}$ to $257 \text{ V}$ at a flow rate of $1200 \text{ sccm}$. The extinction voltage rises with increasing gas flow rate from $128 \text{ V}$ at a flow rate of $100 \text{ sccm}$ to $216 \text{ V}$ at a flow rate of $1200 \text{ sccm}$.

Since the slope of the extinction curve is steeper than that of the constriction curve, the operation range of the abnormal mode becomes narrower with increasing argon gas flow rate. When assuming a linear behavior of the two curves, the upper limit of the gas flow rate for the abnormal mode can be extrapolated to be approximately $1900 \text{ sccm}$. In the graph, this linear extrapolation is represented by two dashed lines.

To analyze the stable operation range and the reasons for this behavior, the transitions are discussed subsequently.
Figure 5.8: Dependence of power density at constriction and extinction on gas flow rate of an argon plasma (pressure 990 mbar).

**Extinction**

The dependence of the point of extinction as illustrated in figure 5.8 shows an increasing linear trend that is similar to the constriction voltage, but the increase is steeper. This behavior is surprising since the extinction of the plasma discharge should follow the Townsend avalanche theory as described in section 2.1. This theory implies that the critical breakdown voltage should be completely independent of the flow and only depend on the pressure and electrode spacing. As described in section 2.1.1, the extinction voltage should behave accordingly. However, the measurement shows that the extinction voltage does linearly depend on the gas flow rate. This behavior suggests that a second mechanism besides direct ionization plays a role. When the extinction voltage is plotted against the residence time (see figure 5.9), the fit shows an exponential decrease with a decay time of 2 ms. This behavior could be explained by a species that delivers energy to the discharge with a lifetime that is long enough to allow slow accumulation in the discharge channel. Since there are supposedly nearly no impurities in the discharge (see chapter 4), these species are unlikely to be built
5.1 Electrical characterization and operational range

Figure 5.9: The extinction voltage decreases exponentially with increasing residence time.

up by a chemical process. In contrary, since only argon is used for the operation, it is reasonable to assume the species have to be long-living argon species. One obvious candidate are argon metastables states that have a lifetime of approximately 119 ns [124]. Thus, an appreciable number of argon metastables can survive from one RF cycle to another and slowly accumulate. Argon metastables can be an energy storage and thus considerably contribute to the discharge. To support this hypothesis, the argon metastable distribution was measured, which is presented in section 5.3.

Constriction

Constriction is most likely caused by one of the two instability mechanisms often found in atmospheric pressure plasmas and described in section 2.1.4, i.e. the thermal instability or the $\alpha$-$\gamma$-instability.

The first possible explanation is the thermal instability. The crucial parameter for this type of instability is the neutral gas temperature $T$ since it is the slowest process in the
Chapter 5  
Physical properties of an argon discharge in the COST-Jet chain as described in the fundamentals (see section 2.1.4). It is determined by the heat balance equation [51]

\[
\frac{dq}{dt} = n c_p \frac{dT}{dt} = j E - n c_p (T - T_0) \nu_c ,
\]  

(5.1)

where \( q \) is the heat energy density, \( n \) is the neutral gas density, \( j E \) is the electrical power density coupled into the discharge, \( c_p \) is the specific heat at constant pressure per molecule, \( T_0 \) is the temperature of the gas entering the discharge (or the wall temperature), and \( \nu_c \) is the heat removal frequency.

A first order perturbation ansatz for the temperature \( \delta T = T_1 \exp(\Omega t) \) and the density \( n \) [74] leads to the instability growth rate \( \Omega \)

\[
\Omega = \nu_h (1 + \nu^* ) - \nu_c \quad \text{with}
\]

(5.2)

\[
\nu_h = \frac{\gamma - 1}{\gamma} \frac{j \cdot E}{n k_B T} \quad \text{and}
\]

(5.3)

\[
\nu^* = \frac{\text{d} \ln \nu_i}{\text{d} \ln (E/N)} ,
\]

(5.4)

where \( \nu_h \) is the heating frequency, \( \gamma \) the heat capacity ratio and \( \nu^* \) is the logarithmic sensitivity of the ionization coefficient \( \nu_i \) on the reduced electric field \( E/N \). \( \Omega \) is defined as the balance of cooling and heating frequency weighted by the dependence of the ionization frequency. The discharge becomes unstable if the instability growth rate is positive (\( \Omega > 0 \)). Using this criterion, a critical input power density \( \varepsilon_{cr} \) can be calculated as an upper limit for thermal instabilities.

\[
\varepsilon_{cr} = (j \cdot E)_{cr} = \frac{\gamma}{\gamma - 1} \frac{\nu_c}{1 + \nu^*} p .
\]

(5.5)

In plasma discharges, the RF voltage applied to the electrodes does not necessarily drop over the bulk plasma. Since the effective sheath is a capacitance in series to the bulk plasma, an important part of the voltage drops over the sheath. Therefore, the critical power density has to be corrected \( \varepsilon_{cr} \) by a factor [137]

\[
R = \frac{V_b^2}{V_s^2} .
\]

(5.6)

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5.1 Electrical characterization and operational range

$R$ can be deduced from the electrical measurements as presented in section 5.2 with the voltage over the bulk plasma $V_b$ and the sheath $V_s$. This results in

$$
\varepsilon_{cr} = \frac{\gamma}{\gamma - \frac{1}{1 + R + \nu^*}} \nu^*_{c}p .
$$

(5.7)

To calculate a realistic absolute value for the critical power density, all parameters have to be estimated. The logarithmic sensitivity $\nu^*$ can be estimated using a Maxwellian electron distribution ($\nu_i \propto \exp(-I/k_BT)$) to be

$$
\nu^* = \frac{I}{k_BT_e} ,
$$

(5.8)

with $I$ being the ionization energy of the feed gas (see section 2.2) and $T_e$ the electron temperature, so that $\nu^*_{Ar} = 15.8$ and $\nu^*_{He} = 24.6$ assuming an electron temperature of approximately $T_e = 1$ eV, as derived in section 5.2.3.

The cooling frequency $\nu_c$ can be dominated either by conductive cooling or convective cooling. In case of conductive cooling, the coefficient is determined by

$$
\nu_T = \frac{\chi}{\Lambda_T^2} ,
$$

(5.9)

$$
\chi = \frac{\lambda}{n \cdot c_p} = \frac{\lambda}{c_p} \frac{k_BT}{p} ,
$$

(5.10)

$$
\frac{1}{\Lambda_T^2} = \sum_{i=1}^{3} \left(\frac{\pi}{L_i} \right)^2 ,
$$

(5.11)

with the thermometric conductivity $\chi$, the characteristic length of the discharge $\Lambda_T$, the thermal conductivity $\lambda$, the specific heat capacity at constant pressure $c_p = 5/2k_B$ and the geometric discharge dimensions $L_i$. This conductive cooling ansatz results in the critical power density being independent of the gas flow rate.

In case of convective cooling, the heat removal frequency $\nu_F$ depends on the gas flow rate. It is determined by

$$
\nu_F \approx 2 \frac{u}{L_1} ,
$$

(5.12)

with $u$ being the feed gas velocity and $L_1 = 30$ mm the length of the discharge channel.
This convective cooling ansatz results in the critical power density being linearly dependent on the gas flow rate and the gas pressure.

**Table 5.1: Critical power densities for thermal instability in argon and helium at a pressure of 1000 mbar.**

<table>
<thead>
<tr>
<th>critical power density / W/m³</th>
<th>argon</th>
<th>helium</th>
<th>Γ' dependency</th>
</tr>
</thead>
<tbody>
<tr>
<td>convective @ 500 sccm</td>
<td>$1.5 \times 10^9$</td>
<td>$4.1 \times 10^8$</td>
<td>$\propto \Gamma'$</td>
</tr>
<tr>
<td>conductive</td>
<td>$1.0 \times 10^9$</td>
<td>$2.5 \times 10^9$</td>
<td>$\propto$ const.</td>
</tr>
</tbody>
</table>

Table 5.1 summarizes the results for the critical power density of the thermal instability and its dependence on the gas flow rate $\Gamma'$ and the pressure $p$. Comparing with figure 5.8 reveals that all of the calculated critical power density values for the argon discharge are at least one order of magnitude above the critical power densities observed in the measurements. However, the values presented in the table are only rough estimates, since for the calculation quite a lot of assumptions have to be made. Therefore, the thermal instability is still a candidate for the observed constriction of the discharge.

Nevertheless, as shown in figure 5.8, the measured power density at the point of constriction is nearly independent of the gas flow rate. This is in contrast to the dependence of the convective cooling ansatz suggesting a directly linear dependence. Therefore, this cooling mechanism can be excluded to be dominating the constriction process of the argon discharge. Instead, if the constriction of the discharge is caused by the thermal instability, it is most probably dominated by conductive cooling resulting in a constant critical power density. In this case, the observation from measurements that the argon discharge constricts at lower power densities than the helium discharge (compare figures 5.4 and 5.5) is reasonable, as the thermal conductivity of helium is a factor of ten higher than that of argon (see section 2.2) and thus peaks can be leveled off faster in helium than in argon.

The second possibility for instabilities in atmospheric pressure plasmas is the α-γ-instability that is due to a sheath breakdown at high voltages. This breakdown mechanism roughly follows Paschen’s law. Since this theory does not depend on the gas flow rate, the critical power density should be constant. However, this mechanism as well as the conductive cooling mechanism of the thermal instability depends on the
5.1 Electrical characterization and operational range

![Graph showing power as a function of voltage for an argon discharge at various pressures.]

**Figure 5.10:** Dissipated power as a function of voltage for an argon discharge at various pressures (gas flow rate 200 sccm).

Therefore, to further analyze whether the constriction of the argon discharge is due to these mechanisms, a variation of the discharge pressure is necessary.

In summary, this section demonstrated that the extinction voltage linearly depends on the gas flow rate. This is an indicator for this process being limited by a long-living species in the discharge channel that is important for the discharge sustainment. In contrast, the constriction voltage is constant. This suggests the conductive thermal instability or the $\alpha$-$\gamma$-instability being the reason for the constriction of the homogeneous discharge. A pressure variation will be performed in the next section, to exclude one of these two mechanisms.

### 5.1.3 Influence of pressure

A second control parameter that determines the behavior of the discharge is the gas pressure. In particular, it should have an influence on the two instability mechanisms.
Figure 5.11: Extinction and constriction voltage as a function of gas pressure (gas flow rate 200 sccm).

To specify the relevance of the instability mechanisms for the argon discharge, the gas pressure was varied. Since the pressure determines the ground state density of the discharge gas, it affects both ionization rate and ambipolar diffusion. A high pressure supports ionization by a high collision frequency but impedes diffusion. At constant electron temperature, a higher ground state density enables more ionization processes and thus encourages ionization. Therefore, pressure is an important operational parameter for the particle balance as well as energy balance.

Figure 5.10 shows the dissipated power in the abnormal mode for gas pressures between 860 mbar and 1020 mbar. In contrast to the flow variation results shown in the previous section, both the operational regime for the abnormal mode and the power dissipation is changed. Briefly, the change in dissipated power can be attributed to the increased number of collisions. As explained in section 2.1, the electrical energy is transferred to the plasma discharge via electron collisions. If the collision frequency is increased, the plasma discharge becomes more resistive, the energy transfer becomes more effective and thus the dissipated power is higher.
The dependence of the extinction and constriction on the gas pressure is shown in figure 5.11. Note, that the voltage is not shown on the right ordinate as in the flow variation (see figure 5.8) since the dependence of voltage and power is not linear as demonstrated in figure 5.10. Again, each data point in the graph is the mean value of at least measurements and the error bars represent the maximum deviation. Whereas the constriction is almost constant for the pressure variation, the extinction power density clearly decreases with increasing gas pressure. In between these limits, a stable operation of the abnormal mode is possible.

\textbf{Constriction}

If the constriction of the discharge was caused by the conduction dominated thermal instability mechanism, the critical power limit should be independent from pressure since the cooling term $v_T$ is proportional to the reciprocal of the pressure. However, the exact form of the pressure dependence cannot be derived from the measurements presented here with high confidence, since the absolute value of the pressure could only be varied by a small range of 16%.

If the constriction of the discharge was caused by the $\alpha$-$\gamma$-instability mechanism, the critical power density would increase with increasing pressure. This is clarified by the following derivation of the formula. With the assumption of the sheath being a discharge gap with size $d_s$ and the plasma playing the role of the anode, Paschen's law can be applied and the breakdown voltage across the sheath $V_s$ is

$$V_s = \frac{B \cdot pd_s}{\ln(Apd_s) - \ln[\ln(1 + \gamma^{-1})]} ,$$

(5.13)

with $A$ and $B$ being the Paschen constants and $\gamma$ the secondary electron coefficient as described in section 2. Breakdown of the sheath occurs when the electric field in the sheath is maximum. This is the case if the sheath thickness $d_s$ equals twice the oscillation amplitude of the plasma boundary $2A_0 = d_s$. At this point, the electrostatic sheath voltage is

$$V_s = 2en_eA_0^2/\varepsilon_0 ,$$

(5.14)
with the elementary charge $e$, the averaged electron density $n_e$ and $A_0 = \mu_e E_a / \omega$, the electron mobility $\mu_e$, the amplitude of the oscillating field $E_a$, the vacuum permittivity $\varepsilon_0$ and the angular frequency $\omega$.

By equating equation 5.13 and 5.14, we obtain the critical electron density

$$n_{cr} = \frac{\varepsilon_0}{e A_0 (\ln(A) - \ln[\ln(1 + \gamma^{-1})] + \ln(p \cdot 2A_0))},$$

from which the critical current density $j_{cr}$ can be calculated by

$$j_{cr} = e n_e \mu_e E_a .$$

Using experimental values for the electron mobility ($\mu_{e Ar} = 4.4 \times 10^{-2} \text{m}^2\text{V}^{-1}\text{s}^{-1}$, $\mu_{e He} = 1.2 \times 10^{-1} \text{m}^2\text{V}^{-1}\text{s}^{-1}$ [51]) and from measurements presented in section 5.2 ($R_{Ar} = 0.03$, $R_{He} = 0.30$), a critical electron density of $n_{cr Ar} = 8.42 \times 10^{17} \text{m}^{-3}$ and $n_{cr He} = 7.15 \times 10^{16} \text{m}^{-3}$ is obtained. This density corresponds to a critical power density of $\varepsilon_{cr Ar} = 1.29 \times 10^8 \text{W m}^{-3}$ and $\varepsilon_{cr He} = 1.81 \times 10^8 \text{W m}^{-3}$, respectively. Even if the argon and helium discharge constrict at a similar voltage (approximately 360 V), the critical power density for argon is lower than for helium since the mobility in argon is lower than the mobility in helium. Thus, the oscillation amplitude $A_0$ is smaller, but the breakdown voltage is higher. However, the electrical field in the sheath affecting the critical electron and power density is smaller for helium than for argon as the voltage drop over the sheath is smaller for helium than for argon.

**Table 5.2:** Critical power densities for thermal and $\alpha$-$\gamma$-instability in argon and helium and the results from the observation.

<table>
<thead>
<tr>
<th>critical power density / (W/m³)</th>
<th>argon</th>
<th>helium</th>
<th>$\Gamma$ dependency</th>
<th>p dependency</th>
</tr>
</thead>
<tbody>
<tr>
<td>thermal instability</td>
<td>$1.0 \times 10^9$</td>
<td>$2.5 \times 10^9$</td>
<td>$\propto \text{const.}$</td>
<td>$\propto \text{const.}$</td>
</tr>
<tr>
<td>$\alpha$-$\gamma$-instability</td>
<td>$1.3 \times 10^8$</td>
<td>$1.8 \times 10^8$</td>
<td>$\propto \text{const.}$</td>
<td>$\propto p$</td>
</tr>
<tr>
<td>observation</td>
<td>$2.2 \times 10^7$</td>
<td>$4.1 \times 10^7$</td>
<td>$\propto \text{const.}$</td>
<td>$\propto p$ ?</td>
</tr>
</tbody>
</table>

Table 5.2 summarizes the two possible instability mechanisms and the observation, its critical power densities as estimated from measured values and the dependencies on pressure and gas flow rate. Comparing the two eligible instability mechanisms, both, the absolute values for the constriction as well as the dependence on the gas flow rate
5.1 Electrical characterization and operational range

Γ and the gas pressure $p$ indicate the $\alpha$-$\gamma$-instability as the underlying mechanism. At least for helium, this is in agreement with a simulation by Chirokov et al. supporting this thesis [70].

**Extinction**

As figure 5.11 shows, the extinction voltage and the power density decrease with increasing gas pressure while the constriction voltage remains almost constant. Consequently, the discharge operation range for argon increases with increasing gas pressure. Due to an experimental outlier, the error of the extinction voltage at 880 mbar is exceptionally high. However, the extinction behavior is in direct contrast to the behavior expected according to Paschen’s law. With $p = 760$ Torr and $d = 1$ mm, $pd = 76$ Torr cm, the discharge should be operating in the emission-free branch where $U_{\text{ext}} \propto pd$.

A first explanation would be the fact that the energy per particle is higher at low pressure, since the number density is lower and the power is distributed among fewer particles. However, this effect is compensated by the residence time that changes (higher gas flow velocity at lower pressure) due to the constant gas flow rate at standard conditions. Thus, the energy provided per atom is exactly constant at a fixed dissipated power (see derivation of equation A.9 in appendix A).

Again, the observed behavior can be explained with long-living, high-energy particles wherein argon metastables are the most probable candidates. In different types of high pressure discharges it was shown that the argon metastable density increases with increasing gas pressure [138]. This means that at atmospheric pressure, the metastable density can contribute to the maintenance of the discharge by stepwise ionization. The higher the argon metastable density, the higher is the ionization rate. If the density is too low, the discharge can not be sustained any longer. Thus, the argon metastable density could cause this behavior. Another supporting hint for this hypothesis is the ignition that has to be initiated by the high voltage gun.

**In summary**, the pressure variation suggests that the extinction of the argon discharge is caused by a gas flow rate depending mechanism such as stepwise ionization via metastables. This hypothesis will be further analyzed in section 5.3. Additionally, the pressure variation excludes the thermal instability as the reason for the constriction of
the argon discharge as the predicted values and trends agree better with the observations. Therefore, constriction is most probably caused by the $\alpha$-$\gamma$-instability. The higher critical power density compared to helium is due to the higher electrical field in the sheath.

In section 5.1, the reproducibility of the measurement of voltage, current and phase-angle was used to describe the global behavior of the COST-Jet operated in argon. Both, phase-angle and power measurements indicate different heating mechanisms in helium and argon. In addition, the limits of the stable operational range for argon are influenced by different mechanisms. The transition to constriction was attributed to the $\alpha$-$\gamma$-instability (excluding the thermal instability) for argon and helium. The extinction of the argon discharge depends on the gas flow rate, while the extinction of the helium discharge is independent of it. This dependence of the gas flow rate may be attributed to metastable particles, which is discussed in detail in section 5.3.

In conclusion, the reproducible measurement of the dissipated power allows to deduce fundamental discharge processes such as the instability mechanism responsible for constriction and extinction.

### 5.2 Plasma parameters

From voltage, current and phase measurements not only the actual power dissipated in the plasma can be calculated. By making assumptions on the electrical character of the discharge, intrinsic plasma parameters such as the plasma impedance, resistance and reactance can be calculated. This even allows to estimate the sheath width and the corresponding electron density in a microdischarge [139, 140]. Since the measurement method presented above provides trustworthy and reproducible values for dissipated power, it can now be used to make resilient calculations. These calculations will be presented in the following section.

The absolute value of the impedance $Z = R + iX$ can be calculated by dividing the measured voltage amplitude $V$ by the current amplitude $I$. To obtain the resistance $R$
5.2 Plasma parameters

Figure 5.12: Measured impedance of argon discharge as a function of the dissipated power (pressure 990 mbar, gas flow rate 400 sccm).

(real part) and reactance $X$ (imaginary part) for a sinusoidal waveform, this value has to be multiplied by the cosine and sine of the phase difference, respectively:

$$|Z| = \frac{V}{I}$$  \hspace{1cm} (5.17)

$$R = \frac{V}{I} \cos(\Delta \phi)$$  \hspace{1cm} (5.18)

$$X = \frac{V}{I} \sin(\Delta \phi).$$  \hspace{1cm} (5.19)

Figure 5.12 shows how the magnitude of the plasma impedance $|Z|$ depends on the power dissipated in the discharge for a gas flow rate of 400 sccm and a pressure of 990 mbar. The differently colored symbols mark the different operating regimes. Additionally, the normal mode region and the constricted mode region are colored in grey. The impedance is maximum when the plasma discharge is not ignited. In normal mode, the impedance decreases linearly with increasing dissipated power. In the abnormal mode, the plasma impedance decreases less steeply than in normal mode. In constricted mode, the impedance decreases linearly again but still less steeply than in normal mode. This behavior of the plasma impedance is reasonable and comparable to impedance measurements from Zhu et al. [141] and Overzet et al. [142].
However, the absolute value of the impedance is striking. When the plasma is not ignited yet, the absolute value of the plasma impedance is around 9 kΩ. Since in this phase, the equivalent electrical circuit only consists of a single capacitor, namely the COST-Jet, the impedance should be purely imaginary and correspond to the capacitance of a parallel plate capacitor with the dimensions of the COST-Jet. However, this is not the case. The capacitance of the COST-Jet is approximately $C_{\text{Jet}} = 0.293 \text{ pF}$, but the plasma off impedance leads to a value of $C = (\omega X_p)^{-1} = 1.297 \text{ pF}$. This is a deviation of 343% and must therefore be taken into account. The evident reason for this observation is a parasitic capacity that cannot be completely avoided by the electrode shielding of the grounded electrode (described in section 3.1.3). It can be caused by the housing or any other grounded or floating material in the vicinity of the Jet. Fortunately, this capacity can be accounted for by simply adding a parasitic capacity in parallel to the COST-Jet as illustrated in figure 5.13 a). This correction only changes the absolute value of the impedance but the overall shape remains the same. The correction complicates subsequent calculations of the impedance but does not affect to the measurements of the power dissipated in the discharge as no power is consumed in the parasitic capacitance. The parasitic capacitance was determined to be $C_{\text{par}} = C - C_{\text{Jet}} = 1.004 \text{ pF}$. Taking this into account, the corrected plasma impedance ($Z_p = R_p + iX_p$) can be calculated from the measured impedance $Z$ and is of the order of $Z_p = 40 \text{ kΩ}$. Comparing to measurements by Overzet et al. [142] and simulation by McKay et al. [113], this value fits much better.
5.2 Plasma parameters

Figure 5.14: a) Plasma resistance and b) reactance of argon discharge as a function of the dissipated power (pressure 990 mbar, gas flow rate 400 sccm) and c), d) for the helium discharge (atmospheric pressure, gas flow rate 1000 sccm), respectively.

To interpret the behavior of the impedance data, the absolute impedance has to be split into reactive and resistive part as shown in figure 5.14. Note, at low power, the dominance of $X_p$ and associated displacement currents.

Figure 5.14 a) shows the resistance as a function of dissipated power. The resistance in normal mode increases linearly. This is first and foremost counter-intuitive, since the resistance $R$ of the plasma depends on its cross-sectional area $A$ via $R = \rho d / A$, where $\rho$
is the specific resistivity and \( d \), in first approximation, the discharge gap. Assuming a constant specific resistivity in normal mode, the plasma resistance is anti-proportional to the cross-sectional area \( A \) of the plasma discharge that increases with increasing power \( R \propto 1/A \). However, when in normal mode, we can only measure the resistance of the whole system including the plasma discharge in parallel to an air-filled capacitor with a reactance \( X_e \) proportional to the area \( X_e \propto (A_0 - A) \), where \( A_0 \) is total electrode area. These competing dependencies on the discharge area and thus the power lead to an overall increase of the resistance.

The resistance in abnormal mode decreases with increasing dissipated power. This is expected as the bulk resistance is associated with the electron density in the plasma \[^{143}\]\. Thus, this is an indicator for an increasing electron density in the bulk plasma. The constricted mode is indicated by a discontinuity in the resistance. As expected, the resistance shows a steep increase. This behavior is due to the constriction of the discharge to an arc-like filament leading to a reduction of the cross-sectional area and thus a higher resistance.

In figure 5.14 b), the reactance is shown as a function of dissipated power. The comparison to figure 5.12 illustrates that the absolute impedance is dominated by the reactance of the discharge underlining the capacitive character of the discharge. The behavior in the normal mode can be explained with the plasma expanding in the discharge channel: The more electrode area is covered with plasma, the less is the capacity of the device. A decrease in absolute reactivity in the abnormal mode can be caused by a decrease in sheath capacitance which means an increase in sheath thickness. In constricted mode, the discharge reactance is even further reduced due to the resistive character of the arc-like filament.

Similar to section 5.1.1, the behavior of the argon discharge is compared with the helium discharge. While the behavior of the reactance (see figure 5.14 d)) is quite similar to the argon trend, the behavior of the resistance differs for the two gases. Figure 5.14 c) shows the resistance of the helium discharge. Surprisingly, the resistance also increases with increasing power. This is confirmed by measurements by Marinov and Braithwaite \[^{114}\]\, who observed the same trend at a similar discharge and attributed it to a dissipation of power in the sheath.
5.2 Plasma parameters

To analyze and interpret these processes in detail and isolate the effect of sheath and bulk plasma, an equivalent electrical circuit is needed, that represents these different zones and is more appropriate to the conditions in the discharge. Figure 5.13 shows the resulting equivalent circuit for the plasma off a) and plasma on b) case. As already described in chapter 2.3, a capacitive coupled atmospheric pressure plasma can be represented by an equivalent electrical circuit of a sheath capacitance in series with a bulk capacitance and a bulk resistance in parallel. The relations between the plasma impedance ($Z_p = R_p + iX_p$) and the components of the equivalent electrical circuit ($X_s$, $X_b$, and $R_b$) are found by solving the system of equations which models the circuit shown in figure 5.13 b) [113]:

\begin{align*}
X_s &= X_p + \frac{R_p^2}{X_p - X_0} \quad (5.20) \\
X_b &= X_0 - X_s \quad (5.21) \\
R_b &= R_p \left[ 1 + \frac{R_p^2}{(X_p - X_0)^2} \right] \quad (5.22)
\end{align*}

$X_0$ in the above equations is the capacitance of the discharge gap without plasma $X_0 = (\omega C_{\text{jet}})^{-1}$. Equations 5.20, 5.21, and 5.22 can be used to calculate the equivalent electrical components from the plasma impedance. Figure 5.15 shows the resistance of the bulk plasma calculated from the measured impedance using the above electrical model as a function of dissipated power for the a) argon and for the b) helium discharge.

In contrary to the plasma resistance, the bulk resistance shows the same behavior in argon and in helium. For both gases, at 0 W, when the plasma is not ignited yet, the bulk resistance equals zero. In the normal mode, the plasma resistance increases. This is due to the expanding plasma as explained above. In this region, the equivalent circuit model is therefore not appropriate. During abnormal mode, the plasma resistance decreases with increasing dissipated power. Since the plasma cannot spread along the electrodes any more, the plasma properties change when current is increased. Thus, the dissipated power can be transformed into a higher electron density which reduces electrical resistance. When the discharge transforms into constricted mode, the resistance is increased again. This is unexpected, because the electron density is expected to be much larger than in abnormal mode and thus the resistance should be
Figure 5.15: Bulk resistance as a function of dissipated power for a) argon (pressure 990 mbar, gas flow rate 400 sccm) and b) helium (atmospheric pressure, gas flow rate 1000 sccm). Note the different scales.

decreased. However, in constricted mode, the discharge is concentrated on a small area of approximately $1 \text{ mm}^2$ at the very tip of the electrodes. This decrease in area compensates for the increasing number of electrons. Thus, the overall resistance is increased even if the specific resistivity is much smaller than in abnormal mode.

In summary, the analysis of the discharge impedance revealed an additional parasitic capacity in parallel to the plasma discharge that has to be accounted for. A more complex circuit model was implemented in this thesis. This resolves the contradiction between the behavior of the helium plasma resistance, also observed by Marinov and Braithwaite, and the argon plasma resistance. The behavior of the helium plasma resistance is ascribed to the ratio between bulk and sheath as the plasma resistance depends on the bulk and sheath impedance $R_p = R_b/\left(1 + \left(\frac{R_b}{\chi_0 - \chi_s}\right)^2\right)$. Yet, the different scales of the graphs should be noted: The bulk resistance of helium is approximately a factor of two higher than in argon which might be attributed to a lower electron density in helium. The interplay of these parameters will be analyzed in the following section.
5.2 Plasma parameters

The results presented above confirm the validity of the model used, which turns out to be well suited for the analysis of measured V-I characteristics. By isolating the influences of sheath and bulk, we can now use the representative components \( X_s \) and \( R_b \) to deduce further plasma parameters. The components of the equivalent circuit were also used to calculate the correction factor \( R \) in section 5.1.3. It was used to determine the critical electron density for constriction of the discharge.

5.2.1 Sheath width

Since the surface-to-volume ratio in atmospheric pressure plasmas is large compared to low pressure plasmas, the plasma sheath in front of the electrodes plays an important role for the stability of the discharge. As the sheath width approaches half of the gap width, the quasi-neutral bulk plasma is suppressed, leading to a collapse of the plasma discharge. Therefore, it is important to assess the properties of the sheath. Yet, due to the large number of collisions in atmospheric pressure plasmas, this is not a harsh limit.

From the components of the equivalent electrical circuit, the sheath width can be extracted based on plasma impedance measurements. Assuming that the sheath capacitance \( X_s \) is the series combination of two nonlinear sheath capacitances, the average sheath width \( s_0 \) can be calculated from the linear sheath capacitance via [52]

\[
s_0 = \frac{\omega \varepsilon_0 A X_s}{2}.
\]  

Because the area of the discharge \( A \) is necessary for the calculations, this formula is only valid in the abnormal mode, since in normal mode as well as in constricted mode, the area changes drastically. Figure 5.16 shows the averaged sheath width \( s_0 \) and bulk width \( d = l - 2s_0 \) in the abnormal mode as a function of the dissipated power for the pure argon and helium discharge. The discharge was operated at a gas flow rate of 400 sccm and a pressure of 990 mbar for argon and 1000 sccm at ambient atmosphere for helium. The graph shows, that for both plasma discharges in abnormal mode, the sheath thickness varies between 350 \( \mu \text{m} \) and 210 \( \mu \text{m} \). For all dissipated power values considered, it is always less than half of the electrode gap of 500 \( \mu \text{m} \). The sheath width decreases monotonically with increasing dissipated power, while the bulk
width increases at the same time. This behavior is in contrast to expectations from low pressure, since in typical capacitively coupled sheath models, the plasma sheath usually increases with increasing applied voltage [67]. However for atmospheric pressure helium plasmas, a decrease was observed [69, 108, 134] and simulated [145] before by various authors. It is most commonly attributed to the weak variation of $T_e$ with dissipated power and the independence of the electrical permittivity of the plasma at atmospheric pressure from the dissipated power [146].

The ratio of sheath to bulk width is a factor of two higher for helium than for argon. This explains the difference in behavior of the plasma resistance in the previous section. For argon, the sheath width only slightly decreases with increasing dissipated power and remains nearly constant. This is due to the smaller abnormal mode operation region compared to the helium discharge. The absolute value of the sheath thickness in argon is in good agreement with results by a global model by Lazzaroni and Chabert [13]. At a gap distance of 1 mm and a power density of $2 \times 10^7$ W m$^{-3}$, which corresponds
5.2 Plasma parameters

to a dissipated power of 0.6 W in the COST-Jet geometry (marked by a dashed line in figure 5.16), the modeled sheath thickness is around 0.22 mm. The calculated sheath thickness from the measured impedance in the experiment was 0.21 mm. This agreement is remarkably good, considering the simplicity of the model used for the measurements. However, it should be evaluated with caution, since the absolute value of the sheath thickness strongly depends on the sheath model. In equation 5.23, a neutral approach (factor 1.0) was chosen, which can be modified depending on the sheath model. For a collisional sheath, for example, the sheath thickness must be multiplied by a factor of 0.76 [147], resulting in a value of 0.16 mm. Nevertheless, the relative trends also agree well with the studies mentioned above.

The results for the sheath thickness of helium are in good agreement with the former mentioned 1D hybrid-model by Waskoenig for the coplanar μ-APPJ operated in helium [144]. For an assumed power density of 3 W cm$^{-2}$ in the simulation, which corresponds to a dissipated power of 0.9 W in the COST-Jet geometry (also marked in figure 5.16), an RF-averaged sheath thickness of approximately 250 μm and an electron density of $n_e = 1.2 \times 10^{11}$ cm$^{-3}$ was calculated. This is again in good agreement with the impedance measurement, which reveals a sheath width of 245 μm. For increasing dissipated power, a decreasing sheath width was observed in experiments by Schaper et al. using phase-resolved optical emission spectroscopy as well as in modeling results [79].

Still, the sheath width for argon is a factor of 0.8 smaller than for helium. The hybrid model by Lazzaroni et al. underlines the dependence of the sheath on the average electron velocity and the ratio of the electron losses by inelastic and elastic processes. So the higher these two variables, the larger is the sheath thickness. So according to the global model by Lazzaroni and Chabert [13], smaller sheath thicknesses in argon can be due to a lower electron temperature, since the sheath thickness depends on the Bohm velocity.

The small sheath thickness of argon can be a stabilizing factor, considering the admixture of oxygen. In their model, Lazzaroni and Chabert demonstrate the increase of sheath thickness with increasing oxygen admixture. As argon generally exhibits a generally smaller sheath thickness than helium, the admixture of oxygen to the discharge should be a smaller problem for discharge stability in argon than in helium. Additionally, the
sheath thickness in argon should be less influenced by the admixture of oxygen, as the elastic electron loss processes are larger in argon than in helium, especially for low electron temperatures. This aspect will be addressed in more detail in section 5.2.3 (compare figure 5.19). The model by Lazzaroni and Chabert predicts a maximum oxygen admixture fraction of 60% before the plasma extincts. The principal behavior of the model predictions concerning the sheath thickness differences could be confirmed by the measurements in this thesis. However, the admixture of oxygen is way more challenging in argon than in helium. Only admixtures below 1% are feasible. This excludes the thickness of the sheath as a potential source of instability.

In summary, the sheath thickness in the argon and helium discharge was calculated from the circuit model to be of the order of 250 $\mu$m. The sheath thickness decreases with increasing dissipated power due to the weak variation of electron temperature with dissipated power. The relative trend, as well as the absolute values, are supported by the available literature. The sheath size in argon is a factor of 0.8 smaller compared to helium. This might be due to a lower electron temperature in argon. As the argon sheath thickness never exceeds half of the discharge gap, this mechanism is excluded as a potential source of instability.

5.2.2 Electron density

One of the most important characteristic plasma parameters is the electron density. It determines the Debye length, the plasma frequency, electrical conductivity and the probability of electron-induced processes such as excitation or chemical reactions.

To estimate the mean electron density based on the measured impedance, the bulk plasma resistance $R_b$ from the homogeneous discharge model can be used:

$$R_b = \frac{l - 2s_0}{A} \rho_b = \frac{l - 2s_0}{A} \frac{1}{\omega \text{Im}(\epsilon_p)} = \frac{l - 2s_0}{A} \frac{\nu_m m_e}{e^2 n_e} \Rightarrow n_e = \frac{l - 2s_0}{AR_b} \frac{\nu_m m_e}{e^2}, \quad (5.24)$$

where $l$ is the interelectrode gap (1 mm for the COST-Jet) and $\rho_b$ is the bulk plasma resistivity. For argon and helium at atmospheric pressure, the electron-neutral collision frequency is $\nu_m = 4.03 \times 10^{12} \text{s}^{-1}$ and $1.52 \times 10^{12} \text{s}^{-1}$, respectively [51].
Figure 5.17: Electron density as function of dissipated power for a) argon discharge at a gas flow rate of 400 sccm and a gas pressure 990 mbar and for b) helium discharge at a gas flow rate of 1000 sccm and a gas pressure 990 mbar. Note the different scales.

The accuracy of the result given by equation 5.24 strongly depends on the precision of the plasma impedance measurements but also on the operation mode of the plasma. Since the equivalent circuit used here does not capture power dissipation in the sheaths, it is not valid in γ-like mode operation.

Figure 5.17 a) shows the resulting electron density for an argon plasma as function of dissipated power. For comparison, figure 5.17 b) shows the electron density as a function of dissipated power for the helium plasma. For better visibility, a different scaling of the ordinate was chosen. As anticipated, the electron density in both discharges increases with increasing dissipated power. However, the absolute values and the shape of the curve are different for both discharge gases. In argon, the electron density is of the order of $5 \times 10^{17} \text{ m}^{-3}$ and increases almost linearly with increasing power. In helium, the electron density is approximately one order of magnitude lower than in argon. This is in good agreement with measurements by Hofmann et al. in a coaxial cold atmospheric pressure RF discharge [148] and the predictions by Jonkers et al. [37]. The argon electron density being higher than the helium density is due to the ionization mechanisms in the discharge gas. In argon, the energy gap between the
argon ground state and the first excited state is less than in helium. Thus, there is less energy needed to produce argon ions by (stepwise) ionization than to produce helium ions. Therefore, the electron temperature in an argon plasma is usually lower than in a helium plasma [37]. Due to the higher mass of argon atoms, the kinetic energy transferred in an elastic collision of an electron with an atom or ion is less in argon than in helium. Consequently, the electron density in helium is lower at the same power density. Additionally, the absolute values estimated here using the electrical model agree well with the predictions from the α-γ-instability model in section 5.1.3.

In contrast to argon, the electron density in helium steeply increases for low dissipated power, but begins to flatten at approximately 0.28 W. This behavior is unexpected, as there is no obvious physical reason for this change in trend. A possible explanation can be deduced from the validity range of the used model. The assumptions for this model are only valid if the discharge is in α-mode. As already seen in figure 5.5, the helium power curve shows a distinct behavior: after a linear increase, the dissipated power increases exponentially with increasing voltage. This can be interpreted as the onset of a γ-like mode characterized by enhanced secondary electron emission. Consequently, the used model is not valid in this region and thus the resulting trends are misleading. This is due to the power dissipation in the sheath that is not captured by the equivalent circuit. In this regime, additional sheath resistors representing the power dissipation by stochastic heating and a dc current source term accounting for the generation of ions have to be included in the circuit [52]. However, these additional circuit elements would make the mathematical problem indeterminate. To mark the region where the model is not appropriate, the graph of figure 5.17 b) has a grey background in this region.

In summary, the electron density deduced from the electrical model is significantly, i.e. one order of magnitude, larger for argon (5 × 10^{17} m^{-3}) compared to helium (5 × 10^{16} m^{-3}) for similar dissipated powers. This results from the lower bulk resistance in argon compared to helium. As expected, the electron density increases with increasing dissipated power for both, the argon and helium discharge. However, the behavior of the electron density underlines that the used circuit model is not appropriate in helium at high dissipated powers due to the onset of the γ-like mode. Yet, the density alone is not sufficient to understand the behavior of a plasma. In addition, the energy distribution function or at least the electron temperature is required.
5.2.3 Electron temperature

In the previous chapter, the difference in electron density was explained by the difference in ionization energy of argon and helium resulting in a different electron temperature. To demonstrate these differences in the electron temperature of argon and helium plasmas, we can now profit from the precise measurements of dissipated power. Using a simplified zero-dimensional power balance for free electrons, a rough estimate of the average electron temperature in the bulk plasma can be performed [37]:

\[
\epsilon = n_e \frac{P}{k_B T_g} S_{CRM} I_1 + n_e \left[ n_+ \left( \langle \sigma^{m}_{ei} v_e \rangle + \frac{P}{k_B T_g} \langle \sigma^{m}_{ea} v_e \rangle \right) \right] \cdot \frac{2m_e}{M} \frac{3}{2} k_B (T_e - T_g),
\]

where \(\epsilon\) is the power density, \(n_e\) the electron density, \(n_+\) the ion density, the quotient \(p/(k_B T_g)\) is the atom density according to Dalton’s law, \(S_{CRM}\) is the ionization coefficient that can be calculated by collisional radiative models (CRM), \(I_1\) is the ionization energy, \(\langle \sigma^{m}_{ei} v_e \rangle\) and \(\langle \sigma^{m}_{ea} v_e \rangle\) are the electron-ion and electron-atom collision rate coefficients for momentum transfer averaged over the electron energy distribution function, \(m_e\) and \(M\) are the electron and atomic mass, \(T_e\) and \(T_g\) are the electron and gas temperature.

Equation 5.25 relates the input power density \(\epsilon\) that can be measured using the miniaturized probes to the power per unit of volume that is lost by inelastic and elastic electron collisions. The energy for heating the cold electrons gained from the ionization process and energy losses due to radiation were omitted. By estimating realistic numerical values for the parameters in equation 5.25, it is possible to calculate the electron temperature from the dissipated power.

For an estimate of the argon neutral gas temperature \(T_g\), the temperature in the effluent was measured using two different techniques (see figure 5.18). Laser schlieren deflectrometry (LSD) and a thermocouple for confirmation of the LSD method were used to measure the temperature in the effluent as a function of the distance to the gas exit. Laser schlieren deflectrometry is a non-invasive technique, whereas the thermocouple can disturb the gas flow and cause energy coupling to the probe. However, it is a standard technique to measure neutral gas temperatures and is therefore used as a cross-check. Thus, the neutral gas temperature in the plasma discharge can be extrapolated. Both methods indicate that the gas temperature in the effluent decreases
Figure 5.18: Temperature in the effluent of the argon discharge measured using a Thermocouple and laser schlieren deflectrometry.

exponentially with increasing distance to the gas exit. This is due to the missing heating of the gas and mixing with ambient air at room temperature. Interestingly, the two methods resulted in two graphs showing the same relative behavior, but with an offset in between. This is most likely due to the laser schlieren deflectrometry measuring the peak temperature, whereas the thermocouple measures integrated values due to the spatial dimensions of the probe tip. Therefore, the averaged value between the two measurements $T_g = 350$ K was used in the following calculation for equation 5.25.

For an estimate of the ionization rate coefficients in the power balance, analytical expressions from fits by Jonkers et al. [37] to results from collisional radiative models were used:

$$S_{CRM}^{Ar} = 7.34 \cdot 10^{-15} \sqrt{\frac{\hat{T}}{T_e}} \exp \left( -\frac{12.06}{\hat{T}} \right) [m^3 s^{-1}] \quad (5.26)$$

$$S_{CRM}^{He} = 3.15 \cdot 10^{-15} \sqrt{\frac{\hat{T}}{T_e}} \exp \left( -\frac{19.38}{\hat{T}} \right) [m^3 s^{-1}] . \quad (5.27)$$
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The electron-ion collision rate

\[ \langle \sigma_{ei} v_e \rangle = \frac{2.91 \cdot 10^{-12}}{\hat{T}_e^3} \ln \left( 1.55 \cdot 10^{13} \sqrt{\frac{\hat{T}_e^3}{n_e}} \right) \text{[m}^3\text{s}^{-1}] \], \quad (5.28) 

and the electron-atom collision rate

\[ \langle \sigma_{ea} v_e \rangle_{\text{Ar}} = (0.084 + 0.537 \hat{T}_e + 1.192 \hat{T}_e^2) \cdot 10^{-14} \text{[m}^3\text{s}^{-1}] \] \quad (5.29)  
\[ \langle \sigma_{ea} v_e \rangle_{\text{He}} = (2.21 + 2.59 \hat{T}_e - 0.344 \hat{T}_e^2) \cdot 10^{-14} \text{[m}^3\text{s}^{-1}] \] \quad (5.30)  

were obtained by Jonkers et al., as well, from fitting cross sections and integrating over a Maxwellian EEDF [37] with \( \hat{T}_e \) and \( n_e \) in eV and m\(^{-3}\). Using the electron densities at 0.3 W calculated in section 5.2.2, we can estimate the electron temperature in the argon and helium plasma by solving equation 5.25 to be 1.18 eV and 1.83 eV, respectively.

As anticipated, the electron temperature in helium is a factor of 1.6 higher than in argon. However, the absolute values are surprisingly low. This might be due to an overestimation of the ionization coefficient. Strictly speaking, equation 5.26 and 5.27 are only valid for electron densities above \( 1 \times 10^{19} \text{m}^{-3} \). Below that value, the ionization coefficients also decrease with decreasing electron density [149]. Additionally, the collisional radiative models used for the fit of equation 5.26 and 5.27 are not optimized for high neutral densities and an extremely low degree of ionization, i.e. they do not account for excited molecular dimer levels and molecular ions [150]. These calculated electron temperatures are only a general orientation, since also all of the collision frequencies were calculated assuming Maxwellian electron energy distribution functions. As will be shown in section 5.3.1, this does not apply to the argon discharge. However, the calculated electron temperatures do show reasonable trends and reflect the physical differences of the two operation gases.

To highlight the differences between the two operating gases, the contributions to the power balance will be separated. As illustrated in figure 5.19 a), the dominating summand in the argon power balance for power densities above \( 1 \times 10^7 \text{W m}^{-3} \) (marked by a horizontal dashed line) is the first term representing energy losses due to ionization. This is because the losses of free electrons due to diffusion and recombination have to be compensated by production of charged species. Consequently, the electron density
is proportional to the power density as observed above for the argon density and can be used to verify the electron density dependency calculated in section 5.2.2:

\[ n_e \approx \frac{\epsilon}{I_1} \frac{k_B T_g}{p S_{CRM}}. \]  

(5.31)

This agrees very well with the observed trend in figure 5.17.

In contrast, figure 5.19 b) shows that for helium, the term representing elastic electron-atom collisions dominates. Only at power densities above \(3 \times 10^8\) W m\(^{-3}\), the ionization term takes over (not shown here). This difference is due to the different cross sections and atomic masses of helium and argon. As described in section 2.2, argon has a lower ionization threshold. Therefore, the ionization term is lower in helium. Even if the elastic electron-atom collision rate is smaller for argon than for helium due to the Ramsauer minimum at low electron energies (compare section 2.2), the electron density in argon is one order of magnitude higher compared to helium, as demonstrated in the previous section, so that the elastic electron-atom collision losses are higher in argon than in helium for electron energies below 1.3 eV. This confirms the assumption by Lazzaroni and Chabert concerning the sheath stability of argon as presented in the
5.2 Plasma parameters

Consequently, the electron density for helium can be simplified to being proportional to the power density as done by many other authors [148, 151]:

\[
    n_e \approx \frac{M}{3m_e} \frac{k_BT_g}{p} \frac{\epsilon}{\langle \sigma_{\text{ea}} n_e \rangle k_B (T_e - T_g)}. 
\] (5.32)

However, the electron density calculated from the impedance measurement as illustrated in figure 5.17 b) does not show linear behavior. Instead, it begins to increase linearly at low powers and then shows a change in steepness. Even when assuming an increasing gas temperature with increasing power, as demonstrated for helium in section 4.3, the electron density should increase over-proportional. This confirms the assumption for the electrical model not being appropriate to describe the physical behavior of the helium discharge.

In summary, the electron temperature in the discharge was deduced using the electron density from the circuit model in combination with a simple energy balance. In argon (1.2 eV), the electron temperature is lower compared to helium (1.8 eV). This is due to the different dominating terms in the power balance. For argon, ionization is the dominating loss process, whereas for helium, elastic electron-atom collisions dominate the loss processes. This is due to the lower ionization energy and the higher electron density in argon compared to helium. This section also confirmed, that the circuit model used in the previous sections is only valid in helium at low dissipated powers.

5.2.4 Influence of molecular admixtures

As already mentioned at the beginning of this chapter, the argon discharge in the COST-Jet is very sensitive to impurities, even if an increasing sheath thickness has already been excluded as the reason (see section 5.2.1). To analyze the underlying processes, it is interesting to evaluate the electron density during admixture of molecular gases. To check the validity of the predictions by the electrical model for the argon discharge, two different molecular gases with exemplary properties were admixed to the feed gas.
Figure 5.20: Electron density in argon discharge calculated from the circuit model as a function of dissipated power a) with oxygen and b) nitrogen admixture (pressure 990 mbar, gas flow rate 400 sccm).

Figure 5.20 a) shows the electron density in the argon discharge with oxygen admixture. Oxygen is a weakly electronegative gas with a dissociative attachment threshold energy of about 4.7 eV and it has several low-lying easily excited metastable molecular states [52]. The electron density for pure argon (black squares) is of the order of $5 \times 10^{17}$ m$^{-3}$ and increases with increasing dissipated power. If oxygen is admixed to the feed gas, the electron density decreases. Due to the electronegativity of oxygen, it tends to form negative ions. Due to quasi-neutrality, the production of negative ions and thus additional negative charge carriers leads to a decrease in electron density. Consequently, the electron density is reduced when oxygen is added to the discharge. Also, the sheath thicknesses increases with increasing oxygen amount as predicted by Lazzaroni and Chabert [13], but is not shown here.

Remarkably, already very small amounts of oxygen strongly influence the discharge properties. This is in contrast to the model by Lazzaroni and Chabert, which predicts an almost constant electron density. The power density of $2 \times 10^7$ W m$^{-3}$ in the model corresponds to an absolute power value of 0.6 W in the experiment. In the model, the electron density decrease per admixed oxygen amount is about $8.9 \times 10^{14}$ m$^{-3}$%$^{-1}$. This decrease is notably less compared to the experiments with $1.1 \times 10^{19}$ m$^{-3}$%$^{-1}$.
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This is an indicator for a fundamentally important interaction mechanism between argon and oxygen that is observed in the experiment, but missing in the model. Species possibly playing a role in these processes are argon excimers, that were not considered in the model. They are strongly connected to the formation of argon excimer ions, which play an important role in atmospheric pressure discharges. This will be investigated in section 5.3.2.

Figure 5.20 b) shows the electron density in the argon discharge with nitrogen admixture. In contrast to oxygen, the admixture of nitrogen tends to increase the electron density. This is due to the molecule being an additional energy sink because of its numerous low-lying vibrational and rotational states. Consequently, the electron temperature is reduced and according to the power balance, this is compensated by an increasing electron density.

In summary, the electron density deduced from the circuit model behaves as expected when molecular gases are admixed: If oxygen is added to the discharge, the electron density decreases due to the electronegativity of the molecular gas. In contrast, if nitrogen is added to the discharge, the electron density increases. This is due to the additional vibrational and rotational energy levels of nitrogen that decrease the electron temperature. The electron density in argon shows reasonable behavior, so this is an indicator for the electrical model being applicable and thus argon being operated in α-mode only. In general, the highest possible admixture rate is significantly lower for the argon compared to the helium discharge. This might be due to the argon excimer species and will be further analyzed in section 5.3.2.

Section 5.2 dealt with the analysis of the electrical measurements using the homogeneous model. It has revealed a general insight into the plasma parameters of the argon and helium discharge. The analysis of the sheath width has confirmed the model of Lazzaroni and Chabert as the sheath thickness in argon is smaller than in helium. However, this difference is not the reason for the observed instabilities of the argon discharge, as it should stabilize the discharge. The analysis of the bulk resistance has shown that, as expected, the electron density in argon is an order of magnitude higher than in helium. However, it also revealed that the electrical model for helium is only valid at low power. The analysis of the power balance demonstrated, that the low ionization energy of argon supports a low electron temperature whereas in helium, the
elastic processes dominate the influence on the electron density. The electrical model correctly reflects the expected dependence of the electron density on molecular gas admixtures. In addition, this study also shows that only very small admixtures are possible, which was not anticipated by models.

In conclusion, the plasma parameters deduced from the circuit model provide a coherent picture of the differences between the argon and the helium discharge. Additionally, the observations agree with expectations in the context of previous results from literature.

To understand the underlying microscopic processes in the discharge, the species in the plasma discharge and their properties and behavior have to be investigated.

5.3 Species composition

Since global measurements are usually difficult to interpret, it is important to link them with further diagnostics. In order to trace the observed macroscopic phenomena back to microscopic processes, it is necessary to determine the relevant players. For this distinction, a diagnostic technique that enables energy resolution is required. Therefore, in this section the species and excited states occurring in the discharge are examined more closely using optical emission spectroscopy and tunable diode laser absorption spectroscopy.

5.3.1 Excited atomic species

Optical emission spectroscopy can help to identify species taking part in the physical processes of a plasma discharge. As already demonstrated in chapter 4, it is a non-invasive diagnostic technique to estimate the stability and reproducibility of the discharge operation as well as the influence of impurities. In this section, optical emission spectroscopy in the visible and ultra-violet range was used to determine relevant species involved in the processes in the argon discharge. To study the response of the plasma processes on different plasma parameters, the plasma emission was measured using a broad band spectrometer (Ocean Optics HR 4000) and fiber optics as described
5.3 Species composition

Figure 5.21: Typical survey spectrum in the visible wavelength range of an argon discharge in the COST-Jet (pressure 990 mbar, gas flow rate 300 sccm, power 0.8 W). Atomic argon lines from the 2p level (696 nm to 965 nm) are most prominent.

in section 3.3.2. If not stated otherwise, all results were obtained with a gas flow rate of 300 sccm argon and a pressure of 990 mbar.

Figure 5.21 shows a typical survey spectrum of an argon discharge in the COST-Jet measured at 0.8 W, 300 sccm argon at a pressure of 990 mbar. The intensity was relatively calibrated using a stable tungsten halogen source (Ocean Optics LS-1-CAL), therefore the wavelength range below 380 nm (grey area) is not covered by the calibration data.

Notably, there is no molecular nitrogen emission of the second positive band (336 nm, 357 nm). This means that conducting the experiments in the discharge chamber reduced most impurities from leakages and made a backflow unlikely. However, the hydroxide emission (308 nm) can be attributed to water (H$_2$O) impurities that are dissociated in the discharge. Even if the cold trap reduces humidity from the gas supply, there are always some water residues left on the chamber walls and in the discharge channel that desorb during operation. Correspondingly, there are two atomic oxygen emission lines (777 nm, 844 nm) visible in the spectrum.
Atomic emission lines from several of the 2p levels of singly excited argon atoms (696 nm to 965 nm) are most prominent in the VIS spectrum. These are usually the most intense lines in the argon emission spectra from plasma discharges.

However, at atmospheric pressure, it is challenging to deduce plasma parameters from individual atomic emission lines. Common techniques such as line broadening measurements fail since the usually dominant collisional broadening (mostly resonance broadening) covers any mechanisms caused by plasma parameters other than the neutral gas density or the gas temperature as demonstrated by Pipa et al. [125]. Therefore, only the analysis of intensities and their relative behavior can give information on plasma processes. To gain information on the electron energy distribution function, it is necessary to compare emission lines originating from different upper levels that exhibit different excitation energies. However, the intensity of emission lines at atmospheric pressure can be notably reduced due to quenching processes. Additionally, in case of the argon discharge in the COST-Jet, ion emission lines or higher excited state emission lines are not detectable. Thus, there is no possibility to extract information on the EEDF from these lines.

Another possibility to gain information on plasma parameters is to rely on plasma emission models such as corona or other collisional radiative models [152–155]. The success of the predictive power of these models strongly depends on accurate electron-atom cross section data. Due to collisional broadening, atmospheric-pressure plasmas are usually optically thin for photons except for non-resonant lines [152, 156]. Therefore, self-absorption was not taken into account, even if the ground state density of argon atoms is comparably high. Consequently, the population density of different levels can be calculated by the ratio of emission line intensities.

\[
\frac{I_1}{I_2} = \frac{A_1 n_1}{A_2 n_2},
\]

where \( I \) is the intensity, \( A \) the Einstein emission coefficient and \( n \) the density of the respective energy level.

Figure 5.22 shows the population density of the 2p excited states of argon for different dissipated power values in the common form of a column diagram. Apparently, the argon 2p_2, 2p_6 and 2p_{10} levels are higher populated than the nearby levels. These
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Figure 5.22: Population distribution of excited argon 2p levels (pressure 990 mbar, gas flow rate 1000 sccm).

levels have small rate coefficients for atom-collision transfer and consequently have a smaller depopulation rate. This is an indicator for the electron density being lower than $1 \times 10^{18} \text{ m}^{-3}$, as in this regime, the excitation from the ground state and atom-collision transfer dominate the rate balance of excited atoms [152]. If the electron density was higher, excitation from the 1s state would be more important, which would result in a strong under-representation of levels $2p_1$ and $2p_5$, which is not the case here. This result fits well to the electron density estimated in section 5.2. However, the attempt to quantitatively compare the experimentally obtained results to collisional radiative models showed that there is no good agreement between the population density results of the experiment and the various models [152, 154, 155]. This is a strong indicator for the temporally averaged electron energy distribution function being far from Maxwellian.

In summary, the deduction of plasma parameters from optical emission spectroscopy at atmospheric pressure is challenging. This is due to the emissions line profile being affected by resonance broadening and the intensity by quenching processes. However, the population density was deduced from relative intensity measurements omitting quenching processes. These measurements confirm the electron density in the argon
discharge lower than $1 \times 10^{18} \text{ m}^{-3}$, which agrees well with the electron densities calculated in section 5.2.2. Additionally, the electron energy distribution function is far from Maxwellian. Apart from that, deducting more information from the use of models is difficult due to the non-equilibrium properties of the discharge. However, excited argon species and a small number of impurities in the COST-Jet discharge could be identified.

### 5.3.2 Excited molecular species

Photons in the UV energy range can play a dominant role in plasma processes since they possess a rather high energy and thus can contribute to many energy transfer processes. For example, VUV photons with energies of the order of 10 eV are capable of breaking chemical bonds of many compounds such as oxygen, hydrogen, water or carbon dioxide. Additionally, the emission of the argon excimer molecules, a potentially interesting specie for argon-impurity interactions, lies in this spectral region. To access the emission below 200 nm, the VUV spectrometer described in section 3.3.4 was used. Due to the setup, the measurements could only be realized in ambient air atmosphere.

Figure 5.23 shows the VUV spectrum of the argon discharge at a dissipated power of 615 mW and a gas flow rate of 600 sccm at atmospheric pressure. Notably, the intensity was not calibrated since this is a complex procedure for the UV wavelength region. The spectrum is dominated by argon excimer continua. The first continuum starts close to the argon resonance line at 104.82 nm marked by a blue dashed vertical line. It corresponds to the transitions from higher vibrational levels of the first excited states $^{1,3}\Sigma^+_u$ of the argon excimer to the ground repulsive state $^1\Sigma^+_g$. Figure 5.24 illustrates the origin of the emission structures of the argon excimer observable in the UV range. The ground state is not stable as the potential curve is repellent. The excited states may form a bound state with a potential minimum. The transitions between the states are always vertical due to the Franck-Condon principle. A more detailed energy diagram can be found in [158].

The second continuum in figure 5.23 corresponds to the transition from the same states, but from lower vibrational levels exhibiting shorter internuclear distances [159–161]. The so-called 'classical Left-Turning Point' (LTP), where the transition probability is
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**Figure 5.23:** The argon excimer continua (1., 2., 3.) are most prominent in the VUV spectrum measured at 615 mW, 600 sccm argon at atmospheric pressure in ambient air atmosphere.

density high, completes this emission sequence. A weak maximum can be suspected at 155 nm [162]. The so-called third excimer continuum, which is not unambiguously assigned yet in literature but might be due to the decay of Ar$_2^+$ [159, 163], can be suspected in the range around 200 nm.

In addition to the continua, there are also several atomic emission lines visible in the spectrum that are marked by vertical dashed lines. All spectroscopic emission line data were retrieved from the NIST database [164]. The lines at 116.7 nm, 117.66 nm, 124.3 nm, 141.2 nm, 149.3 nm and 174.3 nm can be attributed to atomic nitrogen (N I). Around 130.2 nm, three oxygen emissions lines are located that add to the second continuum emission.

Due to the strong excimer radiation, it is also possible that ground state atoms are excited by these photons and thus create absorption lines in the continuum. The following atomic transitions manifest by absorption lines in the second continuum. The absorption lines at 113.5 nm and 119.96 nm correspond to transitions in atomic
Figure 5.24: Simplified energy diagram of the argon excimer schematically illustrating the origin of the emission structures in the UV range (after Gellert and Kogelschatz [157]).

nitrogen (N I). The dip at 121.6 nm corresponds to the Lyman-α-line of atomic hydrogen (H I). These atomic absorption and emission lines result from impurities in the plasma discharge due to the operation at ambient air. Thus, ambient air species such as nitrogen or water (hydrogen, oxygen) can be excited on the way from the discharge channel exit to the slit entrance of the spectrometer. Additionally, impurities from the gas supply lines can contribute to these emission lines.

Remarkably, there is no emission detected below 106 nm. This might be due to the low-lying excited states of the argon atoms. The first resonant state is the 1s$_4$ state at 11.62 eV, which corresponds to a wavelength of 106.67 nm during transition to the ground state. The photoionization threshold is at 78.67 nm, which corresponds to 15.75 eV. The argon resonance lines below 106.67 nm are absorbed due to the high neutral argon density in the ground state.
5.3 Species composition

Figure 5.25: The argon excimer continua are quenched when nitrogen is admixed at 600 mW, 600 sccm argon at atmospheric pressure in ambient air atmosphere.

In summary, VUV emission spectroscopy revealed strong radiation of argon excimers. This supports the hypothesis of these species being important for the discharge processes in argon. As the measurements were conducted in ambient atmosphere, also atomic emission lines from impurities were detected. The high argon ground state density absorbs emission lines below 106 nm.

5.3.3 Molecular admixture

Figure 5.25 shows the VUV spectrum of the argon discharge at several admixtures of nitrogen. Both argon excimer continua strongly decrease with increasing nitrogen amount. In contrast, the atomic nitrogen emission lines increase with increasing amount of nitrogen until the discharge is extinguished. This behavior manifests in the whole observed spectral range. Also, the intensity of atomic argon lines in the visible decreases while the nitrogen rotational band intensity of the second positive system in the range of 300 nm to 400 nm increases (not shown here). The decrease of the
argon excimer emission is probably due to a decrease in its number density. This is an indicator for the reactants important for the generation of argon excimers, namely argon metastables and argon excimer ions (compare section 2.1.2), being reduced, too. As these species are important for the sustainment of the discharge, e.g. via stepwise ionization processes, the discharge becomes less stable.

This decrease of argon metastables and excimer ions is due to increased energy transfer processes from excited argon species to nitrogen molecules and atoms [165]: In contrast to helium, argon has a deep Ramsauer minimum in the elastic scattering cross section around 0.26 eV (compare figure 2.5). At this energy, the scattering cross section dips below $5 \times 10^{-21}$ m$^{-2}$ [166, 167] and the lowest inelastic electron scattering channels require an electron energy of above 11 eV. At the electron energy of the Ramsauer minimum of argon, nitrogen has an elastic scattering cross section which is approximately two orders of magnitude higher than in argon. It even shows a distinct peak in the inelastic electron scattering cross section with maximum values of about $1 \times 10^{-19}$ m$^{-2}$ between 1 eV to 5 eV. At approximately 2.5 eV, the cross section is even higher mostly due to vibrational excitation of the nitrogen molecule [166]. Therefore, the admixture of small amounts of nitrogen into an argon plasma affects the discharge via suppression of the high-energy tail of the EEDF and thus decreasing the electron temperature.

In addition, the nitrogen atom as well as the nitrogen molecule possess energy levels around 11 eV which is very close to the 1s states of the argon atom. This enables crosstalk between these states and allows for an efficient excitation of nitrogen by quenching processes [168, 169]. All of the observed atomic emission lines originate from transitions from these levels. Additionally, the band structure at 337 nm in the visible range increases (not shown here). An informative illustration of these levels can be found in a publication by Masoud et al. [165]. Roughly speaking, the energy necessary for excitation and ionization of the argon atoms is used for vibrational excitation of nitrogen molecules. Consequently, the ionization rate of argon is decreased, even if the electron density increases (see section 5.2.2).

Helium does not exhibit a Ramsauer minimum. As already estimated in section 5.2.3, the electron temperature is higher than in argon from the outset, so that more fast electrons are produced. Additionally, there is no cross-talk between excited levels of
5.3 Species composition

Figure 5.26: The argon excimer continua are quenched when oxygen is admixed at 650 mW at atmospheric pressure in ambient air atmosphere.

nitrogen and helium as the first excited level of helium is at 19.8 eV. Therefore, the electron temperature and density will be decreased as well by adding nitrogen, but the impact on the discharge stability is smaller.

Figure 5.26 shows how the admixture of oxygen influences the emission spectrum of the argon discharge at a power of 650 mW. For the VUV measurements, a different gas supply setup had to be used. In this setup, the oxygen gas flow rate could not be reduced below 1 sccm. However, this is close to the upper limit of stable admixture rates, especially for low argon gas flow rates. Therefore, instead of decreasing the oxygen gas flow rate, the argon gas flow rate was increased from 500 sccm to 800 sccm in order to vary the admixture percentage.

Similar to nitrogen, the argon excimer continua are quenched and the atomic emission lines increase with increasing oxygen admixture. Additionally, the admixture of oxygen induces the appearance of broad emission structures around 150 nm and 190 nm. These could be due to the Schuman-Runge emission bands from excited molecular
oxygen around 200 nm [170]. However, there is no visible band structure nor any other emission bands of molecular oxygen in the visible range (not shown here).

Another possible origin of this emission structure is the generation of an argon-oxygen exciplex (ArO). Emission continua of ArO were observed at 150 nm, 185 nm and 205 nm [171]. The formation is assumed to be a two step process. First, O$_2$ is dissociated by excited argon atoms. In a second step, these oxygen atoms react with Ar$^*_2$ or Ar$^*_2$ to form ArO. The assumption of ArO formation is reinforced by an emission structure at 557.7 nm in the visible range (not shown here), which is also assigned to ArO [172–175]. Additionally, these structures were not observed in the helium discharge with oxygen admixture [84]. Schematic potential curves of the ArO molecule can be found in the literature [176].

However, the amount of oxygen that can be admixed to the discharge before the plasma is extinguished is even less than for nitrogen admixture. This behavior is due to the influence on the electron energy distribution function (EEDF) because of two effects: (i) With 5.16 eV, the energy required for electron-impact neutral dissociation of O$_2$ is considerably less than for the dissociation of N$_2$ 9.79 eV [101] and (ii) the number of electrons in the plasma discharge is reduced due to the electronegative character of O$_2$. It efficiently forms negative ions via dissociative attachment e$^-$ + O$_2$ → O + O$^-$ and thus is an electron scavenger.

**In summary**, the measurements presented above showed, that even small amounts of molecular admixtures strongly affect the argon excimer production. The argon discharge is much more sensitive to impurities compared to the helium discharge for two reasons: Microscopic differences in the cross sections of the gases favor the vibrational excitation of impurities instead of the noble gas. This is mostly due to the Ramsauer minimum in the elastic cross section of argon and its absence in helium. Additionally, the energy levels of impurities overlap with those of argon. Therefore, resonant energy transfer is much more pronounced in argon compared to helium.
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5.3.4 Role of metastables

As already mentioned in the previous section, argon metastables play an important role in the argon discharge as they enhance ionization rates by stepwise excitation. The excitation from metastable levels has been recognized to be important for maintaining the ionization balance of low temperature plasmas \([177, 178]\). This is due to stepwise ionization processes via metastable states which provide a substantial source of electrons, since the threshold is much lower than that of direct ionization. This process is even more important with an increase in pressure \([179]\). Additionally, they might be one of the reasons for the discharge extinction depending on the gas flow rate (compare section 5.1.2).

To verify the hypothesis for long-living species being responsible for the extinction behavior of the argon discharge, tunable diode laser absorption spectroscopy (TDLAS) as described in Section 3.3.6 was used to measure the number density through the absorption of the metastable argon \(1s_5\) state. This is the lower of the two argon metastable levels. In the following, it is denoted as \(Ar_m\). As already described in chapter 2, the potential energy of the \(1s_5\) level is around 11.5 eV. Due to the setup, these experiments were conducted in ambient atmosphere.

Figure 5.27 (reproduced from Spiekermeier \([124]\)) shows a two-dimensional map of the \(Ar_m\) number density in the argon discharge. With \(1.1 \times 10^{12}\ \text{cm}^{-3}\), the metastable density in the sheaths is around one order of magnitude higher than in the bulk with \(9.1 \times 10^{10}\ \text{cm}^{-3}\). The image shows that the density in the sheath is not exactly the same on both sides. The density close to the grounded electrode is slightly lower than the density in front of the powered electrode. However, this difference is only about 10% and can be due to electrode shielding which slightly increases the area of the grounded electrode.

Towards the gas exit, the metastable density expectably decreases due to increased quenching by nitrogen species from the ambient atmosphere. Interestingly, the argon metastable density also increases from the gas inlet (at \(x = -30\ \text{mm}\)) towards the middle of the discharge.

This build-up is illustrated in figure 5.28. In this graph, line profiles of the argon metastable density in the sheath area are plotted for different gas flow rates. The
line profiles were obtained by binning over the sheath area in the region of interest highlighted by a black dashed square in Figure 5.27. As already described in detail by Spiekermeier [124], the method used to measure the metastable density was not ideal for low gas flow rates. Therefore, the curves for lower gas flow rates terminate closer to the gas inlet. Interestingly, the build-up of argon metastables varies with gas flow rate. Except for the line profile at a gas flow rate of 250 sccm, the rise of the metastable density decelerates with increasing gas flow rate. For 300 sccm, the argon metastable density reaches a steady state at position $x = -25$ mm. For 350 sccm, the density is reached at $x = -20$ mm and for 400 sccm, this steady state is reached at $x = -15$ mm. Only the density profile at 250 sccm does not fit into this trend. This is probably due to the low gas flow rate that may allow the back flow of nitrogen into the discharge channel.

If the excitation of metastables is assumed to be mainly due to electron impact excitation, this build-up is surprising as the reaction constant for electron impact collisions is quite large. However, this is an indicator for the important role of other competing processes that populate and depopulate this energy level, thus leading to an effective slow build-up of argon metastables. These processes can include population by dissociative

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**Figure 5.27**: Two-dimensional map of the metastable number density at a gas flow rate of 400 sccm and 0.46 W in ambient atmosphere [124].
5.3 Species composition

Figure 5.28: Line profiles of the argon metastable density in the sheath area for different gas flow rates at 0.46 W in ambient atmosphere.

recombination of excimer ions (equation 2.18), electron impact transfer to other 1s levels or radiative decay of the excited 2p states of atomic argon as detected using optical emission spectroscopy (figure 5.21). This is also in line with Spiekermeier’s observations on the increased lifetime of the metastable state. Thus, the argon metastable build-up might explain the dependence of the extinction voltage on the gas flow rate.

Compared to the helium discharge, the overall metastable density in argon is almost one order of magnitude higher than in helium where the metastable density in the sheath is $6.3 \times 10^{16} \text{ m}^{-3}$ and the bulk density is $1.0 \times 10^{16} \text{ m}^{-3}$ [28]. In helium, no substantial increase of the sheath metastable density within the first millimetres of the discharge channel was identified. Instead, the maximum metastable density was reached directly 1 mm behind the gas inlet. This might be due to the much longer lifetime of helium metastables of the order of 5.8 $\mu$s [20]. This rather long lifetime establishes since quenching reactions in helium are less frequent than in argon.

Although a direct proof is not possible with the available spatial resolution and gas flow range, a strong evidence of this hypothesis could be confirmed.
In summary, TDLAS measurements demonstrate that the argon metastable density in argon is approximately one order of magnitude higher than in helium. Additionally, an increase of the density at the beginning of the discharge channel was observed. This increase depends on the gas flow rate. This argon metastable build-up supports the hypothesis in section 5.1 of metastables being responsible for the discharge sustainment.

In section 5.3, the optical methods revealed the importance of molecular argon ions, excimers and metastable states. After using optical emission spectroscopy in the visible range to calculate the population densities of the excited 2p levels of argon, a strongly non-Maxwellian electron distribution function was confirmed. The measurements in the UV range demonstrated the sensitive response of the argon excimer radiation on small amounts of admixed molecular gases and the consequences for the stability of the discharge. Using TDLAS, the hypothesis of long-living species carrying potential energy that accumulate within the discharge is supported by the measurement of the metastable density in the sheaths.

In conclusion, molecular argon ions, excimers and metastable states apparently play a key role in the homogeneous atmospheric pressure argon discharge.

5.4 Electron kinetics

After the energy levels of the species of the discharge have been considered, the RF cycle itself is resolved in time in this section. Phase-resolved optical emission measurements can give insight into the discharge kinetics. From these measurements, the space and time resolved electron excitation processes within one RF period can be assessed. Since the spectral sensitivity of the used CCD chip is in the visible range, the following lines were selected for observation based on the measurements in chapter 5.3.

As already shown in section 5.3, most of the argon lines in the visible spectral range emitted by the plasma discharge originate from 2p → 1s transitions. This is due to the rather large (1 × 10^{-17} cm^2 to 1 × 10^{-18} cm^2 [180–182]) excitation cross sections of the 2p levels. Conveniently, these levels are well suited for phase-resolved optical emission spectroscopy, since they meet the PROES requirement (see section 3.3.3) of having short lifetimes of 22 ns to 39 ns and they are usually dominated by electron
5.4 Electron kinetics

impact excitation and radiative decay. However, attention has to be paid to cascade contributions from higher energy levels [182].

The argon emission line at 750.39 nm was chosen since it is known from literature (e.g. [183]) that the upper level of this transition (2p₁ → 1s₂) is mainly populated by electron impact excitation from the ground state. Thus, the electron density can be mapped. Unfortunately, there is another emission line at 751.47 nm that is also detected through the interference filter. However, the upper level of this transition (2p₅ → 1s₄) is also supposed to be dominantly populated by ground state excitation [184, 185]. So both emission lines reflect the electron density. This is underlined by the fact that for all measurements discussed below, the emission intensity at 751.47 nm was in the range of 50% to 60% of the emission intensity at 750.39 nm.

In addition to the electron energy and density, the metastables play an important role in the excitation processes of the argon discharge, as demonstrated in the previous chapter. To investigate the role of metastable atoms in kinetic excitation processes, the emissions from a level that is dominated by excitation from metastable levels can be monitored. The argon emission line at 811.53 nm arises from the transition 2p₉ → 1s₅. The upper level has a large cross section for excitation from atoms in the 1s₅ metastable level and thus is most likely to be populated by excitation from the 1s₅ metastable level. Notably, this is the only radiative decay channel for this level. Again, there is another emission line at 810.37 nm originating from the 2p₇ → 1s₄ transition. However, for all measurements discussed below, the emission intensity at 810.37 nm was only about 37% of the emission intensity at 811.53 nm.

As already mentioned in section 5.3.1, the argon emission lines in the visible range do not provide any information of low energetic electrons, since the lowest excitation level of argon is 11 eV. In this situation, the otherwise rather undesirable impurities in the discharge offer a good solution. Due to the small energy distances of the rotational states of molecular gases, they also offer a possibility to probe the low-energy electrons.

The atomic oxygen emission lines around 777.4 nm originate from three transitions (3p)⁵P₁,₂,₃ → (3s)⁵S₂. Atomic oxygen is produced by dissociation of molecular oxygen and water impurities. This is possible by electron impact reactions, but also by collisions with excited argon atoms or radiation, e.g. from the first or second excimer continuum.
Oxygen atoms are excited by electrons via dissociative excitation as well as direct excitation from the atom. The upper energy level of these transitions is at 10.7 eV.

The molecular nitrogen band system at 337.1 nm originates from the 'second positive system' $C^3\Pi_u(v'=0) \rightarrow B^3\Pi_g(v''=0)$. It represents all possible molecular excited states. The short radiative lifetime of 30 ns to 40 ns [186] makes it a good candidate for PROES, the actual lifetime might be even shorter due to collisional quenching. The excitation energy of the lowest vibrational level of the $N_2^*(C^3\Pi_u)$ state is 10.9 eV. As already mentioned in the previous section, this band system can efficiently couple to the argon metastable states via the following reaction scheme [169]:

$$\text{Ar}_m + N_2 \rightarrow N_2^* + \text{Ar} . \quad (5.34)$$

The total rate coefficient of this reaction is $3 \times 10^{-11}$ cm$^3$ s$^{-1}$ [187–190] and about half of this value corresponds to excitation of the $N_2^*(C^3\Pi_u)$ state [191].

The molecular nitrogen ion band structure at 391.4 nm originates from the 'first negative system' $B^2\Sigma_u^+(v'=0) \rightarrow X^2\Sigma_g^+(v''=0)$. The upper state can be populated by direct electron impact collisions with an electron energy of 19 eV. Another pathway is charge transfer $\text{Ar}^+ + N_2 \rightarrow \text{Ar} + N_2^+$ [192, 193] to the ground state and subsequent electron impact excitation to the $N_2^+ (X^2\Sigma_g^+)$ state by low energy electrons with a kinetic energy of 3 eV.

### 5.4.1 Emission patterns

Figure 5.29 shows one-dimensional phase-plots of the emission dynamics within one RF-period between the electrodes. These plots were generated at the central lateral position ($x = -15$ mm) of the discharge channel. All plots are normalized to their respective intensity maximum using linear scaling to highlight their pattern rather than their relative intensity. Except for the measurement of the wavelength-integrated emission (integration time 1 s), MCP gain (600 V) and integration time (2 s) are identical, but the spectral response of the CCD chip and transmission of the filters differ for each measurement. The abscissa comprises two RF half-periods (37 ns each). To guide
Figure 5.29: Phase-resolved emission plots of the respective transition lines at central position in the discharge channel (power 290 mW, pressure 990 mbar, gas flow rate 400 sccm). a)-f) correspond to different observed wavelengths as denoted in the different graphs.
the eye, the estimated boundaries between the plasma sheath and bulk region are indicated by black lines.

Figure 5.29 a) shows a spatio-temporal plot of the spectrally integrated emission. It exhibits two emission structures separated by half of the RF period (37 ns). The emission is at maximum in the bulk plasma during the maximum current density in the bulk. Notably, the two structures in front of the powered electrode are nearly identical to the structures in front of the grounded electrode, which are phase shifted by 180° (36.9 ns). This reflects the good geometrical symmetry of the COST-Jet. The integrated emission is composed of different spectral contributions that are analyzed hereafter.

Figure 5.29 b) represents the spatio-temporal variation of the argon excitation dynamics of the emission at 750 nm. This emission line is expected to reflect the ionization dynamics in the argon discharge. Due to the rapid energy relaxation of energetic electrons at atmospheric pressure ($\tau_e = 1$ ps to $10$ ps $\ll \tau_{rf} = 74$ ns [194]) and the collisional quenching of radiative states, the emission profile is strongly time modulated. The measurements reveal two intensity maxima within one RF half-period (labeled with I and II, respectively). As the electron impact excitation of the 2p$_1$ state requires an electron energy of 13.5 eV, this is an indicator for a high electron energy at the position close the sheath edge. Both maxima and their relative intensity ratios are very similar to the structures observed in the helium discharge [79]. In low pressure plasmas, where similar structures can be found as well, the first maximum is attributed to energetic electrons during sheath expansion. The second maximum is induced by a momentary reversal of the local electric field during sheath collapse [195].

However, at atmospheric pressure, no field reversal could be observed in numerical simulations [27, 66]. According to Hemke et al., ionization during sheath expansion is caused by a high bulk electric field that has local extrema at the sheath edges. This electric field is predominantly a drift field due to the low conductivity of the bulk discharge [27]. According to Liu et al., the processes in atmospheric pressure discharges differ from the aforementioned mechanisms: in contrast to low pressure helium plasmas, the emission structures indicate that the electrons are not only heated during the sheath expansion [52], but may also be considerably heated during the sheath retreat. The additional heating is caused by a field-enhanced region in front of the retreating sheath. Due to collisions preventing electrons from diffusing quickly.
enough, a small number of electrons cannot follow the sheath retraction, accumulates and creates a region of negative space charge. Thus, a self-consistent electric field forms that accelerates the electrons towards the electrode. Thus, heating occurs during the process. In contrast to the low pressure case, there is no local field reversal but an enhanced electric field without changes in polarity.

Hemke et al. named this effect of Ohmic bulk heating of electrons the $\Omega$-mode. However, this term has not been adopted, as most other authors still continue to refer to this mode as $\alpha$-mode. Since in our measurements, the current signal precedes the voltage signal by approximately 90° (compare figure 5.2), the emission maxima (I + II) are also related to the maxima of the current magnitude. Thus, the emission pattern most likely resembles the behavior of the helium discharge.

In figure 5.29 c), the behavior of the 811 nm emission is illustrated. In this image, two emission structures similar to the 750 nm emission are shown. In contrast to the sharp structures in figure 5.29 b), the structures here are blurred in time, but also within the bulk region. Also, the intensity ratio of first and second maximum is less pronounced. This observation can be attributed to the fact that the upper level of this transition (2p$_9$) is also populated by stepwise excitation processes via metastable states. Since metastables have a long lifetime and electrons with lower excitation energies are needed, these broad and hardly modulated structures arise. This measurement agrees well with the measurements already described in section 5.3.4, revealing an increased metastable density at the sheath edges. The emission structures by excited argon atoms closely resemble measurements and simulations by Dünnbier et al., who conducted optical emission spectroscopy at a similar discharge geometry, but at a higher excitation frequency of 27 MHz [46]. Since they used a wider electrode gap and a higher frequency, they observe more concise emission structures due to the smaller oscillation amplitude of the charged species.

Figure 5.29 d) shows the emission structures of the 777 nm line representing atomic oxygen. Compared with the emission at 811 nm, the general emission pattern is similar, but even more blurred and weakly modulated in time. This is an indication for long-living metastables playing a role in the excitation processes. The emission pattern suggests a dissociation of the oxygen molecule via collisions with metastable atoms and a subsequent excitation by fast electrons with an energy of at least 10.7 eV.
Figure 5.29 e) shows the emission pattern of excited nitrogen, which is different to the pattern of atomic oxygen. Even if the excitation energy of nitrogen is similar to the excitation energy of oxygen (10.9 eV), the emission peaks in the center of the bulk discharge during sheath expansion. This is an indicator for the nitrogen molecule being excited by several subsequent electron impact collisions with low energy electrons (several eV). As the number of electrons is higher in the bulk plasma than in the sheaths, this excitation mechanism becomes more likely in the bulk region.

The spatio-temporal emission plot of the excited nitrogen ion molecule transition at 391 nm is displayed in figure 5.29 f). Two emission structures are visible. Comparing with figure 5.29 a), it is obvious that the integrated emission is mostly dominated by nitrogen emission. However, this does not provide any information on the relative fractions of the integrated emission, since the camera and the optical system have not been calibrated. The location of the emission structures in the bulk region is an indication for the excitation not being predominantly caused by electron impact excitation with fast electrons but by a charge transfer process from argon ions and a subsequent electron collision with slow electrons (3 eV).

**In summary**, the emission structures observed in the argon discharge roughly resemble the structures observed in the helium discharge. The 2p states of argon having a rather high excitation energy are mostly excited in the vicinity of the sheath indicating a high electron energy in these regions. Molecular species such as nitrogen having a lower excitation energy are mostly excited in the bulk plasma suggesting a low electron energy.

### 5.4.2 Heating mechanisms

The global measurements presented in section 5.1.1 using electrical measurements revealed differences in the characteristics of dissipated power in the discharge leading to a changing phase difference between current and voltage. This behavior suggests that the temporal and spatial profile of the electron heating and ionization rates is affected. To identify different electron heating mechanisms, the dissipated power in the discharge was varied.
5.4 Electron kinetics

Since the trigger point of the PROES camera usually slightly depends on the amplitude of the applied discharge voltage, two independent but phase-synchronized generators were used: The first generator supplied the RF signal for discharge operation and its amplitude was varied and the second generator supplied a constant trigger signal for the camera.

Figure 5.30 shows phase-resolved emission structures at 750 nm and 810 nm at a typical low (upper row) and high power (lower row) of 260 mW and 540 mW, respectively. The pressure was set to 990 mbar. As expected, the absolute intensity rises with increasing applied voltage (not shown here). However, to emphasize the structure, these images are normalized to their respective maximum. Comparing a) to c) and b) to d), the images reveal that the principal excitation scheme is the same for both wavelengths except for the change in time indicated by vertical dashed lines. For higher operation voltages, emission maximum I appears approximately 6.5 ns earlier in phase than for low voltages. This time shift is less pronounced for emission maximum II. Additionally, for 750 nm, a third emission maximum (marked with III) begins to develop which is approximately as bright as the second maximum (II). The third maximum can be attributed in time to the maximum of the discharge voltage, where the electric field and the sheath amplitude is largest in the cathode region. This is an indication for secondary processes in the sheath region being responsible for the excitation of this maximum (III). Again, this is in agreement with the observations by Dünnbier et al. [46]. However, emission maximum II is rather faint in their measurements. This might be due to a wider electrode gap or the higher frequency used in their experiments.

Contrary to argon, for high voltage and dissipated power, emission maximum III is
more prominent in helium discharges. Comparing the emission patterns of argon and helium, at 540 mW emission maximum III is already more prominent than emission maximum I. For helium, the dissipated power could be even increased to 1000 mW (see figure 5.31 c)), where the argon discharge is not stable any more. Here, this effect is unambiguously observable: Emission structure III is clearly dominating the emission pattern, emission maxima I and II are only faintly visible. This is an indication for a complete mode change, in which secondary electron processes are the main constituent for heating. This behavior also supports the measurements presented in chapter 5.1: For argon, the dissipated power rises linearly with increasing voltage. However for helium, an additional exponential behavior that might be explained by these secondary electron processes was observed.
In helium, these secondary electron processes are more prominent than in argon. In first approximation, for low energies, the secondary electron emission yield is independent of the velocity of the bombarding particles, since the electron emission occurs due to transfer of the incoming ion or atom’s potential energy to an electron in the target \([63, 64, 196]\). Considering that the ionization energies of \(\text{Ar}^+\) and \(\text{He}^+\) are 15.76 eV and 24.59 eV, respectively (see section 2.2), i.e. they differ by about 56\%, we might expect that the potential secondary electron yield to be considerably different. In accordance with this, Hagstrum [63] measured the secondary electron emission yield of helium and argon bombarding clean tungsten. With a bombarding ion kinetic energy of around 10 eV, the secondary electron emission yield of helium is more than two times higher than that of argon. The same effect is triggered by fast neutrals that are created by collisional charge transfer. Therefore, secondary electron emission by impinging particles plays a major role in the helium discharge but not in argon.
However, secondary electron processes responsible for emission maximum III are not only due to electron avalanches initiated by secondary electrons produced by impinging ions, but also by photoionization and electrons generated in pooling reactions near the electrode surface among excimers and atoms in the metastable state ($\text{Ar}^* + \text{Ar}^* \rightarrow \text{Ar}^+ + e^-$, $\text{Ar}_2^* + \text{Ar}_2^* \rightarrow 2\text{Ar}^+ + 2\text{Ar} + e^-$). These excimer states are described in the VUV spectra in chapter 5.3. These reactions are a source of non-thermal electrons, especially if the electrons are created inside the sheath and accelerated by the high electric field. Since the potential energies of excited helium levels and thus the kinetic energy of the released electrons and photons is higher than in argon, re-excitation reactions and thus heating of the discharge is supported.

These differences in heating mechanisms qualitatively agree with observations from the global electrical measurements described in section 5.1.1, as they explain the inverse phase dependence on the discharge voltage as demonstrated in figures 5.2 and 5.3: Whereas the absolute value of the phase difference between current and
5.4 Electron kinetics

Voltage is increasing with higher discharge voltage for argon, it is decreasing for helium. This can be explained by the phase-resolved emission pattern: Figure 5.32 shows the across the discharge gap integrated development of the a) 750 nm intensity of the argon discharge and the b) 706 nm intensity of the helium discharge at different power values. According to simulations by Hemke et al. [27] and Dünnbier et al. [46], the emission maxima can be attributed to the maximum discharge current amplitude. Therefore, the emission intensity is a measure for the absolute value of the discharge current as qualitatively plotted above the graph. Additionally, the qualitative discharge voltage behavior can be deduced from the sheath oscillations and is also indicated above the graphs.

The maxima of the emission are marked in the graphs by vertical lines. With increasing power, the emission maximum (and thus the current) of the argon discharge is shifted to earlier times in the cycle. This results in an increase of the absolute value of the phase difference with increasing power as observed in figure 5.2. In contrast, the emission maximum (and thus the current) of the helium discharge is shifted to later times in the cycle. This results in a decrease of the absolute value of the phase difference with increasing power as observed in figure 5.3. So the microscopic differences in heating mechanisms result in a macroscopic difference of the phase behavior in the global measurements.

**In summary**, the emission patterns of argon and helium are similar, however they are differently pronounced. As emission maximum II during sheath retreat is more prominent in argon compared to helium, the opposite trend is observed for emission maximum III in the sheath. As emission maximum II is due to the electrons not being able to follow the retreating sheath, this is probably caused by the higher collisional cross section for momentum transfer in argon and the higher mobility of helium ions. Emission maximum III is caused by secondary electron processes in the sheath. Therefore, it is stronger in helium, as the potential energy levels of excited states are higher compared to argon. Assuming these emission maxima being a measure for the absolute value of the current amplitude, this explains the different phase behavior observed in section 5.1. This observation represents the bridge between the microscopic differences in heating mechanisms and the macroscopic difference of the electrical measurements.
5.4.3 Pressure variation

Excitation mechanisms in low and atmospheric pressure discharges differ substantially due to the high number of collisions at atmospheric pressure. To verify whether the explanations adopted in the previous chapter apply to atmospheric pressure argon plasma processes, the effect of pressure on excitation mechanisms was investigated. During the pressure variation, the power dissipated in the discharge was kept constant. According to figure 5.10, stable conditions are present in the pressure range between 885 mbar to 990 mbar. However, the voltage had to be decreased with increasing pressure from 242 V at 885 mbar to 220 V at 990 mbar, as the increasing number of collisions increases the resistance of the discharge. Therefore, the total intensity of the emission decreases with increasing pressure.

Overall, there is little change in the emission structures visible in the PROES images, which is not surprising considering the narrow pressure range explored here.

Figure 5.33 shows phase-resolved images of the integrated emission at the a) lowest (885 mbar) and b) highest (990 mbar) investigated pressure at a dissipated power of...
5.4 Electron kinetics

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5.4 & Electron kinetics \\
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5.4 Electron kinetics

$\begin{array}{|c|c|c|c|c|c|c|c|c|c|c|c|}
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$\begin{array}{|c|c|c|c|c|c|c|c|c|c|c|c|}
\hline
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**Figure 5.34:** Ratio of the emission intensity of different maxima (power 540 mW). The insert illustrates the designation of the maxima.

540 mW. Apparently, the emission structure changes slightly. The dominant emission regions in space and time of two different species are indicated by black circles. In the region of the small ellipse, the emission is mainly dominated by argon lines, whereas in the region of the big ellipse, it is dominated by emission of the nitrogen molecule and ion (see figure 5.29). The contribution of argon emission to the overall emission dominates the nitrogen share for all pressures. However, the nitrogen share increases relatively as the pressure increases from 885 mbar to 990 mbar. This behavior is due to the low pressure being more favorable for argon excitation. The higher the gas pressure, the shorter is the mean free path. It varies from 0.76 $\mu$m at 885 mbar to 0.66 $\mu$m at 990 mbar (see appendix B). As a result, a higher pressure leads to a decrease of the overall electron temperature. Consequently, excitation of the nitrogen molecule or ion requiring an electron energy of 3 eV is preferred over direct electron impact excitation of argon requiring an electron energy of 11.5 eV. Therefore, this observation is an indicator for the high energy tail of the electron energy distribution function being more pronounced at low pressures.

To verify the postulated mechanisms responsible for the three different emission structures in figure 5.30, their intensity is compared during the pressure variation. To
compare the emission structures of the 750 nm line, the spatially averaged emission intensity of the structure was calculated by integrating the intensity over all pixels with an intensity above 80% of the maximum emission intensity of the respective structure. The total emission intensity decreases with increasing power. Therefore, figure 5.34 shows the intensity of emission structure II and III normalized to the intensity of emission structure I at a dissipated power of 540 mW. The graph shows different behavior for both maxima which is due to their physical origin. As explained above, emission structure II is induced by accumulation of electrons not being able to follow the retreating sheath due to the high number of collisions. So, the higher the pressure, the higher is the number of collisions. This increases the number of electrons that are not able to follow the electric field, accumulate and generate a higher self-consistent electric field. Consequently, the intensity of emission structure II increases with increasing pressure. For helium, these findings were also confirmed by numerical simulations [66].

Contrary to this behavior, the intensity of emission structure III decreases with increasing pressure. This is due to the secondary electron processes being less effective at higher pressures. Since the particle number density increases, the mean free path decreases and thus the acceleration of electrons becomes more difficult. This differing behavior reflects the different origin of the emission structures and confirms the assumptions from the previous section.

**In summary**, the pressure variation confirmed that the argon emission structures are due to the discharge processes expected from the helium discharge. If the pressure is increased, the argon emission is less pronounced compared to the nitrogen emission. This is due to the higher number of collisions reducing the electron temperature. Emission maxima I and II are due to ohmic heating, whereas emission maximum III is due to secondary electron processes.

In section 5.4, phase-resolved optical emission spectroscopy was used to determine electron kinetics in the argon discharge. The observed emission structures in the argon discharge closely resemble the structures known from the helium discharge. However, they are differently pronounced due to microscopic differences between the properties of argon and helium. By varying the power, it was shown that the argon discharge is mainly operated in the $\alpha$-mode with only a small signature of a $\gamma$-like mode at higher powers thus confirming the observations in section 5.1.1. The pressure variation
5.5 Summary

showed that the emission structures are due to sheath interaction of bulk electrons (maxima I and II) and secondary electron processes in the sheath (maximum III).

In conclusion, electron kinetics in the argon and helium discharge are in principal similar. However, their extent varies depending on the microscopic characteristics of the discharge gas.

5.5 Summary

In this chapter, various diagnostic techniques were used to unravel the processes in argon discharges in contrast to helium discharges. In principal, both gases exhibit similar characteristics. However, analyzing the microscopic processes in the discharge globally, as well as energy- and time-resolved helps to understand the macroscopic discharge behavior of the argon discharge. Finally, the answers to the research questions in the introduction of this chapter could be found by combining all pieces of the puzzle described in the previous sections.

1. Why is the argon discharge more susceptible to instabilities leading to a constricted mode compared to the helium discharge?

As the reproducible electrical measurements in section 5.1 revealed, the instability in the argon discharge as well as in the helium discharge can be attributed to the $\alpha$-\$\gamma$-instability mechanism and the thermal instability mechanism was excluded. The $\alpha$-\$\gamma$-instability mechanism is due to a breakdown of the sheath and a subsequent filamentation of the discharge. The absolute value as well as the dependence on gas flow rate and pressure confirmed this assumption. The helium discharge has a higher critical energy density than the argon discharge, as the electron mobility of argon is lower than in helium, but the critical breakdown voltage in argon is higher. However, the electric field in the sheath affecting the critical power density is smaller for helium than for argon. This was deduced from the electrical model in section 5.2. The critical densities deduced from the instability mechanism agree well with the measured densities from the electrical model in section 5.2.2.
Chapter 5: Physical properties of an argon discharge in the COST-Jet

The power curves (section 5.1.1) and the PROES measurements (section 5.4.2) of argon and helium reveal that the helium discharge exhibits an $\alpha$- and a $\gamma$-like mode. As the $\alpha$-$\gamma$-instability mechanism limits the argon discharge to be operated at high power values, the argon discharge does not exhibit the $\gamma$-like mode.

2. Why does the size of the stable regime of the argon discharge depend on the gas flow rate?

The stable range of the argon discharge coincides with the homogeneous abnormal mode. This mode is limited by the extinction and constriction voltage. Whereas the constriction voltage is constant, the extinction voltage linearly increases with the gas flow rate.

The dependence of the extinction voltage could be attributed in section 5.1 to long-living particles that influence the discharge behavior. These long-living particles were measured by TDLAS and described in section 5.3.4 to be argon metastables slowly building up in the discharge channel. Due to the interplay of argon metastables, argon excimers and excited molecular argon ions, this strongly affects the stability of the homogeneous argon discharge.

3. Why can even a small amount of impurities prevent a homogeneous argon discharge?

As shown in section 5.3.3, argon excimers are efficiently quenched by the admixture of molecular gases to the argon discharge. This is due the different excitation cross sections of helium and argon. In contrast to helium, the elastic excitation cross section of argon exhibits a Ramsauer minimum and thus, nitrogen has an elastic scattering cross section which is approximately two orders of magnitude higher than in argon. Additionally, the energy levels of the molecular rare gases are in the energy range of the excited argon levels, thus enabling effective energy transfer from argon to the molecular gases.

In addition, the admixture of molecular gases reduces the high energy tail of the electron energy distribution function. As the electron temperature in argon is lower than in helium (section 5.2.3), this has an even greater impact on the discharge.
4. Why does the argon discharge directly transfer into the constricted mode after spontaneous breakdown and why does the ignition via a high voltage spark gun avoid this problem?

Answering this question is challenging, as the ignition is a transient process and could not be investigated separately. However, the results in this chapter suggest that for the ignition of a homogeneous argon discharge, a pre-ionization of the feed gas is necessary. This might be due to the importance of argon metastables in the discharge as they serve as an intermediate state for stepwise excitation. According to Massines et al., a homogeneous discharge is possible if the Townsend breakdown instead of the Meek criterion is met. This can occur if enough seed electrons are present in the discharge channel. These electrons result from secondary processes due to impinging particles on the electrode surface prior to breakdown. As already described in section 5.4.2, these processes are more prominent in helium than in argon. Thus, a Townsend breakdown is more probable in helium compared to the argon discharge. A pre-ionization of the argon discharge using the spark-gun can achieve the same effect.
6 Summary and conclusions

This work provides fundamental insights into the atomic and molecular processes considering the stability of a homogeneous RF-excited atmospheric pressure plasma jet comparing argon and helium as plasma gas. This study was enabled by the development of a reliable device - the COST-Jet - and a suitable control parameter - the dissipated power. In combination, these tools allow a reproducible and stable operation of a homogeneous argon discharge at atmospheric pressure. The most important findings of this study are briefly summarized in the following.

In chapter 4, the characterization of the COST-Jet device was presented. The implemented electrical probes allow for an \textit{operando} measurement of the dissipated power. A detailed error analysis of the dissipated power measurement demonstrated its \textit{reproducibility}. Three different measurement scenarios were considered. They revealed that in spite of the challenges that arise due to the capacitive character and small dimensions of the plasma, an \textit{operando} power measurement can be realized by carefully developing the probe design and evaluating the current and voltage waveforms. The \textit{stability} of the plasma in the COST-Jet device was demonstrated in a day-to-day analysis using the effluent temperature as an example. These measurements showed that plasma variations are negligible within the limits of the measurement. If changes occurred, these were caused by external factors such as room temperature or ambient humidity. This is a clear indication that the control of these external factors is crucial and a prerequisite for reproducible scientific results. The \textit{comparability} of five individually manufactured COST-Jet devices was presented in terms of power measurement, temperature and optical emission. All of the devices showed the same distinct behavior and the observed deviations were well within the error bars of the measurements. Thus, the COST-Jet design allows comparing experimental results from different devices operated also in different laboratories. In addition, it was confirmed that the measured
dissipated power in a helium plasma is transferred almost completely into the heating of the discharge gas. Thus, this measurement is only an indication of the possibilities offered by the new control parameter ‘dissipated power’. Lastly, it was shown that the control of impurities in the feed gas by a cold trap has an important influence on the operation of the discharge. Furthermore, it could be shown that external matching has no influence on the discharge parameters in homogeneous mode. However, in the so-called constricted mode, these parameters have to be considered.

In chapter 5, the stable discharge conditions were used to investigate the differences between the main discharge mechanisms in an argon discharge compared to a helium discharge.

First, current and voltage measurements were used for a global classification of the argon discharge into different operating modes: a normal, an abnormal and a constricted mode were observed. The measurements of the phase show that in abnormal mode in argon, the phase decreases with increasing dissipated power. In contrast, in helium, the phase increases with increasing dissipated power. Using these data, the dissipated power in the argon and helium discharge was measured. For both gases, the power is in the range of 0.5 W, which corresponds to a power density of $1.5 \times 10^7 \text{ W m}^{-3}$. However, for argon, the power linearly depends on the applied voltage, whereas for helium, the power dependence exhibits an additional exponential term. The observed differences in phase-angle and power measurements were postulated to be due to different dominating electron heating mechanisms. Using a gas flow rate and pressure variation, the limits of the stable operational range for the abnormal mode in argon were assessed. The transition to constricted mode was attributed to the $\alpha$-$\gamma$-instability, excluding the thermal instability, for both gases, argon and helium. This was deduced by comparing the expected critical power density values and the expected relative dependence of the constriction voltage on gas flow rate and pressure to the observed trends. The higher critical power density for argon compared to helium is caused by the higher electrical field in the sheath. The extinction of the argon discharge depends on the gas flow rate, while the extinction of the helium discharge is independent of it. This dependence of the gas flow rate was attributed to the importance of metastable particles in the argon discharge. In conclusion, the reproducible measurement of the dissipated power allows to deduce fundamental discharge processes such as the instability mechanism responsible for constriction and extinction.
Second, the implementation of an electrical circuit model has revealed an insight into the fundamental plasma parameters of the argon discharge and the differences compared to the helium discharge. This resolves the contradiction between the behavior of the helium and the argon plasma resistance. The sheath thickness in the argon and helium discharge was calculated from the circuit model to be of the order of 250 µm. The sheath thickness decreases with increasing dissipated power due to the weak variation of electron temperature with dissipated power. The sheath size in argon is a factor of 0.8 smaller compared to helium. As the argon sheath thickness never exceeds half of the discharge gap, this mechanism is excluded as a potential source of instability. The electron density deduced from the electrical model is significantly larger for argon ($10^{17}$ m$^{-3}$) compared to helium ($10^{16}$ m$^{-3}$) for similar dissipated powers. This results from the lower bulk resistance in argon compared to helium. The electron density increases with increasing dissipated power for both, the argon and helium discharge. However, the variation of the electron density indicates that the used circuit model is not appropriate in helium at high dissipated powers due to the onset of the γ-like mode. The electron temperature in the discharge was deduced using an energy balance. In argon ($T_e = 1.2$ eV), the electron temperature is lower compared to helium ($T_e = 1.8$ eV). This is due to the different dominating terms in the power balance. For argon, ionization is the dominating loss process, whereas for helium, elastic electron-atom collisions dominate the loss processes. The electrical model correctly reflects the expected dependence of the electron density on molecular gas admixtures. In addition, this study also shows that only very small admixtures are possible, which was not anticipated by models. Argon excimer species are possibly responsible for this behavior. In conclusion, the plasma parameters deduced from the circuit model provide a coherent picture of the differences between the argon and helium discharge. Additionally, the observations agree with expectations in the context of experimental and numerical results from literature.

Third, using optical emission spectroscopy in the visible range to calculate the population densities of the excited 2p levels of argon, a strongly non-Maxwellian electron distribution function was confirmed. VUV emission spectroscopy showed strong radiation of argon excimers. This supports the hypothesis of these species being important for the discharge processes in argon. The measurements in the VUV range demonstrated the sensitive response of the argon excimer radiation on small amounts of admixed
molecular gases and the consequences for the stability of the discharge. The argon discharge was found to be much more sensitive to impurities compared to the helium discharge for two reasons: The Ramsauer minimum of the cross section of argon favors the vibrational excitation of impurities instead of the noble gas. Additionally, the energy levels of impurities overlap with those of argon. TDLAS measurements demonstrate that the argon metastable density in the sheath is $1.1 \times 10^{12} \text{ cm}^{-3}$. This is approximately one order of magnitude higher compared to helium. Additionally, an increase of the metastable density in the sheath at the beginning of the discharge channel was observed. This increase depends on the gas flow rate. This argon metastable build-up supports the hypothesis of metastables being responsible for the discharge sustainment. In conclusion, molecular argon ions, excimers and metastable states apparently play a key role in the homogeneous atmospheric pressure argon discharge.

Lastly, phase-resolved optical emission spectroscopy was used to determine electron kinetics in the argon discharge. The emission structures observed in the argon discharge roughly resemble those observed in the helium discharge. However, they are differently pronounced due to microscopic differences between the properties of argon and helium. By varying the power, it was shown that the argon discharge is mainly operated in the $\alpha$-mode with only a small signature of a $\gamma$-like mode at higher powers. This behavior was correlated to the electrical measurements of the phase-angle. The pressure variation confirmed that the emission structures are due to sheath interaction of bulk electrons (maxima I and II) and secondary electron processes in the sheath (maximum III) as expected from the helium discharge. If the pressure is increased, the argon emission is less pronounced compared to the nitrogen emission. This is due to the higher number of collisions reducing the electron temperature. In conclusion, electron kinetics in the argon and helium discharge are in principal similar. However, their extent varies depending on the microscopic characteristics of the discharge gas.

In this work, the complex atmospheric pressure plasma system was simplified by reducing and controlling the free parameters such as impurities and discharge pressure. Various diagnostic techniques were combined and the results were cross-linked to unravel the processes in argon discharges in contrast to helium discharges. In principal, both gases exhibit similar characteristics. However, analyzing the microscopic processes in the discharge globally, as well as energy- and time-resolved explains the macroscopic behavior of the argon discharge compared to the helium discharge.
The findings in this work have been obtained with a focus on reproducibility, stability and comparability. The results presented in this work represent pure conditions because a cold trap was used and most experiments were conducted in a vacuum chamber under argon atmosphere. These conditions are a unique feature of this work compared to previously published studies. Therefore, they are a valuable benchmark not only for other experimentalists but especially for numerical simulations.

The dissipated power is a suitable control parameter for comparing plasmas operated using different feed gases. Its measurement enables a detailed analysis of the energy consumed in the discharge. It is the basis for an answer to the important question of how much energy is consumed in the system and where. This global measurement even mirrors microscopic processes hidden in the heating mechanisms. The measurement of a reliable absolute value allows the derivation of fundamental plasma parameters. As the electrical characteristics can be measured operando, deduced plasma parameters could be monitored as well. This is an interesting feature for future applications.

Additionally, the use of argon as a feed gas opens up a new field for applications, e.g. in the field of plasma medicine. An economic advantage is the fact that argon is much more affordable than the commonly used helium. A slight drawback is the low amount of molecular admixtures that can be added to generate, for example, reactive oxygen and nitrogen species, as the discharge stability is highly sensitive. However, this is an indicator for an effective excitation of these admixtures which is promising for a rich plasma chemistry.

Future studies may now profit from these stable conditions and focus on the analysis of further diagnostics requiring a stable and reproducible plasma discharge. It might be interesting to analyze the normal and constricted discharge mode or to use other feed gases.

Overall, this work demonstrates how a complex system, such as an atmospheric pressure plasma, can be investigated producing reproducible, stable and comparable scientific results, using the example of the COST-Jet device. The careful design of the device in combination with cross-linking of the used diagnostics provides a holistic picture of the discharge. This allows the detailed observation and isolation of fundamental, microscopic processes leading to an understanding of the discharge's macroscopic behavior.
Assuming continuity of the gas flow, the velocity of the gas in the discharge channel is given by

\[ v_d = \frac{\Gamma}{A_d}, \]  

(A.1)

where \( \Gamma \) is the gas flow rate (volume per time: \( V/t \)) of the inserted gas by a mass flow controller and \( A_d \) the cross-sectional area of the discharge channel. For the COST-Jet, \( A_d \) equals 1x1 mm\(^2\). The mass flow controller is calibrated for operation at standard conditions \( (T_{\text{std}} = 273.15 \, \text{K} \) and \( p_{\text{std}} = 1 \times 10^5 \, \text{Pa} \)). Since the particle number is constant, the gas flow rate equals

\[ \Gamma = \Gamma_{\text{std}} \frac{p_{\text{std}}}{p} \frac{T}{T_{\text{std}}}. \]  

(A.2)

The dynamic pressure in the discharge is given by

\[ p_{\text{dyn}} = 0.5 \rho_{\text{Ar}} v_d^2, \]  

(A.3)

where \( \rho_{\text{Ar}} \) is the argon density at working conditions (with \( \rho_{\text{Ar, std}} = 1.784 \, \text{kgm}^{-3} \) being the argon density at standard conditions):

\[ \rho_{\text{Ar}} = \frac{p}{p_{\text{std}}} \frac{T_{\text{std}}}{T} \rho_{\text{Ar, std}}, \]  

(A.4)

with \( T, T_{\text{std}} \) the gas temperature at working and standard conditions, respectively, and \( p, p_{\text{std}} \) gas pressure at working and standard conditions, respectively.
The residence of the argon atoms in the discharge is given by the duration required to pass the discharge channel:

$$\tau_r = \frac{l_d}{v_d},$$  \hspace{1cm} (A.5)

with $l_d = 30$ mm is the length of the discharge channel. Figure A.1 shows the residence time of argon atoms in the discharge channel for different gas flow rates as a function of the working pressure.

**Figure A.1:** Residence time of argon atoms in the discharge channel for different gas flow rates.
The expressions derived above can be used to calculate the energy per particle in the discharge:

\[
\text{energy per particle} = \frac{P}{N \tau_f} \quad (A.6)
\]

\[
= \frac{k_B T}{pV} \varepsilon V l_d A_d \quad (A.7)
\]

\[
= \frac{k_B T}{pV} \varepsilon V l_d A_d \frac{P}{\Gamma} \frac{T_{\text{std}}}{T} \quad (A.8)
\]

\[
= k_B \varepsilon l_d A_d \frac{T_{\text{std}}}{\Gamma_{\text{std}} P_{\text{std}}} \quad , \quad (A.9)
\]

with \( P \) being the power, \( N \) the number of particles in the discharge, \( V \) the discharge volume and \( \varepsilon \) the power density.
The mean free path in the discharge can be calculated by

$$\lambda = \frac{1}{n\sigma} = \frac{k_B T}{p\sigma} = \frac{k_B T}{p \pi D_{Ar}^2}, \quad (B.1)$$

where $n$ is the gas density, $\sigma$ the collisional cross section (here for hard spheres), $k_B$ the Boltzmann constant, $T$ the gas temperature, $p$ gas pressure and $D_{Ar} = 1.42 \, \text{Å}$ [198] the diameter of an argon atom.

**Figure B.1:** Mean free path for the relevant pressure range.
Figure B.1 shows that the mean free path in the discharge is of the order of µm for the relevant pressure range.

The Reynolds number is given by

$$Re = \frac{v_d D_h \rho_{Ar}}{\eta}, \quad (B.2)$$

where $v_d$ is the velocity of the gas, $D_h$ is the hydraulic diameter of the discharge channel, $\rho_{Ar}$ the density and $\eta$ the viscosity of Argon.

$D_h$ is given by

$$D_h = \frac{4A_d}{U}, \quad (B.3)$$

where $A_d$ is the cross-sectional area and $U$ the perimeter of the channel. For the COST-Jet, $D_h$ equals 1 mm. $v_d$ is given by equation A.1 and $\rho_{Ar}$ by equation A.4.

The dynamic viscosity $\eta$ is given by

$$\eta = \frac{1}{3} n m_{Ar} \bar{v} \lambda = \frac{1}{3} \frac{m_{Ar}}{\pi D_{Ar}^2} \bar{v} = 1.39 \times 10^{-4} \text{ Pa s}, \quad (B.4)$$

where $m_{Ar} = 6.63352 \times 10^{-26} \text{ kg}$ is the specific mass of Argon and $\bar{v}$ the mean particle velocity given by:

$$\bar{v} = \sqrt{\frac{8k_B T}{\pi m_{Ar}}} = 399 \text{ m s}^{-1}. \quad (B.5)$$

Figure B.2 shows the Reynolds number as a function of the gas flow rate. It is much smaller than the critical value of 2300. Consequently, the gas flow is laminar in the whole range of experiments.
Figure B.2: Reynolds number for different gas flow rates at pressure of 100000 Pa.
C Energy level notation

Table C.1: List of the 15 lower energy levels of Ar I after Katsonis et al. [100].

- **i**: level index,
- **c/c**: configuration and core description,
- unprimed for core $^2P_{3/2}$, primed for core $^2P_{1/2}$,
- **jK** description from NIST, **LS** description from [100],
- **PN.**: Paschen notation,
- Energy from NIST.

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<th>l</th>
<th>jK</th>
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</tr>
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Table C.1 gives an overview of the argon energy level characteristics.
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Own Publications


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