TOPICAL REVIEW

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Topical Review

Foundations of atmospheric pressure non-equilibrium plasmas

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Abstract

Non-equilibrium plasmas have been intensively studied over the past century in the context of material processing, environmental remediation, ozone generation, excimer lamps and plasma display panels. Research on atmospheric pressure non-equilibrium plasmas intensified over the last two decades leading to a large variety of plasma sources that have been developed for an extended application range including chemical conversion, medicine, chemical analysis and disinfection. The fundamental understanding of these discharges is emerging but there remain a lot of unexplained phenomena in these intrinsically complex plasmas. The properties of non-equilibrium plasmas at atmospheric pressure span over a huge range of electron densities as well as heavy particle and electron temperatures. This paper provides an overview of the key underlying processes that are important for the generation and stabilization of atmospheric pressure non-equilibrium plasmas. The unique physical and chemical properties of these discharges are also summarized.

Keywords: non-equilibrium plasmas, atmospheric pressure plasmas, discharge generation, plasma instabilities, plasma properties

1. Introduction

Atmospheric pressure non-equilibrium (or non-thermal) plasmas have a long history dating back to the 19th century. Dielectric barrier discharges (DBDs) and corona discharges, for example, have been used in applications such as ozone generation, gas purification, electrostatic precipitation, combustion and surface functionalization of materials for decades [1, 2].

As they do not require expensive vacuum systems, atmospheric pressure plasmas are often proposed as a cost-effective alternative to existing low pressure plasma processes. While this is certainly valid for some applications, it is an oversimplistic and incomplete view of atmospheric pressure plasmas that certainly does not apply to all plasma processes. Atmospheric pressure plasmas present unique opportunities but also face important challenges when compared with their low pressure counterparts.

In recent years, atmospheric pressure non-equilibrium plasmas have received renewed attention in large part motivated by their ability to treat liquids and heat sensitive materials, such as biological targets, that cannot withstand low pressure or vacuum environments. These new treatments have given rise to exciting applications of non-equilibrium plasmas in medicine, disinfection, water treatment, nanoparticle synthesis, food processing and agriculture [3]. Many different plasma generation methods have been devised to address the different requirements of these applications. The properties of the resulting atmospheric pressure plasmas are spread across orders of magnitude in terms of size, time...
scales, temperatures as well as charged and reactive species densities. Figure 1 provides an overview of the range of electron densities and gas temperatures that are encountered in typical atmospheric pressure plasmas.

As is often the case in the literature, in this paper the words plasma and gas discharge are used interchangeably. However, given the exceptionally large range of operational parameters encountered in atmospheric pressure discharges, it is not surprising that some of these discharges fail to develop a quasi-neutral bulk and therefore are not strictly speaking plasmas. This is definitely the case for discharges where the characteristic size of the discharge is comparable to the plasma sheath width (10–100s μm) or when the discharge is highly transient. For example, ions, due to their large inertia, remain practically static in nanosecond pulsed discharges while electrons drift causing significant charge separation. The modeling of some of these discharges using conventional fluid descriptions is problematic as some of the intrinsic fluid assumptions break down.

In non-equilibrium plasmas, the mean kinetic energy of electrons is larger than the gas temperature ($T_e > T_g$). Maintaining this non-equilibrium character is possible because energy transfer from the applied electric field to the electrons is generally much faster and efficient than the subsequent collisional energy transfer between electrons and heavy particles [4]. This latter process is slow due to the large mass difference between electrons and heavy particles. For a steady-state plasma sustained in an atomic gas, the gas temperature $T_g$ can be estimated by balancing the energy electrons gain in an electric field $E$ with the energy they lose through elastic collisions with background neutrals [5, 6]:

$$T_g = T_e \left(1 - \frac{m_e}{4m_e} \frac{\lambda_c e E}{E_e^2}\right).$$

where $m_e$ is the heavy neutral particle mass, $m_e$ the electron mass, $E_e$ the electron energy, $e$ the elementary charge and $\lambda_c$ the electron mean free path. Equation (1) shows that maintaining moderate gas temperatures becomes increasingly challenging with increasing pressure due to the square dependence on the electron mean free path. The high collisionality encountered in atmospheric pressure plasmas not only leads to increased gas heating but it also enhances the tendency to develop spatio-temporal instabilities. Without the use of special plasma excitation methods and/or special plasma electrode geometries, high-temperature (thermal) discharges, such as arcs, will form at atmospheric pressure.

For atmospheric pressure plasma applications where a gas temperature increase is not acceptable, a number of strategies have been developed to minimize gas heating. These include the use of noble gases (higher thermal conductivity and lower inception voltage than most molecular gases), gas flows, reduced plasma size (increased surface to volume ratio), and transient operation of the discharge. An overview of these different approaches and their rationale is provided in subsequent sections. Although non-equilibrium plasmas in which the gas remains close to room temperature have been reported, developing stable non-equilibrium homogeneous large volume atmospheric pressure plasmas remains the focus of active research.

Most applications of atmospheric pressure non-equilibrium discharges rely on their unique non-equilibrium plasma chemistry. This chemistry is driven by energetic electrons (rather than thermal energy) and can be used to initiate and catalyze chemical processes at moderate gas temperatures. This means that with controlling the electron energy distribution function (EEDF) in the plasma one can tune the plasma reactivity. However, the EEDF depends not only on the applied electric field but also on the space charge and the evolving plasma chemistry, and as a result controlling the chemistry in these plasmas is challenging and also remains an area of active research.

The rest of the paper is structured as follows. Section 2 describes scaling laws and time scales of important plasma processes that are relevant to discharge generation and instability development, which are ubiquitous in atmospheric pressure discharges. Section 3 highlights unique properties of atmospheric pressure plasmas and ionization processes leading to breakdown. Common discharge instabilities are discussed in sections 4 and 5. Section 6 discusses different approaches typically employed to stabilize and maintain non-thermal atmospheric pressure plasmas. The conclusions and an outlook are presented in section 7.

The paper is an introductory overview but not exhaustive. For more in depth information, it refers to comprehensive review articles and textbooks. In particular, a detailed description of many aspects of the physics and chemistry of atmospheric pressure non-equilibrium plasmas can be found in [7–14].

## 2. Scaling laws and time scales

Scaling laws are useful proportionality relations that can be used to generalize results obtained at various scales and to provide insights into the origin of fundamental differences between plasma sources. Here the physical meaning of a few scaling parameters relevant to non-equilibrium plasmas are discussed and used to highlight the unique nature of

![Figure 1. Overview of different atmospheric pressure gas discharges spanning a range of more than 10 orders of magnitude in electron density. TD stands for Townsend discharge.](image-url)
atmospheric pressure discharges. Time scales of fundamental processes that are crucial for the understanding of discharge inception, breakdown, plasma kinetics, plasma stability and controllability of plasmas are also discussed.

Arguably the most famous scaling law in plasma physics is Paschen’s law. It states that the voltage necessary to ignite a plasma between two electrodes for a given background gas depends on the product of pressure \(p\) times electrode gap distance \(d\) [16]. The reason behind this experimental observation is that the inception voltage is underpinned by a balance between the generation of electrons in volumetric electron avalanches and secondary electron emission processes and the loss of electrons on the surfaces, which for a DC breakdown ultimately depends on the number of collisions electrons undergo as they transit between the electrodes. This number is proportional to the product of the gas density \((n)\) and the electrode gap distance. Since at inception the gas is typically at room temperature, \(n\) is proportional to \(p\) and hence the inception voltage is typically reported as a function of \(pd\). Paschen curves, i.e., plots of the breakdown voltage versus \(pd\) values, have a similar shape for different gases with a minimum at \(pd\) values in the range of \(1–10\) Torr cm [4, 7, 16]. The increase in breakdown voltage at lower \(pd\) values is due to the reduced ionization and increased loss of electrons that occurs as a result of the electron mean free path becoming comparable to the gap between the electrodes. At large \(pd\) values, the breakdown voltage increases as the energy electrons gain in between collisions for a given applied voltage decreases due to the increasing number of collisions. Most atmospheric pressure plasmas operate in this latter regime \((pd > 10\) Torr cm\) although atmospheric pressure microplasmas (see further) take advantage of the scaling and are operated closer to the Paschen minimum.

Despite its broad applicability, deviations from the Paschen law have been reported and reflect changes in the underpinning mechanisms governing the breakdown. The onset of field emission in small gaps and the trapping of electrons in an oscillatory motion between the electrodes in radio-frequency (RF) discharges are examples of known mechanisms that can cause such deviations [14, 17, 18]. At atmospheric pressure, breakdown often occurs on a nanosecond time scale. This time scale is inconsistent with the Paschen breakdown mechanism since ions remain static on such time scales and thus, secondary electron emission cannot occur.

Besides the \(pd\) product, other important scaling parameters often used in the study of non-equilibrium plasmas include \(E/n\) and \(\omega_{rf}/\nu\), where \(E\) is the electric field, \(n\) the gas density, \(\omega_{rf}\) the (angular) frequency of the applied voltage and \(\nu\) the electron-neutral collision frequency. The reduced electric field strength \(E/n\) is a measure of the energy that electrons gain from the electric field in between collisions. The first Townsend ionization coefficient \(\alpha\) and other parameters that depend on the mean electron energy scale with \(E/n\), which is typically given in the unit Townsend \((Td = 10^{-17}\) Vcm\(^{-2}\)). The scaling parameter \(\omega_{rf}/\nu\) is of interest when comparing discharges that operate at different frequencies and/or pressures as it relates to the number of collisions electrons undergo in one RF cycle. For electrons to gain energy from an alternating field, collisions are needed and for a given field amplitude, it can be shown that maximum power transfer from the electric field to the electrons occurs when \(\omega_{rf}/\nu = 1\) [4]. In atmospheric pressure discharges, the electron-neutral collision frequency is typically in the order of THz and as a result these discharges operate in a regime that is far from this optimum even when sustained at microwave frequencies.

Table 1 compares a low pressure and an atmospheric pressure RF plasma. It is important to note that not only some plasma parameters are different but actually that the scaling parameters differ by orders of magnitude. This indicates that atmospheric pressure non-equilibrium plasmas represent a different paradigm than their low pressure counterparts. Some of the unique aspects of atmospheric pressure plasmas are further discussed in section 3.

Time scales for collisional processes and transport in non-equilibrium atmospheric pressure plasmas span over 12 orders of magnitude. An overview of the most important plasma processes with their typical time scales is shown in figure 2. Electron collisional processes typically take place in picosecond time scales with discharge inception, excitation, dissociation reactions and ionization processes being observed at nanosecond time scales. The large collisionality of atmospheric pressure discharges also leads to short energy relaxation times, which tend to drive electron kinetics in equilibrium with the instantaneous electric field. For example, in helium atmospheric pressure plasmas, the energy relaxation time for low energy and high energy electrons with energies below and above the helium excitation threshold is on the order of nanoseconds and picoseconds, respectively; time scales shorter than the typical period of the applied voltage waveform. As a result, plasma properties such as electron temperature and ionization rates display strong periodic oscillations even in high-frequency atmospheric pressure RF discharges.

Although individual electron-neutral elastic collisions result in little energy transfer due to the disparity in the masses of electrons and heavy neutrals, the large collisionality encountered in atmospheric pressure plasmas \((\nu \sim \text{THz})\) can result in significant energy transfer by elastic collisions to the background gas. Gas heating through elastic collisions (and vibrational excitation in the case of molecular gases) typically takes between 100 ns and 1 \(\mu\)s. Depending on the plasma conditions, faster gas heating can also take place via the recombination of highly excited atoms and molecules, as observed for example in nanosecond pulsed discharges in air [20]. Gas heating does not only represent an undesired energy loss for many applications but it can also drive thermal instabilities. Fast gas heating on nanosecond time scales can also lead to sudden increases in pressure and the creation of shock waves [21]. In addition, the joint action of fast gas heating and dissociation in nanosecond pulsed discharges also initiates radical chemistry on nanosecond time scales [22, 23].

Ionic recombination reactions and metastable induced dissociation reactions, although highly dependent on the electron density of the plasma, typically occur on timescales

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Table 1: Comparison of Scaling Parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Low Pressure</th>
<th>Atmospheric Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>(E/n)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\omega_{rf}/\nu)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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**References**


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Plasma Sources Sci. Technol. 26 (2017) 123002
Table 1. Comparison of a low pressure and an atmospheric pressure RF plasma in helium. Differences in the scaling parameters highlight the different paradigms of the two non-equilibrium plasma discharges [19].

<table>
<thead>
<tr>
<th>Parameter</th>
<th>He low pressure plasma</th>
<th>He atmospheric pressure plasma</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure ($p$)</td>
<td>100 mTorr</td>
<td>760 Torr</td>
</tr>
<tr>
<td>Gas density ($n$)</td>
<td>$3.2 \times 10^{19}$ cm$^{-3}$</td>
<td>$2.5 \times 10^{19}$ cm$^{-3}$</td>
</tr>
<tr>
<td>Electrode gap distance ($d$)</td>
<td>10 cm</td>
<td>1 cm</td>
</tr>
<tr>
<td>Angular excitation frequency ($\omega$)</td>
<td>13.56 MHz</td>
<td>13.56 MHz</td>
</tr>
<tr>
<td>Electron temperature ($T_e$)</td>
<td>3 eV</td>
<td>1 eV</td>
</tr>
<tr>
<td>Electron-neutral collision frequency ($\nu$)</td>
<td>150 MHz</td>
<td>1 THz</td>
</tr>
<tr>
<td>$pd$</td>
<td>$\sim 1$ Torr cm ($\leq pd_{min}$)</td>
<td>$\sim 760$ Torr cm ($\geq pd_{min}$)</td>
</tr>
<tr>
<td>$E/n$</td>
<td>10–100 Td</td>
<td>10–100 Td</td>
</tr>
<tr>
<td>$\omega_\parallel/\nu$</td>
<td>$\sim 0.1$</td>
<td>$10^{-3}$ ($&lt; 1$)</td>
</tr>
</tbody>
</table>

3. Unique aspects of atmospheric pressure plasmas

As shown in table 1, non-equilibrium atmospheric pressure plasmas operate in a very different parameter space than their low pressure counterparts and as a result, they offer new possibilities and present their own limitations. Arguably, the most important characteristic of low pressure non-equilibrium plasmas is their ability to drive ions anisotropically against a target substrate. This anisotropic bombardment is possible because at low pressure the ion mean free path is larger than the plasma sheath width [4]. In the past decades, significant efforts have been made to fine tune and control the ion energy distribution function (IEDF) of ions impinging onto the substrates in order to improve the resolution and repeatability of different low pressure plasma treatments. In general, the IEDF depends on the sheath potential, the sheath width, the ion mean free path, the ion mass and its transit time as compared to the applied RF period. Experimentally, these parameters can be influenced by careful selection of the background gas pressure (ion mean free path), gas composition (ion mass) and applied voltage (sheath potential and sheath width) [24].

As shown in figure 3, the energy of the ions hitting a substrate decreases rapidly with increasing pressure. For the particular case depicted in figure 3, the maximum ion energy decreases from $\sim 1000$ eV at 30 mTorr (4 Pa), to a few hundred eV at 75 mTorr (10 Pa) and to a few tens of eV at 750 mTorr (100 Pa). Ion mean free paths at atmospheric pressure are on the order of $\sim 1$ $\mu$m and therefore hundreds of times smaller than typically sheath widths. As a result, although physical bombardment is critical to the success of many low pressure plasma processes, the high collisionality encountered at atmospheric pressure prevents the collisionless transition of ions across the sheath. As inferred from the trend shown in figure 3, ions reaching the target do so with very little energy in atmospheric pressure discharges [19]. In streamer-based discharges, high-energy ions can reach the electrode when streamers reach the electrode, but their fluxes are typically small. Therefore, one can say that low pressure plasma processes that rely on anisotropic ion bombardment are not easily transferable to a similar atmospheric pressure process.

Although magnetic confinement has been exploited in low pressure plasmas to improve plasma efficiency, the numerous collisions that electrons undergo in a cyclotron period disrupt any effective confinement at atmospheric pressure. Additionally, collisionless electron heating by oscillating sheaths can also be safely neglected in atmospheric pressure discharges as even for small microdischarges, the product of the collision frequency ($\nu$) times the gap distance ($d$) is much larger than the electron thermal velocity $vd > v_{th}$ [4]. The lack of stochastic heating directly impacts on the EEDF and bi-Maxwellian distributions often encountered in low pressure RF plasmas are not found in their atmospheric pressure counterparts.

Nonetheless, the increased collisionality in atmospheric-pressure plasmas brings about many interesting features. For example, collisions between ions and neutral background species result in effective energy and momentum transfer, a

Figure 2. Timescales of relevant collisional and transport processes in atmospheric pressure plasmas.

from a few nanoseconds (in discharges with a high ionization degree) to microseconds. Neutral (radical) induced reactions are often slower and proceed on a microsecond to millisecond time scale with the exception of the above mentioned nanosecond pulsed discharges with a high dissociation degree and fast gas heating. The coupling of transport through diffusion and convection takes typically between 10 s of microseconds up to several seconds and couples mainly with neutral chemistry and can influence pre-ionization in modulated and repetitively pulsed discharges (see further).
feature that has been exploited in plasma actuators to modify the laminar to turbulent transition inside boundary layers and to prevent or to induce flow separation \[26\]. Both AC driven barrier discharges and nanosecond pulsed discharges can for example control boundary layer separation although the main driving mechanisms are completely different. While AC driven barrier discharges cause gas acceleration in the boundary layer due to momentum transfer, nanosecond pulsed discharges cause boundary layer turbulization due to energy/heat release \[27\]. The momentum transfer by plasmas to generate gas flow is often referred to as electrohydrodynamic effect. It can be exploited to create synthetic jets that are perpendicular to a discharge surface, thereby enhancing the transport of reactive species from a surface discharge to the substrate being treated \[28\]. Figure 4(a) shows the formation of one such a synthetic jet by an annular dielectric barrier discharge \[29\]. The interplay between plasma and gas dynamics is in general quite complex and in the same way that plasma can affect flow dynamics, flow conditions also influence the plasma kinetics and formation \[30\]. Figure 4(b) shows four jets operating in parallel in which the presence of plasma triggers a flow instability that enhances the entrainment of the surrounding air and the jets repel each other to a different degree depending on the neutral gas flow rate. As shown in figure 4(c), the energy deposition in pulsed discharges can produce rapid pressure variations and shock waves on submicrosecond timescales, which further complicates the interplay between plasmas and flows \[21, 32\].

Since, as discussed above, physical ion bombardment is not very energetic in atmospheric pressure plasmas due to ion-neutral collisions in the sheath, most atmospheric pressure treatments rely on plasma chemistry. Here again, the increased background density brings about differences with respect to the processes observed in low pressure plasmas and in particular, 3-body collisions become important. In atmospheric pressure plasmas, the collision rates of 3-body processes are four to six orders of magnitude larger than in conventional low pressure plasmas. As a result, atmospheric pressure discharges of atomic noble gases present significant concentrations of dimer ions and molecules including excimers which lead to the generation of VUV radiation \[2, 88\]. The 3-body collisions also lead to the formation of chemical species such as O$_3$ and H$_2$O$_2$, which at low pressure can only be produced through surface reactions. In addition, in the presence of water molecules, positive and negative ions in atmospheric pressure plasmas become hydrated, with larger water clusters at higher water content. This hydration can significantly impact the ion mobility and affect the overall plasma dynamics \[33\].
Although plasma diagnostics fall beyond the scope of this paper, high collisionality causes additional difficulties in the implementation and/or interpretation of conventional plasma diagnostics. For example, the use of a mass spectrometer requires multi-stage differential pumping and optical (laser) diagnostics, and stoichiometric methods need to account for often complex collisional transfer processes. Also, no universal theory exists for the interpretation of Langmuir probe measurements at atmospheric pressure [34–37].

4. Discharge inception and breakdown mechanisms

The inception of non-equilibrium plasmas and gas discharges is based on the development of electron avalanches. The very first free electrons, which are starting the discharge inception, are provided by cosmic rays, radioactivity or leftover charges from previous discharge activity. The main ionization mechanism in most gases is direct electron impact ionization by free electrons accelerated in the applied electric field $E$. In particular, at low pressure the positive ions created in the ionization process drift to the cathode and lead to secondary emission of electrons. This subsequent delivery of free electrons seeds new avalanches and this is the main aspect of the Townsend-breakdown mechanism that leads to the generation of a self-sustained gas discharge. The process can be thought of as successive avalanches crossing the discharge gap without the build up of space charge. The voltage at which a self-sustained discharge is obtained is described by the Paschen law and it is a function of the scaling parameter $pd$ as discussed in section 2. Secondary electron emission due to ion impact cannot play an important role for nanosecond breakdown at atmospheric pressure. Other electrode processes that lead to electron emission from the cathode can, however, occur. Examples include secondary electron emission by photons due to the photo-electric effect and electron emission due to micro-explosions of imperfections at the cathode, the so-called explosive emission centers that lead to the creation of an electron avalanche from the metal electrode [38]. Such an avalanche is sometimes referred to as an eckon. This phenomena typically coincides with a larger energy deposition due to field emission in small and sharp imperfections of metal electrodes or the breakdown of dielectric films and inclusions due to charging by gas discharges.

At higher pressure and thus higher gas density $n$, the number of ionizing collision per unit volume increases and the breakdown mechanism changes significantly. In particular, when electron avalanches create a space charge that locally enhances the applied electric field, secondary electron avalanches are triggered in the gas phase [7, 10, 15]. These are mostly initiated by photo-ionization or (in the case of sufficient electric field strength in electronegative gases) by electron detachment from negative ions previously formed by electron attachment on electronegative molecular species. The ionized region and its perturbation of the electric field grows rapidly and finally a distinct plasma channel, the so-called streamer, is formed. In air and other molecular gases at atmospheric pressure streamer formation occurs on a time scale of nanoseconds. Figure 5(a) depicts schematically the formation of a positive or cathode-directed streamer. The typical small streamer head radius ($\approx 100$ μm) of this ionized channel leads to a significant enhancement of the electric field. Negative or anode directed streamers also exist and have similar properties to positive streamers although the secondary avalanches start at the streamer head and grow towards the anode. Nonetheless, significant differences in the spatial structure and propagation velocities of positive and negative streamers exist. Positive streamers in air propagate faster compared to negative streamers in spite that electron drift acts in the opposite direction of the streamer propagation for positive streamers. This is due to the electron drift causing the growth of the streamer radius for negative streamers. This larger streamer radius reduces the field enhancement [39]. In the case of surface streamer discharges, similar effects are observed with the addition of distinctive different interaction
behavior of positive and negative streamers with a dielectric interface [40].

While the Townsend-criterion provides the inception voltage for the Townsend mechanism, the Meek criterion (sometimes also referred to as the Raether criterion) describes the conditions for streamer initiation. The streamer formation conditions relate to the charge number density in the primary avalanche required for significant space charge field perturbation, namely $\exp(\alpha_{\text{eff}} \cdot d) = 10^9$, where $\alpha_{\text{eff}}$ is the effective first Townsend ionization coefficient. In air, this criterion is typically fulfilled at $pd$ values above 1000 Torr cm.

Streamers can be considered as the initial stage of the electric breakdown of any non-ionized medium (gases, liquids and solids). They can precede sparks, create the path for leaders in lightnings and are responsible for the filamentary discharge structure in many non-equilibrium plasmas at atmospheric pressure. Cathode directed (or positive) streamers are more prominent and anode directed (negative) streamers are only obtained in the case of high over-voltages and sufficiently large discharge gaps. Both types of streamers can exhibit branching and, thus, rather complex spatial structures [41].

The interior of a streamer consists of a conducting, roughly quasi-neutral plasma while a thin and curved space charge layer at its tip is responsible for the screening of the inner ionized area and the strong field enhancement at the streamer head. Electrons in the field enhanced zone around the streamer head can be highly energetic and due to the field enhancement, streamers can propagate into areas where the background electric field is below the ionization threshold of the background gas.

The tendency to form streamers is related to the dependence of the effective reduced Townsend ionization coefficient on the reduced electric field and in particular $\partial(\alpha_{\text{eff}}/n)/\partial(E/n)$, as this determines the increase of the ionization frequency with changes in local electric field strength. Helium or neon are characterized by a relatively high ionization coefficient at a relative low electric field strength and a small gradient $\partial(\alpha_{\text{eff}}/n)/\partial(E/n)$ compared to argon and most molecular gases or gas mixtures. Hence, in gases such as helium or neon, the rapid formation of field gradients is suppressed and it is easier to obtain a diffuse breakdown [42].

The streamer development as described above requires the development of a strong local space-charge gradient that can lead to sufficient field enhancement as to cause the formation of the streamer. This condition is readily achievable when the discharge starts with a single or few electrons leading to well separated avalanches that do not greatly influence each other. However, when the background pre-ionization density is larger, avalanches influence each other and overlap. The overlap of these avalanches smooths out local gradients in the space-charge field and leads to a more homogeneous charge density. Therefore, a sufficiently high level of pre-ionization is a means to inhibit streamer formation. Figure 5(b) schematically depicts the Townsend breakdown in the presence of pre-ionization.

A typical background ionization density in air due to the presence of low levels of radioactive materials and cosmic radiation is of the order of $10^5$–$10^7$ cm$^{-3}$ [43]. The pre-ionization density required for suppression of the Meek condition and therefore the formation of a diffusive breakdown can be estimated by imposing that the distance between avalanches is comparable to the typical radius of the avalanche at streamer formation, which is of the order of 100 $\mu$m in air [44]. Estimating the distance between avalanches by the pre-ionization density ($\times n_0^{-1/2}$), pre-ionization densities in excess of $10^6$ cm$^{-3}$ are typically required for diffuse breakdown at atmospheric pressure. This pre-ionization can be achieved by an electron beam or electrons remaining in the discharge gap from a (potentially non-uniform) discharge used to pre-ionize the discharge gap (see also section 6).

As mentioned earlier, the breakdown at atmospheric pressure proceeds on a timescale of typically several tens of nanoseconds. Changing the applied voltage on the same timescale as the discharge generation by short (usually sub-microsecond) high voltage pulses having a rise time of 100 V ns$^{-1}$ or higher and combined with a high overvoltage (i.e. applied voltage amplitude exceeding the Paschen-breakdown voltage significantly) allows one to strongly impact the discharge formation [45].

The creation of non-equilibrium plasmas in even denser media including liquids, particularly in conductive liquids, requires the application of short high voltage pulses. While it is possible to ignite discharges in liquids with continuous or sinusoidal voltages with moderate frequency, such plasma formation always coincides with a phase change or formation of gas/vapor bubbles [46–48]. It is however much easier to break down liquids with short high-voltage pulses when the pulse duration is shorter than the dielectric relaxation time of the liquid. In this case, the liquid behaves as a dielectric rather than a conductive medium. Many studies have investigated breakdown processes in liquids including liquid Ar, N$_2$, hydrocarbons and water and the reduced Townsend ionization coefficient $\alpha/n$ does typically not scale as in the equivalent gas phase [49]. While not all details are currently understood, the higher density can lead to stepwise ionization processes and two-body collision approximations used in the gas phase breakdown theory are no longer valid in the liquid phase.

5. Discharge transitions and instabilities

In the previous section, we have discussed the transition from an avalanche to a streamer as a result of the build-up of space charge in the discharge volume. Other transitions exist and these are often a result of a plasma instability. An overview of typical transitions in atmospheric pressure plasma discharges is shown in figure 6. Diffuse discharges are obtained when the ignition conditions do not satisfy the Meek criterion. At atmospheric pressure, however, these discharges are prone to instabilities that can trigger the transition from a glow to a spark discharge. Instabilities can be driven by several
mechanisms but they always relate to an unbalance between the ionization and the recombination rate of electrons, leading to excessive ionization [7]. This can be mathematically expressed as:

\[
\frac{dn_e}{dt} = k_{ion}(T_e)n_e n + ... - \frac{D_a}{\Lambda} n_e - k_d n_e^2 - ... \geq 0, \quad (2)
\]

where \( k_{ion} \) is the electron impact ionization rate coefficient, \( D_a \) the ambipolar diffusion coefficient, \( \Lambda \) the diffusion length and \( k_d \) the electron–ion dissociative recombination rate. Many other reactions including attachment, detachment, Penning ionization processes and 3-body electron recombination processes could also play a role, hence the ellipsis in equation (2). Equation (2) shows that in most cases an increase in the electron density does not lead on itself to runaway behavior as dissociative electron–ion recombination, the dominant electron recombination process in many atmospheric pressure plasmas, scales quadratically with \( n_e \) while the ionization scales only linearly with \( n_e \). However, a sudden change in the electron temperature can trigger an instability due to the exponential dependence of the ionization rate coefficient on the electron temperature. This nonlinear dependence of the electron production rate on a changing plasma parameter is necessary to obtain an instability. In most cases, fluctuations in the gas temperature and electron temperature lead to an unbalance in the electron production and recombination, causing the onset of the instability. The ionization rate in equation (2) scales with the neutral gas density \( n \) and therefore, the development of an instability is much faster in atmospheric pressure plasmas than in their low pressure counterparts. An example of the development of an instability in a pulsed atmospheric pressure air glow discharge is shown in figure 7.

The most common instability is the so-called thermal instability. This instability is triggered by small fluctuations in the electron density that lead to the following chain of events. An increase in electron density leads to increased Joule heating and thereby a localized increase in the gas temperature and decrease in gas background density. Assuming that the electric field in the positive column of a glow discharge remains constant, \( E/n \) will then increase, causing an increase in \( T_e \). The increase in \( T_e \) leads to an increased ionization frequency (\( \nu_i \)), which further increases \( n_e \), leading to positive feedback and unstable behavior. The cycle leading to the instability can be summarized as follows:

\[
\delta n_e \uparrow \rightarrow \delta T_e \uparrow \rightarrow \delta \left( \frac{E}{n} \right) \uparrow \rightarrow \delta T_e \uparrow \rightarrow \delta \nu_i \uparrow \rightarrow \delta n_e \uparrow. \quad (3)
\]

Runaway behavior of the ionization rate can also occur due to stepwise ionization. The ionization rate coefficient of metastable species, particularly in noble gases are orders of magnitude larger than direct ionization of the ground state species. Hence, when the density of metastable species reach a critical value, the direct ionization is taken over by stepwise ionization. This can lead to a sudden increase of the ionization rate. Instabilities often occur when the dominant ion is a dimer such as in an atmospheric pressure Ar discharge. In the case of Ar, the electron–ion recombination of \( \text{Ar}_2 \) leads to the production of an Ar metastable atom which is readily re-ionized to \( \text{Ar}^+ \). As the formation of \( \text{Ar}_2 \) from Ar is very fast at atmospheric pressure, intrinsically a very fast recycling between the ion and the metastable occurs which is prone to trigger instabilities. Further considerations about the relation between these reactions and the contraction of a discharge channel in an atmospheric pressure microwave discharge can be found in [51].

Another cause of instability can be encountered when the dominant electron loss process has a strong dependence on \( T_e \). An example of this is an attachment instability. Attachment on its own does not lead to an instability. However, in electronegative plasmas, attachment may be balanced not only by ionization but also by detachment. As the detachment rate is in good approximation independent of \( T_e \), a reduction in \( T_e \) leads to a decrease in the ionization and attachment rates but not the detachment rate. Therefore, if the attachment is mainly balanced by detachment and not ionization, the unchanged detachment rate can lead to an uncontrolled increase in the electron density.

The above description of instabilities suggests that instabilities occur in the bulk plasma and indeed contractions of the positive column of atmospheric pressure glow discharge have been observed. Nonetheless, studies of diffuse

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Figure 6. Overview of the different transitions that occur in atmospheric pressure plasma discharges.
glow discharges in the context of laser at tens to hundreds of Torr have also shown that the anode layer has a voltage current characteristic with a negative slope \cite{52}. Such an anode layer is unstable and similarly to a cathode layer of an abnormal glow discharge susceptible of radial constriction (see e.g. \cite{4}). The shrinkage of the anode layer finally results in the formation of anode spot(s) with high current density that can trigger an instability. Similarly, cathode spot formation has also been observed to trigger instabilities \cite{53}. The instability criterion in these cases has been empirically related to the dissipation of a critical surface energy density. Mesyats reports that the formation of a cathode spot can be triggered by the formation of an ecton (i.e. an electron avalanche from a metal induced by an electron explosive emission center) owing to field emission \cite{38}. Streamer discharges can undergo a transition to more intense spark discharges. A streamer propagates in the discharge gap, but does not necessarily connects the two opposite electrodes. However, when this happens, a conductive plasma channel is formed. The entire gap voltage is across this conductive channel which leads to an increased ionization and subsequent instability. Typical times for excessive gas heating occurs on \(~\sim\)100 ns at atmospheric pressure and a streamer-to-spark transition typically happens on such time scales. However, instabilities in nanosecond spark discharges have also been reported. Despite the potential involvement of fast gas heating, gas heating is not a pre-requisite for the formation of a spark discharge as this could also be due to a sudden increase in the ionization rate due, for example, to stepwise ionization. An intense spark channel can transform into an even more intense arc discharge on a timescale of hundreds of microseconds if the power supply can deliver the necessary power and current.

In filamentary discharges for which the current is limited and the increase in electron density that triggers the spark formation is prevented, a streamer can develop into a transient glow discharge (see further discussion in the context of dielectric barrier discharges).

The rapid increase in electron density observed in some of these instabilities also leads to an increased importance of electron–electron Coulomb collisions. In low electron density plasmas \((n_e \ll n)\), the EEDF is mainly determined by electron-neutral collisions and the high-energy tail of the distribution is typically depleted due to the fast electron energy loss in inelastic processes. In high-density plasmas, electron–electron Coulomb collisions become important and cause a Maxwellization of the EEDF, which in turn increases the ionization rate.

Figure 7. Example of the development of an instability in a nanosecond pulsed glow discharge in air between a metal pin electrode and a liquid surface. Reproduced from \cite{50}. © IOP Publishing Ltd. All rights reserved.

![Image](image110x718 to 487x773)

Figure 8. Schematic of lumped and distributed ballast for stabilizing discharges.

6. Discharge generation and stabilization

6.1. Current limitation (ballast)

The most straightforward approach to avoid spark or arc formation is to limit the discharge current. However, as transitions and instabilities typically occur on submicrosecond time scales, active feedback control approaches cannot respond quickly enough. Instead, passive electrical components in series with the discharge are typically used to limit the discharge current (figure 8). The passive component in the circuit is often referred to as a ballast. For example, a resistor with a well chosen resistance value \((R)\) in series with a discharge will limit the current of the discharge \((I)\) because for a fixed applied voltage \((V_{\text{app}})\), any increase in current due to an increase in plasma conductivity will lead to a drop of the voltage across the plasma \((V_p)\) in favor of an increasing voltage across the resistor \((V_b = IR)\): \(V_p = V_{\text{app}} - IR.\) (4)

Interestingly, similar effect can be achieved with capacitors and inductors. In these cases, the voltage across the plasma is: \(V_p = V_{\text{app}} - L \frac{\text{d}I}{\text{d}t},\) \(V_p = V_{\text{app}} - \frac{1}{C} \int_0^t I \text{d}t.\) (5)

While in the case of a resistor the voltage drop across the plasma reduces proportionally to the plasma current, in the case of the inductor the reduction is more pronounced for fast current changes and in the case of a capacitor the reduction in discharge voltage has a memory effect. Intrinsically, the capacitor and inductor can have a stronger impact on transient phenomena than the resistor. The capacitor is typically used for sinusoidal excited plasmas (as it blocks any DC current)
while a resistive ballast is preferred to stabilize DC operated plasmas.

The above stabilization approach consists of a lumped passive circuit component that is able to successfully stabilize DC corona discharge, dielectric barrier discharges and low-pressure glow discharges. However, this approach is in many cases not able to prevent plasma instabilities such as a contraction of a diffuse plasma into a filament in atmospheric pressure discharges. A more stable and effective approach in this case is the use of distributed ballasts. A distributed resistor is equivalent to the use of a resistive electrode and indeed atmospheric pressure glow discharges have been stabilized by the use of semiconductor and liquid electrodes with finite conductivity [54, 55]. Particularly in the case of a liquid electrode, it has been shown that spark formation due to instabilities in the gas phase can still occur but the contraction of the discharge at the liquid electrode is significantly delayed due to the inability of the electrode to transport the injected charge of a high intensity spark channel because of its finite conductivity [56].

DBDs use a similar principle. In this case, the distributed capacitor is a dielectric barrier placed between the metal electrode and the discharge gap. This approach only works for AC driven or pulsed discharges as a displacement current through the non-conductive dielectric barrier is required to allow for current continuity between the conduction current in the discharge and the metal electrode connected to the electrical circuit. In this case, the voltage limitation across the discharge gap is due to charge deposition on the dielectric that reduces the local electric field in the discharge gap (see also further).

An interesting example of an inductively stabilized DBD which combines the distributed dielectric barrier with a lumped inductance in the circuit has been developed by van de Sanden et al [57]. This approach led to a diffuse discharge which was not possible with the dielectric barrier only. This example demonstrates the potential huge benefit of a detailed design of the electrical circuit on the discharge operation.

The electrical configuration of a DBD is actually very similar to an RF driven discharge between two parallel metal electrodes. In this case, there is no dielectric insulating barrier but instead the plasma sheath acts as a distributed capacitor between the bulk plasma and the metal electrode. A key difference however is the physical interface of the dielectric barrier that allows for charge accumulation. This capacitive nature of the sheath is a typical feature of an RF discharge, as electrons are depleted and the inertia of the ions is too large to respond to the RF field. In this case, current continuity is achieved through displacement current caused by the movement of the sheath in the RF field. This is very different for a DC sheath where secondary emission current through the sheath enables the sustainment of the discharge [4]. However, as the ‘barrier’ in this case is a gas which can be ionized, this configuration is much more prone to instabilities. A breakdown of this sheath can easily occur when for example a thermal instability occurs. This enables the development of an intense filament that connects both metal electrodes. To this end, researchers have investigated RF discharges with dielectric barriers [58]. Nonetheless, this approach is often unpractical as the additional barrier requires higher voltages which are easy to achieve for power supplies operating in the kHz frequency range but needs special amplifiers or circuits for power supplies in the MHz frequency range (RF).

6.2. Transient discharges

Another straightforward approach to prevent thermalization is to limit the discharge duration. A transient discharge can be realized by using short voltage pulses or by exploiting the self-limiting behavior of discharges such as in the DBD. Although time scales are discharge specific, the transient behavior at atmospheric pressure is typically in a time scale of <100 ns, in line with typical time scales for gas heating and glow-to-spark transitions.

6.2.1. Dielectric barrier discharge (DBD).

One of the most used charge-limited, transient atmospheric pressure plasmas is the DBD. As mentioned above, DBD is characterized by an insulating material in the discharge path [9]. Dielectric materials include glass, quartz, ceramics, enamel, mica, plastics, silicon rubber or teflon and in atmospheric pressure plasmas the discharge gap is typically in the range of 0.1–10 mm. The amplitude of the alternating or pulsed high voltage required to sustain a discharge is in the range 1–100 kV and it depends on the gas and the electrode gap dimensions.

A large number of electrode arrangements exists. A so-called volume DBD is shown in figure 9(a). In this arrangement, at least one of the electrodes is covered by a dielectric barrier. Volume DBDs can also be created by placing the dielectric layer in the discharge gap between the two metal electrodes, dividing the gap in two sections [59]. Packed bed DBDs have the space between the electrodes filled with pellets or spheres made of dielectric or ferroelectric material. The polarization of the pellet material generates plasma in the void spaces between the pellets and on their surface. Another DBD electrode arrangement is that used in surface DBDs. Here, both electrodes are in direct contact with the barrier and the plasma forms at the exposed surface electrode (see figure 4(a)) [60]. Alternatively, both electrodes can be embedded inside the insulator to create a coplanar DBD in which the discharge appears in the gas above the dielectric surface. A popular atmospheric pressure DBD structure is that of an atmospheric pressure plasma jet (figure 9(b)) [61]. The gas flowing through the arrangement extends the plasma as an effluent into the surrounding gas. Whether a plasma jet can be considered as a DBD or not is mainly determined by the frequency of the applied voltage as the majority of jets consist of a dielectric tube in between the plasma and at least one of the electrodes. An overview of the large majority of different DBD arrangements and reactors including some additional special configurations can be found in [62].

In most molecular gases but also in argon or mixtures of noble gases with molecular gases, the streamer mechanism lead to so-called microdischarges that visually appear as
filaments (see example in figure 10(a)). The microdischarge development starts with a (Townsend) pre-phase (a weak, localized light spot at the anode) which can last for several 100 ns [63]. When the local electric field strength of the accumulated positive space charge in front of the anode reaches a critical value the propagation of a cathode-directed ionization wave (positive streamer mechanism) starts. Behind the streamer a transient glow-discharge like plasma channel develops [60]. The plasma decays due to the accumulation of charge carriers on the barrier surfaces and the reduction of the axial electric field strength. The microdischarge channels are spreading on the barrier surface covering a region much larger than the original channel diameter. An increase of the voltage amplitude in an AC operated, plane parallel discharge gap DBD leads to a higher number of microdischarge per active phase, but will not necessarily change the amount of charge transferred to a single microdischarge.

The duration of microdischarges is determined by the gas as well as the discharge arrangement (gas gap, type, and thickness of barriers). In air at 1 atmosphere and 1 mm discharge gap the microdischarges have a duration between 10 and 100 ns with a total transferred charge of 0.1–10 nC. Microdischarges in argon can have a duration of a few μs. The maximum current density can reach up to 1000 A cm⁻². While many discharges are filamentary, volume space charge and surface charges distribute plasma filaments across the entire electrode area. In many cases self-organizing patterns have also been observed [59].

At frequencies in the MHz-range the current limitation by the dielectric becomes less effective, the breakdown voltage decreases, and the discharge operation changes significantly [64]. The discharge does not behave anymore as a DBD as discussed above. The role of the barrier is no longer to induce the self-pulsing character in this case and the discharge operates in steady state. Its properties are comparable with RF discharges or capacitively coupled plasmas in the α-mode, i.e. the electron production that sustains the discharges is in the gas phase rather than by secondary electron acceleration across the sheath (γ-mode). Under selected conditions DBDs can be operated in a diffuse mode with uniform plasma formation as it will be discussed in section 6.3.

6.2.2. Partial and nanosecond pulsed corona discharges.
Partial and nanosecond pulsed discharges are typically produced in the close vicinity of a pin or a thin wire electrode, where the electric field is locally enhanced
The asymmetric electrode geometry leads to a decrease in the electric field with increasing distance from the pin or wire electrode. Typically, the applied electric field value drops below the breakdown electric field at a certain distance from the electrode and if the current or voltage is limited the discharge development is inhibited. In this case, the discharge does not extend up to the counter electrode (see the example in figure 10(c)), hence the name partial discharge. Discharges generated in electrode geometries that enable such a local electric field enhancement are often referred to as corona discharges [13].

In the case of DC excited corona discharges, the electrode gap can be divided in two zones: the high electric field region in which highly energetic electrons are produced and the ion drift region in which the electric field is low and the continuity of current towards the second electrode is guaranteed by a flux of positive ions in the case of positive corona or negative ions produced by electron attachment in electronegative gases for negative corona. The morphology of the discharge depends on polarity and the applied voltage [65, 66]. While continuous glow corona exists, many modes of DC corona consists of current pulses and the formation of streamers. An example of a DC transient negative corona discharge mode is the Trichel pulse regime, which consists of current pulses with a nearly regular repetition rate. The pulsating nature of the discharge is due to space-charge effects [67].

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Figure 10. Examples of atmospheric pressure non-equilibrium plasmas. (a) Parallel-plate filamentary dielectric barrier discharge in atmospheric pressure air. (b) Atmospheric pressure He plasma jet propagating in three different ambient gases: nitrogen, air, and O₂. Reprinted from [83], with the permission of AIP Publishing. (c) DC corona in atmospheric air. (d) 50 μs exposure time image of a transient streamer in air. Reprinted from [84]. © IOP Publishing Ltd. All rights reserved. (e) 10 ns pulsed discharge in air operating in corona, glow and spark regimes at 5 kV, 5.5 kV and 6 kV, respectively. Reprinted from [85]. © IOP Publishing Ltd. All rights reserved. (f) Capacitively coupled RF (13.56 MHz) plasma sustained in helium at atmospheric pressure. Reprinted from [86]. © IOP Publishing Ltd. All rights reserved. (g) 3-electrode DC plasma in argon at 160 Torr in which a microhollow cathode (left electrodes) serves as a virtual cathode for a DC discharge sustained between the virtual cathode and an anode (right electrode). Reprinted from [87], with the permission of AIP Publishing. (h) Front view of a 10 cm × 10 cm Xe₂ VUV (172 nm) lamp consisting of an array of encapsulated microplasmas operating in 70% Xe/Ne admixture at 550 Torr. Reprinted from [88]. CC BY 4.0. (i) MW microplasma array operating in 100 Torr argon. Reprinted from [91]. © IOP Publishing Ltd. All rights reserved. (j) 2.45 GHz surfatron operated in argon at atmospheric pressure. Reprinted with permission from [92]. (k) Gliding arc operating in ambient air. Reprinted from [93], with the permission of AIP Publishing.
It is relatively straightforward to achieve conditions satisfying the Meek criterion close to a pin or thin wire electrode leading to the formation of streamers. In addition, steep voltage rise times combined with high overvoltages allows one to strongly impact the plasma parameters. In particular higher number densities of reactive species than in classical DC or AC operated discharges can be generated as the input power can be increased. At sufficiently high field strengths, even runaway electrons can be generated which can lead to the generation of x-rays [68, 69].

For many applications, it is crucial to increase the power deposition in the discharge while maintaining the non-equilibrium character. While overvoltages can be used, they need to be applied for a short time to prevent the streamer-to-spark transition. The short duration of the voltage pulse inhibits streamer growth before it reaches the ground electrode and a spark can be formed. An example of a nanosecond pulsed streamer discharge consisting of branching streamers with a length of several cm is shown in figure 10(d) with corresponding geometry in figure 9(d). Typical streamer velocities in air are in the range \(10^3-10^6\) m/s, depending on applied voltage and polarity. The highest velocity requires 100 ns to bridge a gap of 10 cm hence a well chosen geometry and pulse duration of tens to hundreds of nanoseconds is often able to prevent spark formation. Another approach is to cover the ground electrode with a dielectric barrier.

In recent years, there has been a large interest in the production of nanosecond pulsed glow and spark discharges in pin-pin geometries in the context of plasma assisted combustion. These discharges are typically generated with a high repetition rate in the kHz range (see figures 9(e) and 10(e)). At moderate voltages, these discharges, even in air, are able to operate in a glow mode. However, even for voltage pulses with a duration of 10 ns, spark discharges have been obtained, as demonstrated in figure 10(e) [70]. The transition from a streamer or glow to spark in this case is shown to be enhanced by accumulated effects over multiple discharge pulses. However, fast gas heating on nanosecond time scales in air and stepwise ionization in noble gases can also cause the transition on a nanosecond timescale [71]. The exact discharge geometry, electrode properties, gas composition and potential presence of gas flow have a strong influence on the discharge mode and its instabilities. The transient spark is a non-equilibrium and highly reactive plasma, with an electron density that can be several orders of magnitude higher than for the ionization of Ar. In general, metastable states threshold for Ar metastable production is about 5 eV lower than for the ionization of Ar. In general, metastable states induce a variety of multistage or indirect ionization processes like stepwise ionization and Penning ionization which can affect the discharge formation mechanism and a Townsend discharge can be obtained at elevated pressures [74]. Glow discharges 10

The importance of the gas composition can be illustrated by an example: a DBD in Ar at atmospheric pressure is typically filamentary although when adding a small amount of NH₃ the discharge can become diffuse. This is due to the Penning ionization of NH₃ through Ar metastables. The breakdown electric field reduces in this case as the energy threshold for Ar metastable production is about 5 eV lower than for the ionization of Ar. In general, metastable states induce a variety of multistage or indirect ionization processes like stepwise ionization and Penning ionization which can affect the discharge formation mechanism and a Townsend discharge can be obtained at elevated pressures [74].

Typically, two discharge types are achieved for diffuse discharges: very low density Townsend discharges (with negligible space charge and a homogeneous electric field) and glow discharges that develop from a Townsend breakdown after the formation of a cathode fall [74]. Glow discharges...
have a higher electron density and tend to be unstable often leading to a narrow stable operation window. The applied voltage waveform is thus extremely important for the stability of the diffuse operation of the glow discharge as well.

While in many cases diffuse large scale glow discharges are produced in DBD geometries, there are cases of uniform discharges generated between two metal electrodes. RF driven diffuse glow discharges in He [75], which can also be characterized as a capacitively coupled plasma (CCP, see figures 9(f) and 10(f)) are an example of such discharges. It is difficult to have a pure helium discharge and in many cases the dominant ion is from the impurity making Penning ionization the dominant ionization mechanism. Similarly, a diffuse discharge can also be generated for nanosecond pulsed excitation in the same reactor geometry in helium. The pulse width in this case is smaller than the time scale to develop an instability (~a few 100 ns). It has also been observed that high overvoltages at which the applied electric field is much higher than the breakdown voltage can lead to more diffuse discharge generation in air [73]. The detailed mechanism is in this case still under investigation.

6.4. Flow stabilized discharges and micro-plasmas

Besides limiting the discharge duration and/or current, additional approaches are commonly used to maintain stable non-equilibrium plasmas at atmospheric pressure. For example, many non-equilibrium atmospheric pressure plasmas, specially those in direct contact with temperature sensitive substrates, operate in noble gases. This is because when molecular gases are used, significant amount of energy is lost via vibrational excitation of the background gas. While this may be a desirable process for some applications (e.g. in CO₂ dissociation via vibrational excitation), vibrational states eventually transfer their energy into rotational and translational states (V–V and V–T relaxation), thereby heating the background gas. The use of noble gases as background gas eliminates this heating mechanism. In particular, helium is widely used as a carrier gas because it is not only an atomic gas but it also has a high thermal conductivity (~6 times that of air and ~8 times that of argon).

Other approaches aimed at preventing excessive gas heating in atmospheric pressure plasmas include active cooling of the electrodes, cooling of the inlet gas and modulation of the input power. For example, modulation of the input power with a duty cycle of 20% reduces the average power dissipated in the discharge by a factor 5, hence lowering significantly the final gas temperature. Importantly, as many reactive species have lifetimes of several 10–100 s μs, if the modulation is done at a sufficiently high frequency, it may have only minimal impact on the concentration of the relevant reactive species [76].

Gas flow is an additional parameter that can be used to manage thermal loading of the device and control discharge stability [77]. For example, in plasma jets gas is forced through the plasma, contributing to the removal of heat away from the discharge and at the same time the enhancement of the transport of plasma species away from the discharge and onto the target [61, 78]. Unfortunately, as it is often the case in plasmas, an external parameter affects multiple aspects of the discharge simultaneously, and here varying the gas flow rate does not only control heat removal but also affect mixing of gases and residence time of species, which will affect the overall performance of the plasma source (see figures 4(b) and 9(b)).

Despite being susceptible to chaotic operation and very sensitive to operational conditions, plasma jets have become popular devices among scientists working in the field of material processing and medical applications as these devices are well suited for the delivery of localized treatments [61, 78]. Different electrode configurations and operation frequencies (DC, kHz, MHz and GHz) have been reported in the literature and in nearly all cases a noble gas is used as a carrier gas to generate a channel in which ionization takes place preferentially. Although the visual appearance of most jets is quite similar, the underpinning physics can be quite different. Long plasma plumes observed in kHz and nanosecond pulsed jets are often guided streamers confined in the noble gas channel created by the gas flow [89, 90]. This confinement is due to the spatial gradient of the α coefficient that drastically reduces with increasing air concentration at the edge of the noble gas channel and the electrostatic focusing caused by negative ions (e.g. O₂⁻) in the mixing region. As shown in figure 10(b), the composition of the ambient in which the jet operates has a strong influence on the appearance and properties of these jets.

Thermal dissipation can also be enhanced by having a large surface to volume ratio and as a result many non-equilibrium atmospheric pressure plasma sources rely on creating small discharges in parallel (arrays). The small size not only helps in maintaining a large surface to volume ratio but also favors operation closer to the minimum of the Paschen curve. Advances and popularization of microfabrication techniques in the 1990s triggered the development of the so-called microplasmas and microplasma arrays, reviving the interest in atmospheric pressure discharges. Many different electrode configurations exists and several review papers have been written on this topic [19, 79–81].

Figures 9(g) and 10(g) depict a 3-electrode DC plasma in which a microhollow cathode discharge is used as a virtual ‘plasma cathode’ to maintain a larger volume stable plasma between the microhollow cathode and a third positively biased electrode. In this device, the plasma cathode reduces the cathode fall and allows the generation of a larger and more stable plasma [82, 87]. DC microdischarges have been widely studied and are appealing for their relative simplicity. Operation in DC fields, however, requires large breakdown voltages and the constant bombardment of the cathode required for DC operation limits the lifetime of these devices even when low-sputtering yield materials are used. Nonetheless, this limitation of DC microplasmas can be turned into a strength in applications that use liquids as an electrode because eroded material is easily replenished. DC microplasmas have therefore received renewed attention in applications involving plasma-liquid interactions with applications for both analytical and electrochemical purposes.
Arrays of DC microdischarges have been operated without the need of external ballast resistors when plasmas are operated in the abnormal glow mode. In this mode each discharge displays a positive differential resistance, making parallel operation possible. Uniformity of the arrays, however, is often affected by the current distribution across thin film electrodes, which ultimately limits the number of microdischarges that can be operated in parallel. AC and pulsed excitation, however, enable operation of larger arrays (see e.g. figures 9(h)). An example of a microplasma array operating at 135 kHz is shown in figure 10(h). In particular, the image depicts a 25 W VUV (172 nm) lamp consisting of interlaced arrays of microplasmas operating in 70% Xe/Ne mixture at 550 Torr (at 300 K).

Microwave operated plasmas are well-known in the field of low pressure plasmas as they enable high power absorption resulting in high electron densities. In case of higher pressures the power deposition criterion is even better matched and an efficient plasma generation is possible [8]. Also non-equilibrium and small-scale microwave driven plasmas can be generated at atmospheric pressure. Figure 10(i) shows an example of an array of microwave microplasmas operating in argon at 100 Torr. These MW microplasmas typically use guides such as microstrip lines, coaxial structures or strip lines instead of lumped circuit elements, resulting in compact and robust designs that minimize radiation losses and interference. Interestingly, MW microplasmas self-stabilize, preventing the transition into an arc. The lower sheath voltages encountered in these high frequency plasmas result in efficient discharges and long-lived devices. Although driven at MW frequencies, these microplasmas can be viewed as high frequency CCPs, because the actual plasma dimensions are much smaller than the wavelength of the excitation frequency. Larger atmospheric pressure MW plasmas are typically sustained by surfatrons (see figures 9(j) and 10(j)) or slotted waveguides, devices that have also been adapted to create microplasmas [76, 95–97].

Figures 9(k) and 10(k) show the gliding arc operating in atmospheric pressure air. Gliding arcs are another example of plasma sources that depend on gas flow to reach a non-equilibrium state. Here, the discharge is generated across two diverging electrodes. Initially it ignites at the position of the shortest distance between the electrodes and forms a quasi-thermal plasma. This discharge then moves upwards (glides) between the electrodes due to the applied gas flow and/or the buoyancy force. The diverging geometry of the electrodes causes the length of the plasma to increase and the power supply eventually is not able to deliver enough input energy to maintained the increasingly longer discharge. As a result, the discharge intensity decreases and the original quasi-thermal plasma is converted into a non-equilibrium plasma before the plasma extinguishes and a new arc is formed [93, 94].

While heat losses are important to prevent an excessive rise of the gas temperature and maintain the non-equilibrium character in atmospheric pressure plasmas, losses of charged and metastable species also play an important role in maintaining discharge stability, for example, by reducing the effective ionization rate. Many of the techniques described above (e.g. use of helium, forced flows and large surface to volume ratios) simultaneously affect both heat and particle losses, thereby contributing in more than one way to the non-equilibrium nature of the discharge.

7. Conclusion and outlook

An extremely rich variety of non-equilibrium atmospheric pressure plasmas exists ranging from Townsend discharges to spark discharges that span a range of ionization degrees of 10 orders of magnitude. This paper attempts to provide an introductive overview of the main aspects of these plasmas but is far from being complete. We did for example not deal with thermal atmospheric pressure plasmas that in spite their name have often significant non-equilibrium effects as has been discussed in the related foundations article on this topic.

While the ability to generate stable low temperature, atmospheric pressure plasmas is well established, new operation approaches and plasma regimes are continuously being explored. The physics and chemistry of these complex discharges are less understood and studied than those of their low pressure counterparts. A strong coupling between plasma kinetics, heat transfer, chemistry and fluid dynamics makes these plasmas an intrinsic multidisciplinary problem. The particular properties and unique conditions of these discharges underpin many applications that would not be possible by other technologies. In addition, the self-organizing nature and filamentation of atmospheric pressure plasmas leading to significant spatial and temporal gradients in plasma properties provides many additional challenges and interesting scientific questions. The high collisionality and non-equilibrium nature of the plasma are also strongly complicating factors for the interpretation of diagnostics.

New applications continuously drive to explore the interaction of plasma with previously unexplored substrates including living tissue and complex solutions, which only increases this challenge. While detailed characterization starts to emerge for a few atmospheric pressure plasma sources, the plasma properties and kinetics for higher gas densities, including liquids and supercritical fluids remain relative unexplored.

Despite their long history, recent developments in state-of-the-art diagnostics and modeling capabilities will provide the unique opportunity to tackle these challenges and move the important field of non-equilibrium atmospheric pressure plasmas towards new exciting science and unique applications that will without doubt be of great benefit for our society.

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References

[37] Mesyats G A 1995 Phys.—Usp. 38 867–91
[67] Loeb L B 1952 Phys. Rev. 86 256
[92] van Gessel A F H 2013 Laser diagnostics on atmospheric pressure plasma jets PhD Thesis Eindhoven University of Technology