Plasma Agriculture

Plasma Agriculture:

Oxygen Plasma Effects on Garlic

By

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and Miran Mozetič

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PREFACE

This book examines the effects of gaseous plasma treatment on garlic cloves. The idea to expose garlic to the effects of plasma stems from the concept of "plasma agriculture", which has been a part of agricultural research trends for the last decade or so. Today, the physical phenomenon of non-thermal, highly reactive gaseous plasma is already widely employed in a variety of industrial applications, from microelectronics to medicine. The beneficial effects of plasma are mainly attributed to its unique mixture of reactive species, charged particles (ions, electrons), electric field, and ultraviolet radiation. In recent years, it has additionally become clear that, when properly applied, plasma can have a variety of beneficial effects on living organisms. In humans, this includes medicinal or cosmetic applications such as improved wound healing or effective teeth whitening. In the field of agriculture, however, many studies now show how exposure of seeds to plasma can boost plant germination, growth, or resistance of plants to disease. This includes important food crops such as wheat, corn, soy, and many more. These crops are all routinely propagated using seeds. Most garlic used in agriculture, however, is sterile and cannot produce seeds. Instead, it is propagated using cloves – the most well-known edible part of the plant, but also a vegetative propagation material, genetically identical to the parent plant, but simultaneously very different from the typical agricultural seed in size, weight, and water content.

By using garlic as a model organism to explain plasma agriculture principles, this work shows that many of them hold true for garlic cloves just as well as for seeds of agricultural plants. To illustrate this, it considers the physico-chemical effects of oxygen plasma on the garlic clove surface, together with the biological effects of such treatment. Plasma increases wettability of the clove surface; this is a result of functionalization, as the reactive oxygen species in the plasma oxidize the cuticle surface. Etching and the resulting nanostructuring of the surface additionally contribute to increased wettability. As a result of this hydrophilicity increase, water uptake of cloves increases as well. The biochemical mechanisms activated in this way accelerate clove germination and early growth of sprouts and roots. The garlic plants grown from optimally plasma-treated cloves also exhibit a higher yield than plants grown from untreated cloves. The behavior of unpeeled and peeled cloves differs due to surface chemistry and biological function differences.

The garlic used as sample material throughout this book is the Slovenian autochthonous cultivar *Ptujski spomladanski*. The improvements in growth and yield could strengthen its presence and availability, which are threatened by imported varieties. Thereby, local and sustainable agricultural practices could be supported by innovative technology practices. At the same time, the plasma technology is ecologically more acceptable than traditional, chemical-based approaches, as it uses abundant materials and does not introduce toxic compounds into the environment.

In addition to the specific effects of plasma on garlic, the book further seeks to explain the physical basics of low-pressure oxygen plasma. It stresses the importance of analyzing plasma characteristics directly, as opposed to simply adjusting discharge parameters. Non-thermal plasmas with conditions suitable for biological material treatment are commonly formed in laboratory environments, as well as scaled up to industrial-size reactors, both of which are used to generate the results presented in the course of this book. We show that by properly tuning the plasma and discharge parameters, as well as studying the physico-chemical effects of plasma on the treated material, it is possible to achieve the desired biological responses of the treated garlic cloves – that is, stimulation of garlic germination, growth, and improvement of its yield. As such, the book provides insights on the current understanding of plasma agriculture and encourages further steps in exploring the effects and benefits of this unique approach.

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1. GARLIC

1.1 Cultivation

Garlic (*Allium sativum* L.) is an important agricultural crop, with world production totaling over 24 million tons in 2013 (Food and Agriculture Organization of the United Nations 2015). Garlic growers aim to produce a high yield of a high-quality crop (Brewster 2008), but production remains limited by the region and climate (Wu et al. 2015, 43-52).

The main difference between the production of garlic and other crops is in the propagation. Cereals and other agriculturally cultivated plants are propagated sexually, through seeds. But while researchers have indeed discovered fertile clones of garlic some three decades ago in central Asia (Etoh 1986, 312-319), the commercially cultivated varieties of garlic remain sterile. As such, they do not produce seeds, and must be propagated vegetatively (Rabinowitch and Brewster 1989) – by planting individual cloves which germinate and produce new, genetically identical plants (Brewster 2008). This means that while it is possible to improve crops such as cereal, and even other alliums, by conventional or innovative breeding techniques (Mondal et al. 2016, 991), these are not applicable to agriculturally produced garlic, where we must consider alternative methods of crop improvement. Using such methods, we can improve garlic germination and growth without the need for genetic engineering, and propagate established or autochthonous cultivars instead.

Depending on climate and cultivar, garlic is typically planted either in the fall (September to November) or in the spring (January to March), both for a harvest in the summer. Ideally, the timing should be such that development begins after planting, but the plant does not emerge from the soil before the first frost (Kamenetsky 2007, 123-172). The local Slovenian garlic cultivars are either fall- or spring-planted. Among them, the cultivar *Ptujski spomladanski* was specifically adapted for long bulb storage time to enable spring planting. However, any garlic planted in the spring lacks the advantage of starting its development in the fall, and therefore requires early planting to properly develop its root system in time. Further, it may lack the low temperature exposure required to break dormancy and initiate clove formation and bulbing (Kamenetsky 2007, 123-172). External conditions such as wet soil or freezing of the soil due to low temperatures often hinder planting at the optimal time. To overcome these uncertainties brought on by external factors, it is beneficial to strengthen the garlic plant and improve its germination so that bulbs may grow efficiently, leading to high yields.

1.2 Anatomy

1.2.1 Bulbs and cloves

The underground part of a garlic plant is commonly called a bulb. Each bulb consists of several cloves. A clove is a storage bud consisting of a sprout leaf, found within a storage leaf, which is further covered by a protective leaf. The clove anatomy is schematically shown in Figure 1.1. The sprout leaf is the first leaf to emerge when the plant begins to actively grow, and is followed by foliage leaves. The storage leaf provides the food reserve required for the early growth. The protective leaf envelops the storage leaf of each clove, protecting it with its tough surface; it remains tightly wrapped around the clove when the bulb is broken apart. The cloves are further enveloped by layers of dry, white sheaths, which are the bases of the foliage leaves growing over ground. The anatomy of the protective leaf is very similar to that of the foliage leaf sheath (Mann 1952, 195-251). Leaves comprise of an upper and lower epidermis, and the mesophyll in between, with vascular bundles distributed throughout the latter (Evert and Eichorn 2012). In garlic, the epidermal cells are arranged in one row; a cross section of the top layers of the protective leaf is schematically shown in Figure 1.2. The storage leaf surface, which is the surface of the peeled clove, appears similar. However, its epidermis is comparably thin and delicate (Mann 1952, 195-251).

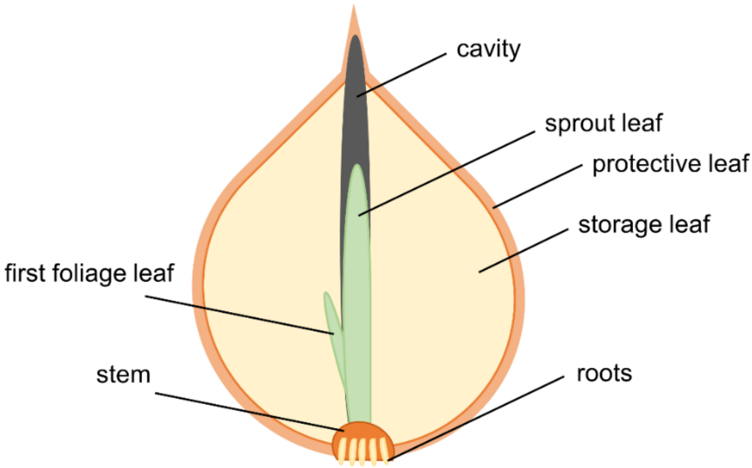

Figure 1.1: Garlic clove anatomy. Schematic representation. Adapted from (Mann 1952, 195-251).

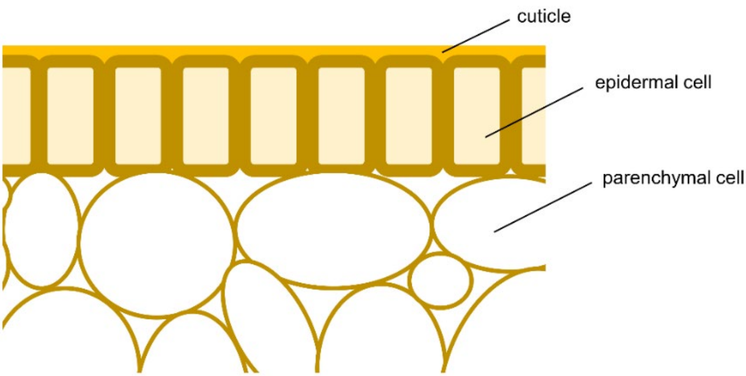

Figure 1.2: Schematic cross section of the protective leaf. Top layers are shown; the upper layer presents the sclerified epidermis, which is then further covered by a cuticle. Adapted from (Mann 1952, 195-251).

1.2.2 Clove surface chemistry

To understand how garlic cloves are affected by external treatments, such as exposure to gas plasma, we need to look at the composition of the very surface of clove components. The outer cellular layer of plant surfaces is the epidermis. As shown schematically in Figure 1.3, the epidermis is covered on the outer side by a cuticle (Mann 1952, 195-251), which is a layered, continuous non-cellular membrane composed of a polymeric lipid matrix embedded and covered with wax. In general, plant cuticle thickness is 0.1 – 10 µm (Riederer and Müller 2006). In garlic, this layer is known to be relatively thin (Mann 1952, 195-251).

Cuticular waxes are complex mixtures of compounds. As the name "wax" suggests, they consist of hydrophobic organic compounds. Chemically, the term wax usually refers to long-chain alkyl esters. However, in the cuticular context, it is used to also encompass compounds with different or additional functional groups, as well as other potential compounds present in this layer (Riederer and Müller 2006). Cuticular wax is additionally divided into two separate sub-layers: epicuticular waxes, which coat the outer surface of the cuticle, and intracuticular waxes, which are embedded in the cuticle matrix below. In a given plant species, chemical composition differs between the two sub-layers (Buschhaus and Jetter 2011, 841-853), but mainly in the relative amounts of the particular compounds (Riederer and Müller 2006). A standard array of cuticular wax compounds, found in virtually all plants studied to date, comprises fully saturated, unbranched hydrocarbon chains, from 20 to almost 40 carbon atoms in length, either as *n*-alkanes or containing a single terminal oxygen functional group: a hydroxyl, carbonyl, or carboxyl group, which gives a *n*-alcohol, *n*-aldehyde, or a fatty acid, respectively. In addition, the fatty acids and primary alcohols form an array of homologous esters, dimers of the aforementioned monomer compounds. The polymeric matrix of the cuticle is the biopolyester cutin, a primarily aliphatic polymer with long chains of methylene units linked by primary and secondary ester bonds (Riederer and Müller 2006). Glycerol is another monomeric component of cutin, and represents between 1 and 14 % of the total polymer composition (Graça et al. 2002, 205-215).

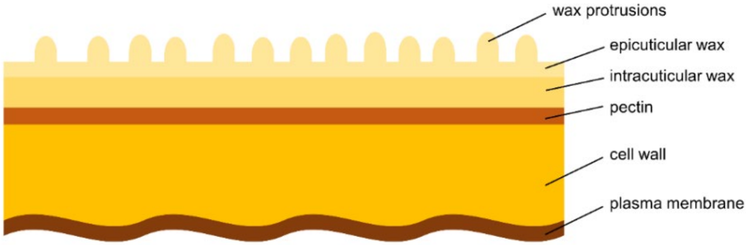

Figure 1.3: Anatomy of the outermost layers of plant epidermis. A pectin layer links the cuticle with the underlying cellulose cell wall of epidermis cells. Adapted from (Koch and Barthlott 2009, 1487-509).

1.2.3 Dormancy and germination

Germination is typically associated with emergence of the sprout from a seed. However, formally speaking, germination is the process from the first water uptake by the dry seed to the emergence of the radicle, which is the embryonic root of the plant. Further growth of the seedling, both sprout and root, after emergence of the radicle is called seedling establishment.

Before germination and growth may begin, plant propagation material of many species is in a resting state. Indeed, in a variety of plant seeds, as well as in garlic cloves, a phenomenon known as dormancy exists. The purpose of dormancy is to prevent germination in unfavorable seasons even if conditions are temporarily favorable. Dormancy needs to be released by additional environmental signals, such as light and temperature, before germination may begin. Release of dormancy allows for germination, which is the resumption of plant embryo growth after water uptake (Taiz et al. 2014; Graeber et al. 2012, 1769-86).

Garlic cloves are dormant when freshly harvested, and will not readily germinate (Mann 1952, 195-251). This period lasts for about 50 to 70 days, after which growth of the sprout leaf begins within the clove. As with seeds, dormancy of garlic cloves is controlled by the balance of plant hormones (Argüello et al. 1983, 1559-1563), and their external application to the clove accelerates germination (Rahman et al. 2006, 63-65). Roots emerge more rapidly than sprouts, even with dormancy breaking pre-treatment (Mann and Lewis 1956, 161-189). One important factor affecting garlic dormancy is temperature, as seed cloves need to be exposed to low temperatures for an optimal amount of time to achieve proper sprouting and bulbing. Normally this occurs after planting in the field, as garlic is planted in the autumn and harvested in the spring, thus experiencing the low temperatures during wintertime. Instead, cloves can also be exposed to low temperatures during storage, which affects both dormancy and bulbing (Brewster 2008).

2. PLASMA AGRICULTURE

2.1 Applications of plasma agriculture

Due to increasing food demands, and various factors affecting production, an improvement in the germination and growth of food crops is desired as a mechanism of increasing yields. Agricultural sustainability is desired to meet increasing food demands without harmful environmental effects (Araújo et al. 2016, 646). For example, wheat (*Triticum aestivum* L.) is one of the key cereal crops worldwide, and a major source of food. In 2015, an estimated 733 million tons of wheat were produced. In 2016, its required productivity growth was estimated at 1.1 % to meet consumption demands until 2020, while factors such as climate change, unpredictable environmental events, and various diseases or pests reduce yields and thereby further increase the need for production growth (Mondal et al. 2016, 991).

In agricultural research trends of the last decade, the discipline named plasma agriculture is a rapidly expanding field. It utilizes the processing capabilities of plasma treatment to improve properties of biological and food materials throughout the entire agricultural process, from seed to table. The aim of this research is to achieve optimal yields and increase food production, while simultaneously providing a high-quality, safe, environmentally friendly and affordable final product (Puač et al. 2018, 1700174). Plasma agriculture encompasses a variety of important applications such as disinfection of biological materials and food packaging materials, enhancement of seed or plant properties (Randeniya and de Groot 2015, 608-623), production and use of plasma-activated media (Thirumdas et al. 2018, 21-31), as well as plasma treatment of food (Thirumdas et al. 2015, 1-11).

2.2 Germination and growth improvement of agricultural seeds

In an attempt to avoid the excess use of fertilizers or chemical growth stimulants to improve plant performance in the field, plasma agriculture has delivered an environmentally acceptable alternative. The use of non-thermal plasma in agriculture is ecologically benign, does not introduce toxic compounds into the environment, and does not damage the sensitive planting material.

So far, gas plasma treatment of various agricultural seeds has been shown to affect many stages of plant germination and growth (Randeniya and de Groot 2015, 608-623). Germination rate, which is the percentage of germinated seeds at a given time point, has been improved for a variety of species, including seeds of quinoa (Gómez-Ramírez et al. 2017, 5924), rapeseed (Li et al. 2018), and peanut (Li et al. 2016, 1027-1033), using RF plasmas. After germination, various parameters of seedling growth were also improved, including sprout length, root length (Stolárik et al. 2015, 659-676; Dobrin et al. 2015, 255-260; Li et al. 2014, 5859), seedling dry weight (Stolárik et al. 2015, 659-676; Jiang et al. 2018, 044007), root fresh and dry weight (Henselová et al. 2012, 490-497), as well as other parameters. The selection of species included wheat, pea, maize, soybean, tomato, and other crops. A wide variety of plasma configurations has been used to achieve these effects, ranging from dielectric barrier discharge plasmas in atmospheric air to low pressure radio frequency discharges using a variety of process gases.

Further, planting of plasma-treated seeds can result in improved yield of agriculturally important crops. Increase in wheat yield was achieved by use of low-pressure helium plasma (Jiang et al. 2014, 54-58), low pressure air or air/helium plasma (Saberi et al. 2018, 11655; Zhang et al. 2018, 37-42), medium pressure air and air/oxygen plasma (Roy et al. 2017, 13-28), and an atmospheric pressure gliding arc discharge (Roy et al. 2018). Tomato yield was improved by treating seeds in an atmospheric pressure air plasma, either an arc discharge (Yin et al. 2005, 3143-3147) or a dielectric barrier discharge (Zhou et al. 2011, 23-27). A low pressure helium plasma improved peanut (Li et al. 2016, 1027-1033) as well as rapeseed yield (Li et al. 2018), while the seed yield of *Arabidopsis thailana* was improved by using air in an atmospheric pressure dielectric barrier discharge (Koga et al. 2016, 3).

2.3 Mechanisms of germination and growth improvement

Published research on plasma-induced seed germination and growth improvement currently focuses on the elucidation of physico-chemical and biochemical mechanisms by which plasma exerts its influence on the seeds. Plasma is uniquely suitable for modifying the outer layer of the seed surface, influencing its physico-chemical properties, without disrupting the bulk of the seed. As with polymer materials, the organic materials of the seed surface are targets for functionalization and etching by the reactive plasma species. In particular, treatment with a plasma that uses an O- or N-containing working gas increases the density of polar groups on the seed surface (Gómez-Ramírez et al. 2017, 5924; Bormashenko et al. 2012, 741). At the same time, plasma etching affects seed surface morphology by increasing its roughness (Meng et al. 2017, 1105-1119; Wang et al. 2017, 5601). Both increase the seed surface energy, causing hydrophilization (Zahoranová et al. 2018, 969-988). There appears to be a direct correlation between seed wettability and water uptake (da Silva et al. 2017, 280-285; Ambrico et al. 2017, 305401), which is the necessary first step in the seed germination process (Taiz et al. 2014). Increased hydrophilicity of the surface is therefore desired to enhance or accelerate seed hydration. Additionally, effects of etching may further facilitate seed coat permeability by the formation of cracks and pores on the seed surface (Stolárik et al. 2015, 659-676; Chen et al. 2012, 74-79).

In addition to these physico-chemical surface effects, the exposure of the seed to the plasma environment appears to activate certain biochemical pathways, thereby triggering a biological response. While the molecular mechanism of seed dormancy and germination are reasonably well known (Graeber et al. 2012, 1769-86), research in the field of plasma agriculture has only recently begun to investigate the effects of plasma on the seed biochemistry. These effects may be either specific, affecting certain signaling pathways, or part of a non-specific stress response of the seed to plasma treatment (Hayashi et al. 2015, 06GD01). The accelerated water uptake is a biological factor in itself, as it enables cell component mobility, restarting the seed metabolism after a period of quiescence or dormancy (Taiz et al. 2014). Further, concentrations of plant hormones involved in germination and dormancy are affected by plasma treatment (Ji et al. 2016, 117-28; Pérez Piza et al. 2018, 82-91; Stolárik et al. 2015, 659-676), an effect which may be related to the redox status and reactive oxygen species (ROS) signaling pathways of the seed. ROS are proposed to act as transmitters of environmental cues during germination, and the concept of an "oxidative window for germination" has been proposed to describe a critical range of ROS content in seeds that allows for dormancy release and germination (Bailly et al. 2008, 806-814). Exposure to the reactive plasma species could thus affect these mechanisms, and thereby, germination and growth.

By all of the above, plasma treatment of seeds can be considered a physical seed priming approach. Effect of plasma on both germination and yield varies with the selected plasma parameters, as well as plant species, and should be optimized for each specific treatment case.

3. GASEOUS PLASMA

3.1 Fourth state of matter

Gaseous plasma is one of the four fundamental states of matter, following the solid, liquid, and gaseous states. Adding sufficient additional energy to a gas results in a plasma – a state in which a substantial amount of molecules is dissociated and ionized, while the gas remains macroscopically neutral. The plasma state is abundant in nature. It is found on Earth in the form of lightning and aurora borealis, and comprises the majority of the remaining universe, such as the interior and corona of stars, or the solar wind (Fridman 2008). On the other hand, plasma is commonly formed in laboratory settings in various ways, typically by applying heat or a strong electric or electromagnetic field to a gas. Laboratory plasma systems vary widely in the possible selection of power sources, electrode configurations, reactor size, process gas, working pressure, etc. (Conrads and Schmidt 2000, 441-454). The purpose of such man-made plasmas is often tailoring of surface properties. Scaled up to an industrial level, they are applied in material, medical, electronic, and other sciences.

3.2 Thermal plasma

A plasma state achieved by gas heating is a thermal plasma. If a material is in a gaseous state, and the temperature of a gas is further increased, the molecules of the gas will dissociate into atoms, which at even higher temperatures will further dissociate into charged particles: electrons and ions. This effect is called ionization. Very high temperatures, in the range of several thousand Kelvin, are required for this to occur (Lieberman and Lichtenberg 2005). As such, thermal plasmas are unsuitable for direct treatment of biological materials or polymers, as at the required temperatures, thermal degradation of the treated material would take place. Thermal plasma is, however, a rich source of chemically reactive species such as atoms, radicals and metastable molecules. Thus, indirect treatment with thermal plasma may be of benefit, while also allowing to avoid substantial temperature increases and thermal degradation of treated materials.

For example, one hot plasma source of cold reactive gaseous species is a gliding arc discharge (Fridman et al. 1999, 211-231). The device is schematically presented in Figure 3.1. The distance between its electrodes is gradually increasing. There is a pressure difference across the device, which causes drifting of the gas through the narrowest gap between the electrodes and the gas expansion thereafter. The discharge is ignited by a simple DC power supply connected to one electrode, while the counter-electrode is grounded. This discharge, ignited at the narrowest part between the electrodes, causes formation of an electric arc (a hot plasma) in the gap between the electrodes. The gas flow pushes the arc towards the wider gap between the electrodes, where the gliding arc is observed. The gas temperature in the gliding arc is much lower than in the original arc in the narrowest gap, but charged particles as well as radicals persist even far away from the narrowest gap. The materials to be treated by the reactive gaseous species are placed at the widest gap between the electrodes, where the plasma is not thermal any more, but still rich in reactive gaseous species capable of interacting chemically with organic matter.

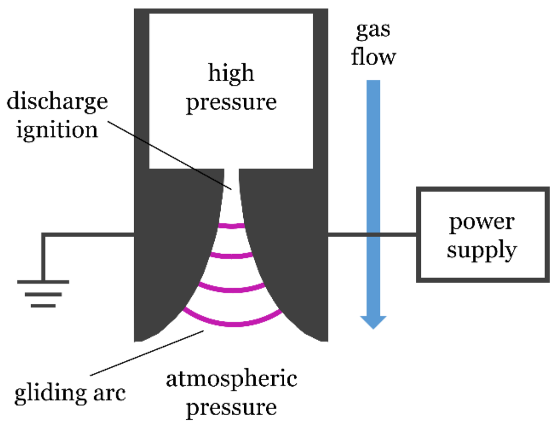

Figure 3.1: Gliding arc discharge. Schematic representation.

An alternative to the gliding arc is application of a hot plasma which expands into a vacuum chamber (Engeln et al. 2002, A100-A104). Figure 3.2 shows such a plasma expansion configuration schematically. There is a narrow nozzle between a dielectric tube and a vacuum chamber. The gas flows through the dielectric tube and expands into the vacuum chamber. Hot gaseous plasma is sustained in the dielectric tube with a suitable electric discharge, while inside the vacuum chamber, there is an expanding plasma whose temperature decreases rapidly as the gas expands into the vacuum chamber. The configuration in Figure 3.2 is similar to that in Figure 3.1, except that the vacuum conditions inside the vacuum chamber suppress the loss of chemically reactive species in the gas phase. Namely, the life-time of reactive species depends inversely on the square of the pressure. The speed of gas expanding into the vacuum chamber reaches the sound velocity at the nozzle, so the transport of reactive plasma species from the hot plasma to the vacuum chamber is extremely efficient.

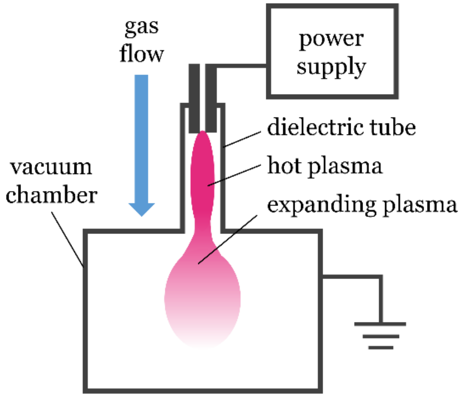

Figure 3.2: Plasma expansion. Schematic representation.

3.3 Non-thermal plasma

In contrast to thermal plasmas, non-thermal plasmas are formed at temperatures near room temperature. They can be initiated by several types of discharges, and at a wide range of pressures. The most common distinction is between atmospheric pressure and low-pressure discharges; both are considered in detail in the following chapters. The discharges are electrically driven, and the primary recipients of the energy transfer are electrons, which are mobile and charged (Lieberman and Lichtenberg 2005). This results in a pronounced inequality between the kinetic temperatures of electrons and the heavy particles (ions, neutral particles) in the plasma. The electron temperature is much larger, typically several 10,000 K, while the temperature of other species remains close to room temperature. Furthermore, the concentration of reactive species in non-equilibrium plasma is much larger than the value one can calculate based on room temperature using Boltzmann distribution. Therefore, the plasma is not in thermodynamic equilibrium, and cannot be described by the basic laws of equilibrium thermodynamics (Gorjanc and Mozetič 2014). In this environment, numerous reactions occur between the plasma particles. Electron collisions with atoms and molecules bring on processes such as dissociation, excitation and ionization, which results in the occurrence of heavier particles with relatively high potential energy (Lieberman and Lichtenberg 2005).

In fact, one should be cautious when using the term "temperature" while describing non-equilibrium gaseous plasma. Strictly, temperature is not defined for non-equilibrium systems, but in practice, it is used to describe the average kinetic energy of gaseous species which assume the Maxwell-Boltzmann distribution. In scientific literature, various temperatures have been adopted for description of non-equilibrium gases: the neutral gas kinetic temperature, the electron temperature, the ion temperature. All these temperatures indicate the distribution of corresponding particles over kinetic energy (Lieberman and Lichtenberg 2005). The distribution over excited states is rarely referred to as "temperature", although the terms "vibrational temperature" or "rotational temperature" have been adopted (Britun et al. 2007, 1022-1029). Most authors mean "neutral gas kinetic temperature" when using the term "temperature" to describe non-equilibrium gases. This was also adopted in the present monograph, unless stated otherwise.

3.4 Atmospheric pressure plasma

3.4.1 Collision phenomena

Non-equilibrium gaseous plasma can be sustained in different gases at different pressures. The voltage between the two electrodes should be high enough to enable acceleration of free electrons, where as a result they gain enough energy to cause ionization, dissociation, or excitation of gaseous molecules upon inelastic collisions. A high concentration of charged particles as well as atoms or molecules in highly excited states at low gas temperature is against the rules of thermodynamics, so the reactive species tend to neutralize, relax, or associate to stable molecules (Fridman 2008). The concentration of reactive gaseous species obviously depends on the production and loss rates. The production depends of various parameters, but the major one is the applied discharge power. A higher power will generally lead to a higher concentration of the reactive gaseous species (Zaplotnik et al. 2012, 3857-67).

There are numerous channels for the loss of reactive species, some of them taking place in the gas phase and some on the surfaces of any material facing plasma. A collision of an electron and a positively charged ion in the gas phase usually does not lead to neutralization. The reason is the requirement for conservation of energy and momentum. Before the collision, there is high potential energy in the electron–positive ion system. This potential energy is equal to the ionization energy of the parent molecule, which is often above 10 eV (National Institute of Standards and Technology 2019). If neutralization occurs, the potential energy prior to the collision should appear as the energy of the newly formed molecule. The requirement for conservation of momentum prevents the potential energy before the collision to appear as the kinetic energy of the molecule. It can appear only as the internal energy of the neutral molecule. Since the potential energy before the collision is large, the large internal energy would lead to immediate dissociation, a reaction that is regarded useful for plasma chemistry. Still, the probability for such dissociative neutralization in the gas phase is low.

Similar considerations should be taken into account for the case of association of two atoms to the parent molecule. The potential energy before the collision between two neutral atoms in the ground state is equal to the dissociation energy of the parent molecule. The potential energy before the association in the gas phase cannot be transferred to the kinetic energy of the newly formed molecule due to the requirement for the conservation of momentum. The atoms are therefore rather stable in the gas phase, despite numerous collisions among them.

An effective channel of dissipation of the potential energy of colliding particles in the gas phase are three-body collisions. Suppose a simultaneous collision of three particles, two atoms and a molecule, occurs. The collision proceeds as: atom + atom + molecule → two molecules. These resulting two molecules easily take the potential energy before the collision in the form of kinetic energy, which is shared equally between the molecule involved in the collision and the newly formed molecule (Lieberman and Lichtenberg 2005). In the case of three-body collision, the momentum is conserved, since the two molecules simply move apart after the collision. The kinetic energies of the two molecules after the collision should obviously be equal to the potential energy before the collision. Such a collision therefore ensures conservation of energy and momentum, and so such an association of two atoms to the parent molecule is likely to occur as long as the frequency of three-body collisions is large.

The probability that three particles meet at the same time in the same place depends on the mean free path of gaseous particles between subsequent collisions, which in turn depends on the density of gaseous particles and their speed of thermal motion (Misra et al. 2017, 1832-1863). The higher the gas temperature, the more frequent the collisions. The density of gaseous molecules depends on the pressure. The standard equation is $p = n\, k_B\, T$, where p is the gas pressure, n the density of gaseous particles, k_B the Boltzmann constant, and T the gas temperature (measured in K). The collision frequency therefore increases with increasing pressure.

Of particular importance are three-body collisions that lead to association of atoms to parent molecules. The frequency of three-body collisions increases with the square of the pressure. At atmospheric pressure, the frequency is roughly about 1 MHz, while at the pressure of 1 mbar, it is solely about 1 Hz. There are about one million collisions per second that may lead to the loss of reactive plasma particles at atmospheric pressure. The loss of such particles at atmospheric pressure is thus much more intense than at low pressure (Zaplotnik et al. 2018, 1800021). This is the major reason for choosing low-pressure plasma for treatment of various materials on the industrial scale.

3.4.2 Heating

The loss of reactive plasma particles by three-body collisions causes localized heating. As explained above, the potential energy before the three-body collision is transferred to the kinetic energy of the molecules (Lieberman and Lichtenberg 2005). The original and newly formed molecules therefore move apart at rather high kinetic energy. The dissociation energy of a gaseous molecule is usually several eV. For example, the dissociation energy of the oxygen molecule is 5.2 eV (Luo and Kerr 2012). This energy is shared between the original and newly formed molecule equally, so the kinetic energy of each molecule after the three body collision is about 2.6 eV. An energy of 1 eV corresponds to the temperature of about 11,000 K. The molecules are therefore super-fast, or super-thermal, after the three-body collision. This is why such collisions are often called super-elastic collisions.

After a super-elastic collision, the molecules collide with other (thermal) molecules. The collisions are often elastic: the molecules keep their original internal energy (in view of vibrational and rotational states), but a significant fraction of the kinetic energy of the fast molecule is transferred to the slow molecule (Lieberman and Lichtenberg 2005). The fast molecules formed at super-elastic collisions therefore quickly lose their energy and the rest of gaseous molecules gain the energy. The energy gained from the super-fast molecules therefore causes heating of the gas – an increase of the neutral gas kinetic temperature.

Not only fast molecules formed upon super-elastic collisions, but also other reactive gaseous particles in plasma share their energy with thermal molecules. For example, molecules that have been excited to electronically excited states will de-excite upon collisions with other gaseous molecules, and the potential energy is often shared between the colliding particles in view of the kinetic energy. As explained above, the collisions are numerous at atmospheric pressure, so the gas is heated extensively.

There are methods for suppressing extensive gas heating upon plasma conditions at atmospheric pressure. One method was already explained: drifting gas (typically at room temperature) through gaseous plasma. As long as the discharge power is rather low and the gas speed high, the heating of the gas passing plasma is tolerable.

In any case, practically all power spent for sustaining the gaseous plasma at atmospheric pressure is transformed to the increases in gas temperature. One can estimate the temperature of gas passing an atmospheric pressure plasma from a simple equation: $\Delta T = P / (\varphi_V \rho c)$. Here, ΔT is the temperature difference between the gas before and after passing plasma, P the discharge power, φ_V the gas flow rate, ρ the gas density, and c the gas specific thermal capacity. For air at ambient conditions, the density is roughly 1 kg/m^3, and the specific thermal capacity is roughly 1000 J/kg K. In Figure 3.3, the temperature difference is plotted versus the discharge power for two different gas flows often used in experiments with plasma jets, i.e., 1 and 10 standard liters per minute (slm).

The results of the simple calculation indicate that gas heating in atmospheric pressure plasma may not always be neglected. For example, air passing plasma sustained by a power of only 1 W at the flow of 1 slm will be heated for 60 K. If the original gas is at room temperature (about 20 °C), the gas will heat to 80 °C. The gas will heat for only 6 K if the air flow is 10 slm and the discharge power remains 1 W. Many plasmas sustained in air jets are powered with much larger powers. In such cases, the gas heating may be prohibitively high.

These simple calculations, summarized in Figure 3.3, assume that all discharge power is spent for heating the gas, neglecting any cooling. The gaseous plasma glows, so part of the discharge energy is always emitted by radiation (Cvelbar et al. 2007, 224-227). This effect is negligible at low powers, but becomes important at low flow rates and/or large discharge powers. The emission appears in a range of wavelengths and arises from radiation transitions from high to low excited states (sometimes to the