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The essential role of the plasma sheath in plasma-liquid interaction and its applications—A perspective p

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ABSTRACT

Based on the current knowledge, a plasma–liquid interface looks and behaves very differently from its counterpart at a solid surface. Local processes characteristic to most liquids include a stronger evaporation, surface deformations, droplet ejection, possibly distinct mechanisms behind secondary electron emission, the formation of an electric double layer, and an ion drift-mediated liquid resistivity. All of them can strongly influence the interfacial charge distribution. Accordingly, the plasma sheath at a liquid surface is most likely unique in its own way, both with respect to its structure and behavior. However, insights into these properties are still rather scarce or uncertain, and more studies are required to further disclose them. In this Perspective, we argue why more research on the plasma sheath is not only recommended but also crucial to an accurate understanding of the plasma–liquid interaction. First, we analyze how the sheath regulates various elementary processes at the plasma–liquid interface, in terms of the electrical coupling, the bidirectional mass transport, and the chemistry between plasma and liquid phase. Next, these three regulatory functions of the sheath are illustrated for concrete applications. Regarding the electrical coupling, a great deal of attention is paid to the penetration of fields into biological systems due to their relevance for plasma medicine, plasma agriculture, and food processing. Furthermore, we illuminate the role of the sheath in nuclear fusion, nanomaterial synthesis, and chemical applications. As such, we hope to motivate the plasma community for more fundamental research on plasma sheaths at liquid surfaces.

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I. INTRODUCTION

In 1928, Langmuir introduced the term *plasma* to describe the body of an ionized gas where free electrons and ions occur in about equal numbers.¹ This balance corresponds to a nearly negligible space charge, which is now known as the plasma criterion of quasi-neutrality. Already in 1923, Langmuir distinguished this quasi-neutral zone from the thin layer with an appreciable space charge formed at any plasma boundary, for which he used the term *sheath*.² For instance, at the interface between a plasma and a solid object on a floating potential, the free electrons reach the surface by diffusion on a much smaller time scale than the ions. Therefore, the object obtains a negative surface charge, while a thin region around it gets depleted from electrons and thus forms a positively charged plasma sheath. Consequently, an electric field is built up in the sheath, repelling electrons back into the plasma and accelerating positive ions toward the negatively charged surface.

In many applications, this leads to undesirable effects, like damage to the plasma reactor wall by sputtering or an increased heat flux.³ In other applications, such as plasma etching, sputtering, and ion implantation, the sheath plays a central role, because it determines the energy and angular distributions of the incident ions, which are largely responsible for the surface modification.^{4,5} The sheath generally contributes to the interfacial physical and chemical processes working during any type of plasma treatment of materials, further illustrating its technical importance. Moreover, its properties govern the plasma boundary conditions, as well as the emission of particles from the surface into the plasma volume, which both influence the overall plasma behavior. All these effects

have motivated numerous investigations since the dawning of plasma physics. The study of the plasma sheath has developed accordingly into a fully fletched subdomain.

Nonetheless, less attention has been paid to the plasma sheath in research on plasma-liquid interactions. This remarkable observation is readily substantiated with a quick exploration using any scientific search engine. Combining the search terms "plasma-liquid interactions" and "plasma sheath" or "Debye sheath" in Google Scholar, for example, provides a total of only 36 publications at this moment of writing, as opposed to nearly 1000 results with the former term alone. Yet, even with these publications, a careful analysis of the plasma sheath at a liquid surface is still lacking in scientific literature. A profound understanding is urgently needed, because of the rapidly increasing interest in the fundamentals of plasma-liquid interaction, for applications ranging from water treatment,⁶⁻¹⁰ nanomaterial synthesis,¹⁰⁻¹³ polymer solution treatment,^{10,14-16} and chemical analysis^{10,17,18} to food processing,^{19–21} plasma agriculture,^{22–24} and plasma medicine.²⁵⁻³² The latter three applications, namely, also fall under this overarching research field because biological tissue is naturally surrounded by a liquid layer. They deserve a special mentioning as important drivers of the field, with promising applications for sterilization;^{33,34} for enhanced seed germination and plant growth;²²⁻²⁴ and for skin, wound, dental, and cancer treatment.^{25–32} Modeling and optimizing the plasma treatment in these processes require the appreciation of the sheath under the corresponding conditions.

With the present Perspective, we aim to provoke a higher level of awareness regarding the importance of the plasma sheath at a liquid surface, by exploring the peculiarities for the situation at a liquid surface. First, Sec. II emphasizes the general importance of the sheath for plasma-liquid interactions. After discussing the fundamental considerations (Sec. II A), we explore the role of the sheath in bidirectional mass transport (Sec. II A) and the chemistry (Sec. II C) at a plasma-liquid interface. Doing so, we argue why the fundamental study of the sheath at a liquid surface is not only interesting but also essential for an accurate understanding of plasma-liquid interaction, as well as for a faster progress in the various applications. Afterward, we discuss the variability of sheaths, with special attention to anode sheaths (Sec. II D). Next, Secs. III-V illustrate these claims for a few selected processes. We start with the role of the sheath as an electric field regulator for food processing, plasma agriculture, and plasma medicine (Sec. III). According to the second example, the sheath can also serve as a mass transport regulator at liquid metal walls in a nuclear fusion reactor (Sec. IV). Third, we zero in on the effect of the sheath on the chemistry of nanomaterial synthesis and other applications (Sec. V). Subsequently, Sec. VI deals with several insights and gaps in knowledge regarding liquid-related sheath properties, including electron emission from a liquid surface (Sec. VI A) and droplet formation at the interface (Sec. VI B). Finally, Sec. VII concludes this review with a summary of the newly obtained insights and recommendations for future research. Accordingly, we hope to increase awareness on the essential role of the sheath in plasma-liquid interaction, as well as to provide a starting platform for advanced models and theories describing the underlying physics.

II. THE GENERAL IMPORTANCE OF THE PLASMA SHEATH IN PLASMA-LIQUID INTERACTION

A. Fundamental considerations

In Sec. II, we argue why the plasma sheath deserves a place in the spotlight in both fundamental and applied research on plasmaliquid interactions. Since this perspective builds further on the insights obtained in our previous review paper,³⁵ there will be several occasions in this section where we refer to it for more detailed information. For a structured discussion, we limit Secs. II A–II C to ion sheaths with a positive space charge at a negatively charged surface. Such sheaths are, for instance, encountered at a cathode or at a material on a floating potential, submerged in a plasma. Section II D will deal with the situation at a liquid anode and the ways in which sheaths can differ.

From a fundamental point of view, the plasma sheath at a liquid surface is more than simply a theoretical curiosity. Similar to the case at a solid surface, it determines the boundary conditions of the plasma phase. According to the fluid dynamics continuity equations, this includes the mass and energy transport across the boundary. More specifically, the sheath plays an active role in these equations, as it generally accelerates positive ions toward the surface, increasing the heat flux into the material, which on its turn influences the emission of particles and heat into the plasma. Besides that, the sheath governs the boundary conditions for Maxwell's equations, which do not only dictate the local potential drop across the sheath but also affect the behavior of the plasma and the liquid due to their electrical coupling. In simplified terms, the sheath thus forms an essential part in the equivalent circuit of the entire plasma reactor. A change in its properties will, therefore, determine the electrical potential distribution over the plasma and liquid phases. More specifically, rapid fluctuations of the sheath potential regulate the field penetration into the liquid phase. We will explain and illustrate this in Sec. III in more detail for field-induced processes in biological materials. For a more fundamental discussion on the electrical coupling in plasma-liquid systems, we refer to our previous review.

Furthermore, the plasma sheath regulates the mechanisms behind secondary electron emission from a surface in multiple ways. First of all, it defines the local electric field, which is largely responsible for the kinetic energy distributions of the charged plasma species bombarding the material. The fast incident ions can subsequently transfer their energy to bound electrons in the surface through a kinetic electron emission mechanism.^{36–38} Second, the electric field at the interface can modify the local electronic structure of the material. The sheath field is, namely, closely related to the local field of the electrical double layer in the liquid, which can reach toward the order of 10⁹ V/m at submerged electrodes and electrocatalysts.³ This approaches the threshold of 3.0×10^9 V/m for dielectric break-down of water without bubble formation.⁴² Local fields as low as 10^7 V/m have been observed to induce a refractive index change, which could be attributed to reorientation of the water molecules or the excitation of their OH stretch vibration.43,44 Such effects may translate themselves into the bending of the band scheme or the shifting of individual surface levels. Note in this regard that an amorphous semiconductor model is frequently used to explain laser-induced breakdown in dielectric liquids (see, e.g.,

Refs. 45–52). In our previous review paper, we have promoted this view for plasma initiation in the liquid phase and plasma–liquid interaction.³⁵ Recently, Delgado *et al.* adopted a similar band structure model for the plasma–water interface to explain their experimental study on secondary electron emission at a water electrode.⁵³ For a field aiming toward the liquid phase, band bending or the surface level shifts lower the energy required for the release of electrons. The sheath may, therefore, give rise to field-enhanced ion-induced secondary electron emission, as further explained in Sec. VI A.

As a side note for the case of hydrated electrons at the airwater interface, a reduction of the vertical binding energy with a few tenths of an eV may actually already be naturally present relative to the bulk species. This is suggested by simulation results independently obtained with several quantum mechanical methods (see, e.g., Refs. 54-58). As a possible explanation, interfacial solvated electrons may be subject to a strong naturally present local field. Remarkably large field strength values have, namely, been obtained in several computational studies for the vapor-water interface: 10^8 V/m with quasichemical theory,⁵⁹ 8 × 10^8 V/m with classical molecular dynamics simulations,⁶⁰ 10⁹ V/m with density functional theory,⁶¹ and 1.5×10^{10} V/m with *ab initio* molecular dynamics simulation.⁶² These high values were mostly attributed to the arranged orientation of water molecules at the water surface, in analogy with recent electrical field measurements for the water-oil interface of aqueous microdroplets by means of stimulated Raman excited fluorescence microscopy.6

Third, a sufficiently large number of emitted electrons alter the electron density and thus the space charge in the sheath. On its turn, this adjusts the sheath properties. In this way, a feedback loop emerges between the sheath and the electron emission. The possible mechanisms behind electron emission from a liquid surface are also more elaborately discussed in our previous review.³⁵

Additionally, the liquid surface structure adapts to the presence of the sheath field in a myriad of ways (see Fig. 1). The microscopic structure is expected to diverge from the more familiar gas-liquid interface due to the appearance of the net surface charge. Analogous to a liquid adjacent to a solid electrode or surface, an electrical double layer forms in contact with the plasma sheath. Such reorganization of the liquid determines which condensed species are directly exposed to the incoming plasma particles. This may strongly influence the mass transport across the interface. In contrast to solids, liquids generally conduct electricity through ion drift, giving their surface a distinct resistive behavior. In Sec. III C, we will discuss an experimental indication that this may lead to a more diffuse type of plasma than usually observed at a solid surface, the so-called resistive barrier discharge. Moreover, the liquid surface can deform by the Coulomb attraction from the sheath to generate capillary waves or Taylor cones.^{35,64-68} When these deformations become extreme or get combined with other violent plasma processes, such as sputtering, droplets will be released toward the gas phase. Likewise, droplet emission is also expected when the sheath generates a sufficiently strong heat flux onto the liquid to initiate local boiling. Many liquids generally display stronger evaporation than solids, modifying the composition of the contacting gas phase. Similar to electron emission, these liquid-specific phenomena affect the electric field and space charge distribution over the surface, creating a feedback loop between them and the sheath. Since these processes are absent for solids, the plasma sheath at a liquid surface is expected to have a unique character and behavior, depending on the liquid properties. In other words, classical sheath models are likely inapplicable to the plasma-liquid interface. The fundamental study of plasma sheaths at liquids is, therefore, highly required in order to scrutinize how this multitude of factors affects the plasma-liquid interactions. Our previous review introduces the general role of evaporation, droplet ejection, and surface deformation in further detail.³



FIG. 1. Schematic summary of the processes at a plasma-liquid interface, which are expected to affect the plasma sheath. On the contrary, the sheath also affects these processes, creating a feedback loop.

B. Bidirectional mass transport across the plasma sheath

Apart from the fundamental considerations in Sec. II A, a detailed understanding of the plasma sheath over a liquid is also crucial for an efficient and goal oriented optimization of the numerous related technologies. A large portion of these methods are predicated on transferring reactive plasma species into the liquid phase. Atmospheric air plasma, for instance, produces several types of reactive oxygen species, such as ozone, hydroxyl radicals, and hydrogen peroxide. When brought into the liquid phase, these species readily react with the solvent or solutes, changing the molecular structure. Organic pollutants in water can be decomposed in this manner, ideally down to CO2 and H2O as harmless end products. This makes plasma treatment one of the advanced oxidation techniques considered for water purification. Similarly, plasma treatment has been proposed for the decomposition of pesticides on the surface of seeds before germination.^{24,69} Next to that, reactive oxygen species can be used to kill bacteria for sterilization purposes, in food processing or plasma medicine. Plasma-generated reactive oxygen and nitrogen species often contribute to the liquid chemistry as well. They are particularly crucial in plasma treatment of cancerous tumors^{25,30-32} and in plasma agriculture for fertilizer synthesis.^{22,23} Besides this, plasma gases other than air have been applied for polymer solution treatment, as a preparation step before spin coating.^{10,14-16} The Plasma-Liquid Interactions Roadmap from 2016⁶⁸ puts a strong emphasis on these types of applications, where the plasma forms a means to induce chemical reactions in the liquid.

Correspondingly, the primary reactive species in the solvent need to be either generated directly in the liquid phase or transferred into the liquid from the gaseous phase. Regarding the former pathway, absorption of plasma-produced UV photons by the solvent or solutes is generally considered the main mechanism (see, e.g., Ref. 68). For the latter pathway, the reactive plasma species need to cross the sheath before they enter the liquid phase. Particularly, the transport of ions and electrons is expected to be affected by the sheath due to the presence of the electric field. Their collisions with neutrals additionally amend the overall plasma species transmission. At atmospheric pressure and room temperature, ions have a mean free path l smaller than $1 \mu m$, which is significantly smaller than the expected sheath thickness.⁶⁸ The ions will anisotropically transfer their kinetic energy to the neutrals in the thin sheath section with a thickness l right above the liquid surface. Charge transfer reactions between the ions and neutrals additionally produce hot neutrals traveling toward the surface. Accordingly, the pressure and temperature of the neutrals in this layer are better expressed as tensors, instead of scalars. This likely affects their interaction with and transport into the liquid surface.

Analogously, the sheath mediates the reverse transfer of liquid species into the plasma as well, as summarized in Fig. 2. For instance, a local electric field of a few kV/cm perpendicular to the liquid surface increases the evaporation rate of water,^{70,71} while a parallel field causes a decrease.⁷² Solutes may also be emitted into the gas phase in their entirety or in fragments, in which the sheath may play an important role. Electrical discharge is even able to extract non-volatile species from a solvent, in agreement with numerous experiments using a wide variety of plasma sources (see, e.g., Refs. 17 and 18). This observation has laid the foundation for plasma-liquid systems in analytical chemistry. An example with a rich research history is the electrolyte cathode atmospheric glow discharge (ELCAD), where an electrolytic sample serves as the cathode of a diffuse plasma.⁷³⁻⁷⁶ ELCAD allows the detection of aqueous trace metal ions, implying the transfer of the metal species from the liquid to the plasma phase. In theory, the metal species



FIG. 2. Schematic summary of the aspects of the bidirectional mass transport across the plasma sheath that are mostly affected by the presence of the electric field.

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can be emitted into the plasma as ions or atoms, but the relative dominance and underlying physics of these mechanisms are still unclear. Inspiration can be taken from the mechanisms proposed for ion desorption by lasers, for which several uncertainties remain as well (see, e.g., Ref. 77).

The transfer of liquid species into the plasma phase is, however, relevant too for all other applications. Traces of compounds in the gas phase may, namely, contribute significantly to the overall plasma features, ^{17,78–82} affecting the desired effect. The decomposition of organic pollutants in a plasma reactor for water treatment can, for instance, occur for an important part in the gaseous phase. A detailed study on this topic has been performed by Ognier *et al.*, who used an AC powered coaxial dielectric barrier discharge (DBD) reactor for the decomposition of four volatile compounds (acetic acid, phenol, ethanol, and 1-heptanol).⁸³ When the plasma was switched on, the mass transfer increased for each pollutant from the liquid to plasma, proportionally to the corresponding Henry law constant. According to the measurements, minimally 95% of the pollutant decomposition took place in the gas phase.

This effect is often neglected, but deserves special attention in applications, for a comprehensive insight into the overall process. In order to reach the plasma phase, liquid species have to cross the sheath, which acts as a barrier for positively charged droplets or ions and facilitates the extraction of negative particles. This filter function of the sheath will be illustrated in Sec. IV for fusion reactors with liquid walls. Furthermore, the electric field strength at the liquid surface regulates the incident ion energy and heat flux, which determine the extent of sputtering, desorption, evaporation, and droplet ejection. Therefore, an accurate description of the plasma sheath is required to understand the bidirectional mass transport through it. Current models ignore this effect, for example, by assuming species transmission as dictated by Henry's law (see, e.g., Refs. 84-89). The validity of Henry's law at a plasmaliquid interface is, however, highly questionable, exactly due to all of the aforementioned plausible mechanisms. Even if the mass transport of certain solutes across the interface appears sensitive to their Henry's law constants, as in the experiments of Ognier et al.,⁸³ the law itself may be violated, in the sense that the constants need to be recalibrated. For example, Henry's law constants might depend on the local electric field.

C. Plasma sheath chemistry

Kinetic models neglecting the plasma sheath are at risk for another oversimplification. Such models simulate the chemical reactions in the system by means of separate chemistry sets, each corresponding to one region in the reactor. Obviously, at least two regions must be distinguished: the gaseous plasma and the liquid phase. In recent years, a few computational groups, including ours, have developed plasma–liquid models that limit their chemistry sets to these two zones (see, e.g., Refs. 84–88). The sets are coupled with one another through the boundary conditions at the plasma– liquid interface, describing the mass transport across the surface with, for instance, Henry's law and Raoult's law. Although such a straightforward approach allows us to obtain a first estimation of the reactive species densities, it disregards the chemistry in two crucial zones. First of all, the liquid surface is known to host its own chemistry, acting as a catalyst for both gaseous and liquid reactants.^{90,91} This surface chemistry is expected to significantly depend on the surface charge, which is closely related to the sheath properties. Moreover, the reactions of gaseous or liquid species at a solid surface or electrode can tremendously change under an applied electric field, as well-known from electrochemistry and surface science.^{92–95} A similar influence may, therefore, take place at the plasma–liquid interface.

Second, the plasma sheath forms another zone with a unique chemistry. Its difference with the chemistry in the plasma bulk has several causes. To start with, a sheath is generally poor in electrons, which eliminates a large part of the electron impact reactions at low kinetic energies.^{96,97} Some sheaths or sheath regions, on the contrary, contain a negative space charge region where the reverse effect can occur. Examples are the anode sheath (see Sec. II D) and the thin Aston dark space at the cathode in a glow discharge.⁹ Additionally, the strong electric field accelerates the electrons to far higher kinetic energies than in the bulk plasma, bringing their chemistry in a higher kinetic regime. The ion chemistry similarly shifts to a higher kinetic regime as well, allowing endothermic reactions that do not take place in the plasma bulk.⁹⁸ Based on experimental research, the energetic collisions of positive ions in the sheath are, for example, an important source of negative ions, even in low-pressure plasmas.⁹⁹⁻¹⁰¹ At a non-evaporative solid surface, a fully collision-free sheath is observed only at pressures below 1 Pa.^{102,103} At a liquid surface, a substantially larger portion of liquid species is expected in the sheath as compared to the bulk plasma, due to evaporation, desorption, and sputtering processes. In principle, these differences do not necessarily imply reactions of a different nature in comparison to the plasma bulk, as they only mean a shift of the chemistry to a different regime in the sheath. Following this line of thought, it seems reasonable to describe both regions with the same gas chemistry set, as long as it covers a sufficiently wide range of conditions for the electron and ion energies, as well as the species densities.

There are, however, two factors that might cause an essential contrast in chemistry between the plasma sheath and plasma bulk (see Fig. 3). As the first factor, the sheath may be populated with numerous microdroplets, acting as catalysts or miniscule reaction vessels. That is, reactions can be accelerated by orders of magnitude in microdroplets relative to their liquid bulk counterparts, as demonstrated in several investigations.¹⁰⁴⁻¹⁰⁷ Interestingly, the droplets allow a voltage-dependent chemistry acceleration and a reversible electrochemical derivation.¹⁰⁸ This makes the plasma sheath an interesting reaction environment for microdroplets, with a promising application for chemical synthesis. When coupled with mass spectrometry, these features also allow an in situ mechanistic study and capture of key radical intermediates, applicable for chemical analysis purposes.¹⁰⁸ Moreover, the aforementioned remark on the distinct surface chemistry at a liquid surface remains valid for a droplet boundary. All of these droplet-related chemical principles should be strongly dependent on the presence of an electric field. Therefore, microdroplets can lead to an essentially different chemistry in the plasma sheath with respect to the plasma bulk.

As a second factor, a strong electric field like the one in the sheath can alter the rate and pathway of reactions also in the absence of any droplets. In fact, the electric field dependence of

PLASMA CHEMISTRY



FIG. 3. Schematic summary of the aspects in the plasma sheath chemistry and liquid surface chemistry that are mostly affected by the presence of the electric field. The thin black arrows denote reactions and the green downward arrows represent the electric field.

chemical reactions involving charged functional groups is heavily pronounced in the gas phase, in comparison to its muted effect in a solution due to dielectric screening.¹⁰⁹ For an introduction to such field effects, we recommend the tutorial by Shaik *et al.*¹¹⁰ This tutorial explains the impact of the field on a reaction by means of its orientation relative to the axis of the bond to be broken and the so-called reaction axis. The latter is defined as the direction along which electron pairing undergoes reorganization from reactant-like to product-like bonding. A field along the bond axis facilitates bond breaking. A field along the reaction axis catalyzes the reaction. Moreover, forbidden-orbital mixing can be removed and stereo-selectivity can be controlled with a field component perpendicular to the reaction axis.¹¹⁰ Since polar molecules orient themselves along a strong electric field, a net modification of their chemistry may be expected in a plasma sheath.

In other words, the sheath chemistry is expected to diverge significantly from the bulk plasma chemistry due to the dissimilar particle densities and charge carrier kinetic energies and due to the presence of microdroplets and field-dependent reactions. The products created in the sheath need to travel less of a distance to enter the plasma bulk or the liquid surface than particles crossing the entire sheath thickness. They are, therefore, of prime interest for a description of the species and charge transport through the plasma–liquid interface. Moreover, the sheath forms an electrostatic and chemical barrier for plasma and liquid species coming from the bulk phases. As such, the question arises how much the bulk species contribute to the fluxes onto the liquid surface or into the plasma in comparison to the species generated in the sheath.

The answer will of course strongly depend on the pressure and ionization degree of the plasma. For low-pressure plasmas with solid boundaries, ion-neutral reactions in the sheath become noticeable at 1 Pa for increasing pressure, based on studies of the incident ion energy distribution functions.^{102,103} Below 1 Pa, the sheath is often considered collisionless for ions. However, collisions and reactions between the neutral species will still occur with a high frequency. At atmospheric pressure, the sheath is strongly collisional for both ions and neutrals, providing numerous opportunities for any particle to react while crossing the sheath. An interesting study in this regard has been performed by Liu et al., using a one-dimensional fluid model with a chemistry set of 17 species and 60 reactions, for the simulation of a radio frequency atmospheric pressure He-O2 plasma with solid boundaries.¹ From a detailed analysis of the particle transport in the sheath region, the wall fluxes were found to originate from a 3 to $300 \,\mu m$ thin boundary layer contacting each electrode, i.e., only a fraction of the sheath thickness of $472-489\,\mu\text{m}$. As such, the chemistry in the thin boundary layer supplied the species incident to the surface. More studies are required to test this hypothesis for other plasma

sources. Unfortunately, the research domain of plasma sheath chemistry has remained remarkably inactive up to now, also for gas discharges with solid boundaries. With the present Perspective, we therefore hope to motivate the plasma community to breathe new life into this topic. For this purpose, a few examples are discussed in Sec. V on how the sheath can regulate the chemistry for nanomaterial and chemical synthesis by varying the ion or electron kinetic energy at a liquid cathode or anode, respectively.

D. Sheath variability and anode sheaths

In general, the sheath features depend on the plasma and liquid properties, as well as any externally applied fields. At low pressure, for instance, collisionless ion sheaths at a positively biased solid surface can be described with a one-dimensional steady-state two-fluid model, from which a sheath thickness l is deduced as¹¹²

$$l = \frac{\lambda_D \sqrt{2}}{3} \left(\frac{2e\Delta\phi}{T_e}\right)^{3/4},\tag{1}$$

where λ_D is the Debye length, *e* is the elementary charge, T_e is the electron temperature and $\Delta \phi$ is the sheath potential drop determined from the global current balance. Equation (1) implies the sheath scale to be several Debye lengths thick if $e\Delta\phi \gg T_e$. Its deduction is based on the Bohm criterion, which states that ions need to enter the sheath from the plasma with a velocity of at least the ion sound speed $c_s = \sqrt{k_B T_e/m_i}$, with k_B being the Boltzmann constant and m_i being the mass of the ions. However, a waterproof analytical formulation of the sheath is mathematically complicated in this way, which formed the subject of a heated discussion at the start of this century.¹¹³⁻¹¹⁶ The transition point where the Bohm criterion needs to be applied, namely, does not coincide with the sheath edge, i.e., the boundary between the and the quasi-neutral plasma as defined by sheath Langmuir.^{113,117} In order to avoid inconsistencies, the equations for the sheath and plasma can be coupled to one another with the method of matched asymptotic expansions by introducing an additional transition region between the plasma and the sheath.¹¹⁸⁻¹²⁰ Alternatively, patching methods may be applied to force the equations together at the transition point.^{114,121} Considering that ion sheaths at solid surfaces are the most intensely studied types of plasma sheaths, this illustrates the challenging character of this research domain.

As another example of this complexity, the distinct types of plasma sheaths formed at a biased solid electrode at low pressure have been identified only recently. Figure 4 shows the qualitative electrical potential profile of five types, including the well-known ion sheath. Electron sheaths are thin regions of negative space charge, emerging near a positively biased electrode for a sufficiently small effective surface area of the sheath edge.¹¹² Double sheaths additionally possess a positive space charge region at the side of the quasi-neutral plasma. They can arise under various conditions, related to the electrode configuration or due to secondary electron emission.^{112,122-127} An anode glow emerges from an electron sheath when the potential difference between the electrode and the plasma rises, enhancing the ionization rate in the sheath by accelerated electrons. Due to the inertia of the ions, they leave the sheath



FIG. 4. Electrostatic potential profile of five plasma sheath types that can form at a biased solid electrode. Regions of negative and positive space charge are denoted by minus and plus signs, respectively. Reprinted with permission from Baalrud *et al.*, Plasma Sources Sci. Technol. **29**(5), 053001 (2020). Copyright 2020 IOP Publishing.

much slower than the electrons, causing a positive space charge at the side of the electrode. The higher electron energy in this region results in a larger number of excitations, making it glow. When the bias voltage, or alternatively the pressure, is further increased, the positive space charge region expands, leading to an abrupt fireball onset. A fireball is a transient phenomenon, after which the sheath and plasma potential are adjusted. For an excellent overview of these different types of sheaths at low pressure, we refer to the recent review of Baalrud *et al.*¹¹²

An important subsequent question is how these insights need to be translated for sheaths at higher pressures. In this regard, we also highly recommend the assessment made by Baalrud et al.¹¹² They have suggested a similarity between fireballs at low pressure and anode spots or anode glow at atmospheric pressure, taking into account the nearly identical reactor geometry and power system used to generate them. The two phenomena, namely, involve a selforganized, highly luminous, and localized secondary discharge generated near biased electrodes in a plasma. The underlying mechanisms may, therefore, display similarities as well. However, Baalrud et al. point out a clear contrast between their usual theoretical descriptions. On the one hand, kinetic effects associated with details of the velocity distribution functions, i.e., beyond the assumptions in fluid or thermodynamics models, are essential in the fireball model. On the other hand, spots in atmospheric pressure plasmas seem well represented by means of fluid models, such as the ones including reaction-diffusion or drift-diffusion descriptions. According to these models, spots are formed due to a thermal instability coupled with the boundary condition of the electrode temperature, a parameter absent in the fireball model. As such, Baalrud et al. proposed to investigate the transition between the low and high pressure regimes in order to elucidate these differences. Analogously, they bring forward the same considerations for

the transition from a low-pressure ion sheath to a complex cathode spot structure at higher pressures.

At a liquid surface, the situation may be very different, due to the processes presented in Fig. 1. Therefore, the sheath models for solid surfaces may be inaccurate or perhaps even invalid at a liquid surface. Currently, assessing the differences is a matter of speculation, because several properties of the plasma-liquid interface are still poorly understood. Sections VI A and VI B will illustrate this for electron emission and droplet generation at the liquid surface, which can involve evaporation, surface deformation, the electrical double layer, and ion drift in the liquid phase. Validated fundamental knowledge on these processes is crucial to obtain a trustworthy description of the plasma sheath in plasma-liquid interactions. The present uncertainties regarding the sheath are also demonstrated by comparing a few recent models for plasma interaction with a water anode. Figure 5 displays some characteristics of the anode sheath at the water surface according to an analytical model developed by Rumbach et al.,¹²⁸ a one-dimensional particle-in-cell Monte Carlo collision (PIC-MCC) model with liquid chemistry by Gopalakrishnan et al.,¹²⁹ and a onedimensional PIC-MCC model by Levko et al. describing plasma species in both the gas and liquid phases with computational macro-particles.¹³⁰ Although the three models show some agreement with each other and with the experimental study by Rumbach et al.,¹³¹ they predict a different sheath structure. The model by Levko et al. calculated a positive space charge region in contact with the surface, based on the interaction between an anode-directed streamer in humid nitrogen and de-ionized water. This corresponds with an anode spot, as often observed over a water anode (see, e.g., Refs. 132-141). The model by Gopalakrishnan et al. instead found an electron sheath without a positive space charge in argon over an electrolyte electrode. The model by Rumbach et al. simply assumed an electron sheath at the aqueous anode, as displayed in Fig. 5.

This dissimilarity may be the result of the different operational conditions or the distinct computational methods, which would be interesting to investigate with a dedicated comparative study. In any case, it clearly shows that the currently available data on sheath properties cannot simply be generalized for all combinations of plasma-liquid interactions. A key question will be what type of plasma sheath is formed at the liquid. Obviously, the sheath type will strongly influence the plasma-liquid electrical coupling, the species transport across the interface, and the sheath chemistry.

For an anode sheath, the schemes in Figs. 2 and 3 need to get modified accordingly. As an important difference with cathode sheaths, the electric field strength in the gas phase near an anode is often estimated to be weaker. For an anode sheath at a liquid, values ranging from 10^4 to 10^6 V/m are reported (see, e.g., Refs. 128–130, 138, and 142), corresponding to an electron impact energy up to 10 eV with the surface. Contrarily, ion sheaths at a water cathode are often thought to contain a field around 10^7 V/m.^{68,73,143} The latter value originates from the measured cathode voltage drop, which usually lies within the interval from 400 to 700 V (see, e.g., Refs. 73 and 143–149), and the implicit assumption of a sheath thickness around $40-70\,\mu$ m. According to the plasma–liquid interaction roadmap by Bruggeman *et al.*, the ions bombarding a liquid cathode surface are, therefore, expected

to obtain a kinetic energy of a few eV, up to perhaps tens of eV at most, based on an ion mean free path smaller than 1 μ m at atmospheric pressure.⁶⁸ This stands in contrast with values around 100 eV mentioned elsewhere (see, e.g., Refs. 150 and 151). A strikingly lower field strength of $2-4 \times 10^5$ V/m has been observed in the cathode sheath of an atmospheric air plasma between two streams of tap water, implying two orders of magnitude lower ion energies.^{152,153} These are exciting observations, demanding further investigation, because the ion energy distribution provides essential insight into the possible electron emission mechanisms. Fields in the order of 10^5 V/m, namely, seem to contradict the current theories of ion-induced secondary electron emission, as discussed in more detail in Sec. VI A. Next to that, the field strength in the sheath strongly determines the likeliness and prevalence of the processes depicted in Figs. 2 and 3. Obtaining accurate values for it is, therefore, of primary importance.

III. THE SHEATH AS AN ELECTRIC FIELD REGULATOR FOR FOOD PROCESSING, PLASMA AGRICULTURE AND PLASMA MEDICINE

A. Plasma-induced electric fields for electrostatic disruption

Section II discussed the relevance of the plasma sheath for plasma–liquid applications in general, in terms of the electrical coupling between the plasma and liquid phases (Sec. II A), the species transport through the sheath (Sec. II B), and the sheath chemistry (Sec. II C). In Secs. III–V, we zero in on a few specific applications, where the sheath plays a particular role to obtain the desired effect. The list of these examples is far from complete but serves as an extra emphasis on the importance of the sheath in plasma–liquid interactions and as a motivation for more research on this topic. Section III puts the looking glass over the electric field penetration into the condensed phase, which is tightly linked to the electrical coupling function of the plasma sheath.

Any object under plasma treatment is subject to ions, electrons, photons, neutral species, and the local electric field of the sheath at the contact surface. The latter may, on itself, cause modifications in the material, apart from or in synergy with the plasma particles. Its effect in the treatment process should, therefore, also be analyzed for a complete understanding of the observed effects. In the domain of plasma-liquid applications, this has mainly attracted the attention of researchers working on the treatment of biological material. Indeed, electric fields are known for a long time to affect biological organisms. To explain the observed effects, several mechanisms have been proposed in the literature. Throughout Sec. III, we zoom in on these mechanisms for fields ranging over the orders of 10^{-1} till 10^5 V/cm in amplitude and 10^{-12} till 10^2 s in duration. Doing so, we want to illustrate how crucial it is to know the exact parameters of the field penetrating into the condensed phase. Although the focus lies on biological materials, a part of the presented knowledge also applies to liquid matter in general. More specifically, Sec. III C deals with field penetration into the liquid phase, and its relationship with the plasma sheath. Section III F presents field-induced effects on a molecular level, which may also occur in non-biological plasma-liquid systems.



FIG. 5. Anode sheaths at a water surface according to three different models. (top left) The assumed qualitative gradient of charged species and the resulting space charge density and electrostatic potential across the electrolyte surface normal in the model by Rumbach *et al.* (Top right) The electric field and electric potential calculated with the model by Gopalakrishnan *et al.* in the Ar plasma phase over an electrolyte anode. The cathode fall voltage is around 100 V. The electric field in the bulk plasma region remains nearly constant around the value -1.5×10^5 V m⁻¹. The inset shows the field strength increase in the electron sheath. (Bottom) The electron field profile obtained with the model by Levko *et al.* along the liquid surface normal of de-ionized water in contact with a humid nitrogen plasma under steady-state, with a cathode voltage of -2 kV. (Top left) Reprinted with permission from Rumbach *et al.*, Phys. Rev. E **95**(5), 053203 (2017). Copyright 2017 the American Physical Society. (Top right) Reprinted with permission from Gopalakrishnan *et al.*, J. Phys. D: Appl. Phys. **49**(29), 295205 (2016). Copyright 2016 IOP Publishing. (Bottom) Reprinted with permission from Gopalakrishnan *et al.*, J. Phys. D: Appl. Phys. **12**(2016). Copyright 2016 IOP Publishing. (Bottom) Reprinted with permission from Levko *et al.*, Phys. Plasmas **25**(3), 033515 (2018). Copyright 2018 AIP Publishing LLC.

As a first example, electrostatic disruption of the cell membrane was introduced by Mendis *et al.* to explain *E. coli* inactivation under atmospheric pressure glow discharge treatment.¹⁵⁴ This mechanism assumes the cell membrane to acquire a sufficiently large electrostatic charge, so that the resulting outward electrostatic stress exceeds its tensile strength. An estimation of the required membrane potential gives several to tens of volts.¹⁵⁴ Electrostatic disruption has frequently been suggested to explain immediate cell death under plasma treatment.^{155–159} Outside the plasma community, however, field-induced inactivation of micro-organisms or biological tissue is more commonly attributed to electropermeabilization, which forms the topic of Sec. III B.

B. Plasma-induced electric fields for electroporation

The membrane of cells under treatment can be understood as a capacitor filled with a low dielectric constant material.¹⁶⁰ In the presence of an electric field, the intra- and extracellular ions move along the field direction, accumulating free charges at the opposite sides of the membrane. This process plays an important role in signal transduction between the cell's interior and exterior.¹⁰ For a rising field strength, the transmembrane potential increases, up to a certain threshold value of usually around 0.2-1.0 V.^{160,162,163} At and above this threshold, pores are formed in the membrane, either reversibly or irreversibly, an effect known as electroporation (see Fig. 6). In the case of temporary pores, mass transfer occurs between the intra- and extracellular solutions, including water molecules, minerals, and larger particles, depending on the pore size. Such reversible perforations have a lifetime of several milliseconds to hours.^{164,165} Permanent pores, on the other hand, correspond to the rupturing of the cell wall. Accordingly, reversible and irreversible electroporation (IRE) can result in apoptosis (delayed, programmed cell death) and necrosis (immediate, unprogrammed cell death).

Based on this mechanism, electric fields can be used to inactivate hazardous or undesirable micro-organisms in biological materials. In practice, this type of treatment is most frequently performed with pulsed electric field (PEF) technology. PEF has found widespread application for food processing^{166–170} and has been proposed as a novel method for enhanced seed

germination,^{69,171–174} wound healing,^{175–178} and cancer treatment.^{179–181} Note that, coincidently or not, these resemble some of the most popular applications in plasma agriculture and plasma medicine. For food processing and wound healing, the inactivation of micro-organisms due to electroporation is generally considered the main underlying mechanism. 168-170,176-17 ⁸ For seed and cancer treatment, in contrast, the positive impact has frequently been attributed to reversible electroporation in the multicellular tissue.^{108,179–181} Reversible electroporation, namely, enables the extraction of intracellular molecules and the infusion of water or foreign materials into and within the cell, which may benefit the subsequent germination process in the case of seeds or the healing process in the case of tumors. Such a mechanism may also be used for gene delivery in wound or cancer treatment, a technique known as gene electrotherapy.^{175,180} An alternative is electrochemotherapy (ECT), where the membranes of the malignant cells are permeabilized for the infusion of cytotoxic drugs.^{182,183} Interestingly, a few recent studies have tested the combination of pulsed electric fields with plasma treatment of tumors.^{182,184-188} In an *in vitro* study with a three-dimensional cell model, pulsed electric fields were found to greatly potentiate the cytotoxic effect of plasma-activated phosphate-buffered saline.¹⁸⁴ Reversely, a second study demonstrated a reduction in the required pulsed electric field intensity after a pretreatment of two cell lines with plasma-activated medium.¹⁸⁷ In a third investigation by our group, such a medium in combination with electric field treatment caused cell death, while the field alone turned out to be nonlethal.¹⁸⁶ In another



FIG. 6. Schematic description of electroporation. A biological cell is located in an electric field E. For a field below the critical value E_c , charge separation occurs in the intra- and extracellular liquids, but the cell membrane remains intact. Beyond this threshold, reversible pores develop in the membrane, represented with the dashed line (RE: reversible electroporation). For increasing field strength, the pores become irreversible, corresponding to the rupturing of the cell wall (IRE: irreversible electroporation). In contrast, keeping the field strength at sublethal values can stimulate the growth of cells (SEF: stimulating electric fields). When biological material is treated with pulsed electric fields, these processes occur over a certain range of the treatment time t_{PEF} (in s) and the total specific energy *U* (in kJ/kg), as indicated at the right. (Left part) Reprinted with permission from Donsì *et al.*, Food Eng. Rev. **2**(2), 109–130 (2010). Copyright 2010 Springer Nature. (Right part) Adapted with permission from Galván-D'Alessandro and Carciochi, Fermentation **4**(1), 1 (2018). Copyright 2018 Author(s), licensed under a Creative Commons Attribution (CC BY) license.

study on direct cell culture medium treatment with the kINPen plasma jet, the killing potential increased when the cells were pretreated 3–5 min in advance with pulsed electric fields.¹⁸⁸ In yet another investigation using direct treatment with the kINPen, more cells were killed when the plasma process preceded the pulsed electric field.¹⁸² In a sixth investigation, the sequence of treatment did not seem to play a significant role.¹⁸⁵ However, a parallel combination turned out to be more effective than a serial application with a 15 min pause in between both regimes. Interestingly, cell membrane permeabilization was induced by pulsed electric fields but not by plasma.

This shifts forward the question whether plasma treatment alone can cause electroporation under different circumstances. Obviously, electroporation can only take effect for a sufficiently large electric field applied over the cells, in agreement with Fig. 6. For this reason, several sources in the literature have proposed a comparison between plasma-liquid interaction and pulsed electric field treatment with respect to the electric field (see, e.g., Refs. 189-192). A strongly simplified reasoning could go as follows. On the one hand, plasma treatment of biological materials is generally performed by means of atmospheric pressure plasma jets and dielectric barrier discharges. Atmospheric pressure plasma jets can generate fields in the order of 10 kV/cm in a propagating plasma bullet, with local values approaching 100 kV/cm.¹⁹³⁻ The field at the head of a propagating streamer filament in a dielectric barrier discharge can reach even higher, ranging from tens to around 200 kV/cm.^{192,196-198} On the other hand, pulsed electric field treatment is often described in terms of a few operating conditions, one of which is called the applied electric field. It refers to the voltage applied over two metal electrodes in contact with the cell culture medium, divided by the inter-electrode distance. The critical value E_c of this parameter required for electroporation is typically found to range in the order of 0.1-10 kV/cm.^{166,199-202} For animal cells, for instance, values around 0.4-0.5 kV/cm are often cited. Comparing these values with the local ones found for the plasma sources, it appears as if electroporation is accessible with plasma treatment. As a necessary condition according to this logic, the cells should be positioned sufficiently close to the location where the electric field is considered, e.g., the plasma sheath. However, a high field strength is an insufficient condition for electroporation, because its time-dependency needs to be added in the equation as well. We will discuss this further in Sec. III C.

Still, electroporation has been proposed as an important mechanism in plasma treatment of various biological systems, based on numerous experimental observations. Ouf *et al.* studied the inactivation of *A. niger* spores in wastewater from the washing process of cherries, grapes, and strawberries by means of a 25 kHz AC powered double atmospheric Ar plasma jet.²⁰⁵ After the treatment, pores were detected in the spore walls, which they attributed to electroporation. Similarly, Devi *et al.* treated inoculated *A. parasiticus* and *A. flavus* on groundnuts in an RF powered capacitively coupled plasma reactor at 0.2 mbar.²⁰⁶ They attributed the disintegration of the fungal spore membrane to a combination of electroporation and plasma etching. Also for plasma treatment of individual unicellular organisms or adherent cell cultures in buffer solution, electroporation is often proposed to explain experimental results. Jinno *et al.*, for instance, investigated the

mechanism behind plasma-induced gene transfection, which they partly attributed to the direct effect of the electric field.²⁰⁷ Such claims are supported by the experiments of Tero *et al.*, who detected pores in the order of 10–1000 nm in an artificial cell membrane system at a plasma–liquid interface after irradiation of the solution with plasma.²⁰⁸ However, direct evidence for plasma-induced electroporation is hard to obtain, since also several other mechanisms can underlie the pore formation, like chemical or biochemical triggers.

C. Plasma-induced electric field penetration into the liquid phase

Several points of caution need to be addressed regarding the simplified reasoning in Sec. III B in the comparison between plasma treatment and pulsed electric fields. First of all, the electric field in the plasma or sheath at a liquid surface refers to local conditions in the gas phase, while the field strength in the liquid phase is expected to be very different. In fact, the liquid is electrically coupled with the plasma phase through the potential at the liquid surface as a boundary condition, rather than by the local electric field. Analogous to the formation of the sheath in the gas phase, an electric double layer will form in the liquid phase. Under steadystate conditions, this double layer blocks the electric field generated by the positive space charge in the sheath and the liquid surface charge by means of dielectric screening. Most of the potential drop over the liquid phase then occurs over the double layer, similar to how the potential drop in the gas phase lies focused in the sheath. As should be noted, the electric double layer in aqueous solutions is very thin in general, in the order of nanometers.^{39,41} The corresponding local electric field can reach up to 10^7 V/cm,³⁹⁻⁴¹ somewhat comparable to the field strength around 10^6 V/cm naturally present at a cell membrane.²⁰⁹ These local values should not be directly compared with the applied field strength values given in the literature for pulsed electric field treatment, as the latter does not take into account the variation of the electric potential in the liquid phase. In summary, the potential drop in the liquid phase is expected to be small under steady-state conditions, with the exception of the electric double layer.

Second, the time-dependent behavior of the plasma-induced voltage over the liquid needs to be taken into consideration, especially when its variation occurs faster than the adjustment of the compensating electric double layer. Note that it is indeed the voltage over the liquid that needs to be compared with the one in electric field treatment. Here, the important role of the plasma sheath becomes apparent. Indeed, the voltage over the liquid phase is directly coupled to the sheath potential. Therefore, knowledge on the temporal evolution of the latter is required to deduce the evolution of the former. This time-dependency is crucial for a full understanding of the electric field-induced processes in biological applications. That is, the critical field E_c for electroporation strongly depends on the applied voltage waveform characteristics. DC fields display the lowest threshold in the order of a few hundreds of V/cm.²⁰³ For AC fields, the peak amplitude E_c can be double this value, yet still well below 1 kV/cm at low frequency, but significantly increasing beyond 10 kHz.^{210–212} For pulsed electric fields, E_c decreases with the number of applied pulses and with the pulse

width.^{166,199-202} Millisecond pulses generally induce larger pores at moderate field strengths in the order of some hundreds of V/cm, as opposed to the smaller pores induced by microsecond pulses with strong fields in the order of 1 kV/cm.^{180,201,202} For this reason, the former are often used to stimulate the uptake of large molecules such as nucleic acids into cells, which has laid the foundation of the so-called gene electrotransfer.¹⁸⁰ Microsecond pulses, on the other hand, are more fit for the injection of small molecules or ions, forming the basis of electrochemotherapy.¹⁸⁰ An interesting situation emerges when characteristic times, such as the pulse width or voltage rise time, fall below the duration required for the ionic redistribution and thus charging of the cell membrane, which lies in the order of $1 \mu s$ (see Fig. 7).^{180,213} In this case, the slow charge redistribution can no longer compensate the external electric field on the sub-microsecond scale. The same reasoning counts for the modification of the electric double layer at the liquid surface. Accordingly, the rapidly changing field can penetrate into the biological tissue, to exert their force on intracellular material, such as organelle membranes.¹⁸⁰ We will discuss this further below.

Third, the total treatment time used to obtain reversible electroporation with repetitively pulsed electric field typically ranges from 10^{-10} to 10^{-4} s, 160,170 which lies multiple orders of magnitude below the plasma treatment times of several seconds to minutes. When using a DC or AC voltage for electroporation, the treatment duration is generally limited to the order of 0.1 s, which is still lower than for plasma treatment.^{210–212} In practice, long electric field treatment times are often avoided to obtain electroporation, as they lead to ohmic heating and possible thermal damage to the treated biological material.²¹⁴ Therefore, the threshold value E_c for conventional electric field treatment may not be an ideal reference for plasma-induced electroporation, where a synergy or

counteraction may take place between the pore formation and other longer term effects. For instance, if an electric field deforms a cell from a circular shape into an elliptical one, the field orientation relative to the longer cell axis will influence the threshold for electroporation.²¹⁵ Fourth, electroporation cannot be considered independent from the plasma-induced chemistry. Oxidation of the cell membrane by reactive oxygen and nitrogen species is, namely, able to facilitate pore formation.²¹⁶ According to a computational study where a direct contact is assumed between an air plasma and a cell wall, pores can also be formed by the bombardment of the membrane by ions, electrons, and radicals.²¹⁷

In other words, the simplified reasoning in Sec. III B lacks in two crucial aspects regarding the electroporation: the timedependency of the voltage over the liquid as well as the potential synergies and counteractions with other plasma-induced effects. Therefore, the role of electroporation in plasma treatment is still not entirely clear up to now. However, multiple recent investigations have added conviction to the belief of its relevance. From a theoretical point of view, strong voltage fluctuations can be expected over the liquid phase in many plasma-liquid systems due to the rapid pulsed-like nature of the applied electrical discharge source. In plasma medicine, for instance, one of the most commonly studied atmospheric plasma jets for cancer treatment is the kINPen, which is AC powered with a frequency ranging from 0.8 up to tens of MHz.²¹⁸ This frequency on its own can generate voltage fluctuations on the sub-microsecond time scale, i.e., below the charging times of the electric double layer and cell membranes in biological tissue. Moreover, the luminescent plasma plume is known to consist of the so-called plasma bullets of a high field intensity, which indeed interact with the liquid surface in a submicrosecond time frame.^{35,218-220} Figure 8 shows that this time



FIG. 7. Ion redistribution in the cell cytoplasm during the application of an external electric field. This charging process takes about 1 µs for cells packed together in a tissue. After the redistribution and charging is complete, the local electric field in the cell has diminished, as long as the external field remains present and fixed. However, imposed electric fields with temporal variations shorter than a microsecond can penetrate into the cell and organelles until the ion redistribution comes to a stationary state. Note that this thought experiment can be repeated for the rapid quenching of an external field and thus also counts for the capacitive discharging of the plasma membrane. Reprinted with permission from Nuccitelli, Bioelectricity 1(1), 30–34 (2019). Copyright 2019 Mary Ann Liebert, Inc.

frame remains valid for lower power frequencies as well. This may enable the incident electric field to penetrate into the liquid phase and intracellular solution. Still, when the interaction of the plasma bullet with the liquid surface takes place over a few hundreds of nanoseconds, the surface potential fluctuations most likely do so as well. This time frame remains rather close to the characteristic charging times around $1\,\mu s$ in biological matter, which limits the actual field penetration.

Another commonly studied plasma source for biomedical applications is a dielectric barrier discharge driven by high-voltage pulses or AC power. This discharge type consists of filamentary streamers, which typically interact with an electrode surface on a nanosecond time scale.^{222,223} Since the propagating streamer heads bring with them an intense field, strong fluctuations in the electric potential are also expected at the liquid surface. According to a series of simulation studies by Babaeva et al., this can result in local electric fields well beyond 100 kV/cm in biological tissue under treatment [Fig. 9(a)].^{192,198,224,225} Yet, these simulations did not include all of the possible microscopic effects at the liquid surface as presented in Fig. 1, i.e., evaporation, microscopic surface deformation, and droplet emission. Such effects may be decisive to the plasma-liquid interaction, in agreement with an experimental investigation by Vanraes et al. on a single dielectric barrier micro-discharge filament in contact with a thin water layer [Fig. 9(b)].²²⁶ Time-resolved imaging of the filament, namely, revealed a continuously present glow-like plasma spot at the liquid electrode, which is generally not observed in the case of solid electrodes. Based on the electrical analysis of the single filament, this unique behavior may be attributed to a so-called resistive barrier discharge, a less known type of plasma with more diffuse features as compared to the usual dielectric barrier discharge.² The resistive nature of the surface, whether it be purely liquid or biological tissue, may thus play an essential role in the plasma properties, both on a local and general level. More specifically, it likely smooths out the temporal evolution of the surface potential, in comparison to a dielectric barrier discharge with solid electrodes. Correspondingly, the voltage over the liquid phase may fluctuate over a time frame of hundreds of nanoseconds instead of a few or tens of nanoseconds, as suggested by the photomultiplier tube (PMT) signal in Fig. 9(b) and the measured voltage waveforms.²²⁶ Analogous to the plasma bullets of a plasma jet, this could limit the actual field penetration into the condensed phase.

D. Plasma-induced electric field effects on skin tissue

A process similar to electroporation can also take place in the skin, at transdermal voltages beyond 100 V, promoting the tissue's permeability.^{229,230} This can explain the pores seen after skin treatment with an atmospheric plasma jet or dielectric barrier discharge, although plasma etching and Joule heating have been suggested to play a role as well.^{231,232} These pores were found to enhance the skin permeability for oxidative species dissolved in a solution, whereas they are not as effective for the transdermal delivery of gaseous plasma species.²³³

Nonetheless, electroporation is but one of the multiple effects electric fields can have on cells and biological tissue. Skin can also absorb species with transdermal DC voltages in the order of 0.1-10 V through a process called iontophoresis. This transfer

mechanism consists of three components: enhanced passive diffusion, electromigration (EM), and convective solvent flow, also known as electroosmosis (EO) (see Fig. 10).²³⁴ The diffusion component is often neglected due to its comparatively minor contribution to the total species transport.^{234,235} In contrast, electromigration stands for the effective ordered ion movement in the presence of the applied electric field. Since the ions prefer the pathway with the lowest electrical resistance, electromigration mainly transpires through the existing skin pores, such as sweat glands or hair follicles.^{230,236–239} The stratum corneum, on the other hand, usually forms a strong barrier for this type of transport. However, such pathway may become effective in the presence of pore formation, e.g., induced by other mechanisms, such as plasma etching or electroporation. The smaller the ion and the higher its charge, the more effective its electromigration. Therefore, monoatomic ions like Na⁺ and Cl⁻ are transferred faster through this process than the charged peptides and proteins with a lower mobility.²³⁴ Electroosmosis, as the third transport component, stems from the isoelectric point (pl) of the human skin, which lies around 4-4.5, well below the physiological pH of about 7.4. Correspondingly, skin is negatively charged and acts as a cation-selective ion-exchange membrane.²³⁴ As a consequence, the flow of water is favored under an electric field in the anode-to-cathode direction.^{234,240-} This facilitates the transport of positive ions and counteracts the electromigration of negative ions into the skin, as depicted in Fig. 10.

Besides the three transport mechanisms contributing during iontophoresis, an increased skin permeability has frequently also been observed after its application *in vitro*. This increased permeability partly corresponds to a disorganization of the stratum corneum. At low current densities, this perturbation remains local, whereas it expands at higher values.²⁴⁴ Several long-term structural changes have been reported, including a decrease in intercellular lamellar ordering and intralamellar packing. Additionally, iontophoresis increases the electrical conductivity and hydration of the skin tissue. In their strongly recommended review,²⁴⁴ Jadoul *et al.* distinguish four possible mechanisms for the increased disorder in the stratum corneum:

- An alteration in the ion concentration and ion type can lead to changes in skin integrity. Also the pH can affect the local lipid organization.
- Water is a known dermal conductivity and permeability enhancer, which reduces lamellar ordering. The increased skin hydration may, therefore, partly explain the observed structural changes in the skin.
- Since the stratum corneum has a higher electrical resistance than the underlying viable skin layers, it forms the place of preference for Joule heating. The general temperature increase by iontophoresis is expected to be minimal, but current flow within localized pathways may lead to confined heating effects and structural perturbations.
- The electric field may also interact in a direct manner with the constituents of the stratum corneum. Electroporation has, for instance, been proposed as a possibility at the low applied voltages in iontophoresis. Although such voltages induce an average electric field that is too low for electroporation, field enhancement at the appendages might enable it at a very localized level.



FIG. 8. Plasma bullet evolution in three different He plasma jets. (Top) The electric field strength E as a function of time and distance from the nozzle, for (left) a jet without a target and (right) a jet at a distance of 2 cm from a grounded active electrode. Both jets are AC powered with a voltage of 4 kV and a frequency of 12.65 kHz. (Bottom) Experimental snapshots with an exposure time of 5 ns, showing the propagation of a plasma bullet onto a water surface, for a jet powered with 7 kV pulses of 800 ns at a frequency of 8 kHz. (Top) Reprinted with permission from Sretenović *et al.*, J. Phys. D: Appl. Phys. **47**(10), 102001 (2014). Copyright 2014 IOP Publishing. (Bottom). Reprinted with permission from Sretenović *et al.*, Plasma Med. Sci. **2**(3), 223–228 (2018). Copyright 2018 IEEE. 800 ns at a frequency of 8 kHz. (Top) Reprinted with permission from Sretenović *et al.*, J. Phys. **47**(10), 102001 (2014). Copyright 2018 IEEE. 800 ns at a frequency of 8 kHz. (Top) Reprinted with permission from Sretenović *et al.*, J. Phys. **47**(10), 102001 (2014). Copyright 2018 IEEE. 800 ns at a frequency of 8 kHz. (Top) Reprinted with permission from Sretenović *et al.*, J. Phys. **47**(10), 102001 (2014). Copyright 2018 IEEE. 800 ns at a frequency of 8 kHz. (Top) Reprinted with permission from Sretenović *et al.*, J. Phys. **1**(2014). Copyright 2014 IOP Publishing. (Bottom) Reprinted with permission from Sretenović *et al.*, J. Phys. D: Appl. Phys. **47**(10), 102001 (2014). Copyright 2014 IOP Publishing. (Bottom) Reprinted with permission from Sretenović *et al.*, J. Phys. D: Appl. Phys. **47**(10), 102001 (2014). Copyright 2014 IOP Publishing. (Bottom) Reprinted with permission from Sretenović *et al.*, J. Phys. D: Appl. Phys. **47**(10), 102001 (2014). Copyright 2014 IOP Publishing. (Bottom) Reprinted with permission from Yang *et al.*, IEEE Trans. Radiat. Plasma Med. Sci. **2**(3), 223–228 (2018). Copyright 2018 IEEE.



FIG. 9. Temporal behavior of a dielectric barrier micro-discharge filament in contact with a liquid electrode. (a) Simulated snapshots of the electron density and electric field around the moment where the filamentary streamer reaches a wound covered in a liquid, having a relative permittivity of $\varepsilon_r = 60$. The maximum values for the snapshot series are 1.2×10^{16} cm⁻³ and over 400 kV/cm, respectively. The latter value corresponds to the momentary sheath at the liquid surface. (b) Experimental photomultiplier tube signal and snapshots of an AC powered filament between an upper high-voltage needle included in a spherical quartz barrier and a thin water film over a grounded grid, (left) during the negative and (right) positive voltage half cycle. The blue panels present images obtained with an OH filter. The applied voltage amplitude was 6.7 kV, except for the most left bottom panel, where the discharge for 8.5 kV is shown for comparison. (a) Reprinted with permission from Babaeva *et al.*, J. Phys. D: Appl. Phys. **47**(23), 235201 (2014). Copyright 2014 IOP Publishing. (b) Reprinted with permission from Vanraes *et al.*, Sci. Rep. **8**(1), 1–11 (2018). Copyright 2018 Author(s), licensed under a Creative Commons Attribution 4.0 International License.

The electric field may also interact directly with the polar groups in the cell membrane lipids. As an example, this mechanism has been held responsible for the non-linearity in the currentvoltage relationship of phospholipid bilayers, corresponding to a growing number of structural defects at higher voltages and ultimately a first-order phase transition of the membrane.²⁴⁵ In such a way, the electric field may force the stratum corneum components to adopt high energy configurations, which enlarge pre-existing channels or create new ones. Consequently, pathways can be created for the electrical current, which may be physically long but less resistive.²⁴⁶

Even though the mechanisms of species transport in iontophoresis and electroporation are believed to be different, their effect



FIG. 10. The roles of electromigration (EM) and electroosmosis (EO) in the transport of charged (D^+ and D^-) and neutral (D) molecules during transdermal iontophoresis with an applied DC voltage V under physiological conditions. The size of the gray arrows represents the transport intensity of the considered species. Reprinted with permission from Gratieri *et al.*, Expert Opin. Drug Delivery **8**(5), 645–663 (2011). Copyright 2011 Taylor & Francis Ltd. (http://www.tandfonline.com).

on the stratum corneum minutes after their application is very similar.²⁴⁴ In plasma treatment of skin, the combination of both phenomena may occur. Indeed, the plasma-induced voltage over the skin may be understood as the sum of a DC component, resulting in iontophoresis, and a time-dependent component with sub-microsecond fluctuations, responsible for electroporation. This may open the door for synergetic effects.

E. Plasma-induced electro-endocytosis

Electric fields can also influence the transport of species between the intracellular and extracellular solutions in less violent ways. Kaneko et al. detected a higher transfection efficiency under plasma-liquid interaction in a cell solution serving as an active electrode in comparison to an identical solution on a floating potential.²⁴⁷ The observed fluorescent dye injection into the cells could not be explained with electroporation. The authors, therefore, suggested an enhanced transport through channels that selectively act on the dye, induced either by reactive oxygen species or by the electric field. In several other investigations, plasma treatment turned out to have an important effect on endocytosis, one of the most fundamental physiological functions of cells (see Fig. 11).^{248,249} Jinno et al. investigated the mechanism behind plasma-induced gene transfection and found clathrin-dependent endocytosis to have a dominant contribution.²⁰⁷ The other part of the species transport was attributed to electroporation, while the permeation did not seem to transpire through ion channels or chemical poration. In follow-up research by the same group, the electric field was discovered to be essential for the gene transfection, with a threshold value around 100 V/cm.² Vijayarangan et al., on the other hand, did not notice a significant contribution of poration by the electric field.²⁵¹ In their experiments, endocytosis was also revealed as a dominant mechanism for plasma-induced drug delivery into cells. He et al. suggested a similar process for the uptake of gold nanoparticles in cells under plasma treatment, based on their measurements.²

Note, in this regard, that endocytosis may be induced or enhanced by low electric fields, sometimes referred to as electro-endocytosis.^{253–256} A transmembrane voltage below 1 mV may be sufficient to influence endocytosis and endocytic vesicle recycling,²⁵⁵ since field strengths as low as a few V/cm already provide a clearly noticeable effect.^{253,254,256} The mechanisms behind this process are still under debate, more specifically regarding which type of endocytosis is stimulated by the fields. However, a growing interest can be noticed in recent years in fundamental research on this topic. Perhaps not coincidentally, clathrinmediated endocytosis has been reported as one of the main underlying principles of gene electrotransfection.^{254,257,258} Next to that, caveolin/raft-mediated endocytosis and micropinocytosis were demonstrated to be important as well in a study by Rosazza et al.,²⁵⁸ while the caveolin-dependent pathway did not play an obvious role in the experiments by Moisescu et al.²⁵⁴ Interestingly, endocytosis may be preceded by the binding of the genetic material to the cell wall. According to the experimental data of Wu and Yuan,²⁵⁹ ⁹ the presence of divalent cations such as Ca²⁺ and Mg²⁺ enhances gene adsorption to the membrane, thus facilitating the electrotransfer. Based on these insights, the endocytosis observed under plasma treatment might largely be due to relatively weak electric fields penetrating into the biological material, possibly enhanced by iontophoresis. As should be noted, such field-induced effect is somewhat reminiscent to vesicle electroformation, whose underlying mechanism is still under debate (see Fig. 11).² Artificial vesicles actually form interesting test systems to study the effect of electric fields on the cell membrane. A great deal of inspiration on these effects can be found in numerous review papers (see, e.g., Refs. 262-266). Schubert and Römer, as well as Madl et al., for instance, discussed how synthetic membrane systems contribute to the understanding of lipid-driven endocytosis.^{267,268} For more information on electro-endocytosis, we refer to the reviews by Kolosnjaj-Tabi et al. and by Baluška and Wan.

F. Other effects of plasma-generated fields on biological materials

Electric fields can influence biological materials in many more ways. Figure 12 summarizes some of the most important effects on a cellular level as a function of the electric field strength and pulse duration, based on the recommended review by Kolosnjaj-Tabi *et al.*²⁵⁶ As a tentative rule of thumb, the pulse duration gives an indication of the part of the cellular structure that will be affected by the field. Microsecond pulses have a preferential impact on the cell membrane. Nanosecond pulses, in contrast, shift the aim toward the nuclear matter, by inducing DNA and chromosome damage,²⁷¹ by altering nuclear processes and by increasing gene expression.²⁷² Picosecond pulses have recently been made possible with novel high-voltage generators. Their application inhibits the growth of HeLa cells *in vitro* and induces apoptosis, which is believed to follow the mitochondria-mediated route.^{273,274} Note that a shorter pulse in these experiments generally implies a higher



FIG. 11. Comparison of (top) clathrin-mediated endocytosis, a mechanism observed in electro-endocytosis, and (bottom) vesicle electroformation on indium tin oxide (ITO) coated glass. As indicated by the horizontal blue line, clathrin-mediated endocytosis is a multistage process, regulated by multiple factors at multiple stages, some of which may be intensified by the field. The electroformation of vesicles can be understood as a field-enhanced version of the natural swelling of a lipid film into vesicles. An electric field stimulates the swelling due to an interplay between electrostatic interaction, bilayer counterion redistribution, changes in the membrane surface and line tension, as well as electroosmotic processes. (Top) Republished with permission from Mettlen *et al.*, Annu. Rev. Biochem. 87, 871–896 (2018). Copyright 2018 Annual Reviews, Inc. Based on Ref. 269. (Bottom) Reprinted with permission from Stein *et al.*, Front. Physiol. 8, 63 (2017). Copyright 2017 Author(s), licensed under a Creative Commons Attribution (CC BY) license.

field strength. At the lower intensity range around the order of 1 V/cm, the cellular effects become subtler and less destructive. Examples are cell deformation, contraction, elongation, reorientation, alignment, and migration. Curiously, cells can also change

from one type into another by the electric field, a process known as cellular differentiation. Another peculiar process is cell electrofusion, where the membranes of two cells merge into one.²⁵⁶ As already mentioned in Sec. III B, electric fields are also able to



FIG. 12. Electric field effects in biological material at a cellular level (top) as a function of the electric field strength and (bottom) as a function of the field and the pulse duration. The used abbreviations stand for picosecond pulsed electric fields (psPEF), nanosecond pulsed electric fields (nsPEF), irreversible electroporation (IRE), and electrochemotherapy (ECT). (Top and bottom) Reprinted with permission from Kolosnjaj-Tabi *et al.*, Adv. Drug Delivery Rev. **138**, 56–67 (2019). Copyright 2019 Elsevier. (Bottom) Adapted with permission from Weaver *et al.*, Bioelectrochemistry **87**, 236–243 (2012). Copyright 2012 Elsevier.

stimulate cell multiplication, often referred to as proliferation. The current knowledge on the fundamental mechanisms behind these effects is more thoroughly discussed in Refs. 256 and 275.

One should not forget that the fields can also affect the biological matter on a molecular level. Figure 13 presents a few examples. Similar to iontophoresis in skin tissue (see Sec. III D), electric fields facilitate ionic and molecular transport through biological membranes in other types of biological liquids and tissue via electrophoresis and electroosmosis.²⁷⁵ Polarizable neutral molecules such as DNA and proteins may be transported and separated in inhomogeneous fields too by dielectrophoresis.^{276–279} Furthermore, fields can orient polar molecules and modify their conformational structure. This is especially relevant for proteins, whose function depends on their quaternary structure. Strong pulsed electric fields



FIG. 13. Examples of electric field effects in liquid matter at the molecular level, i.e., (left) transport mechanisms present already at low field intensities and (right) modification of conformational structure at higher intensities. Strong fields can unfold a protein and lead to a higher exposure of an internal hydrophobic pocket. This can lead to either denaturation and a better digestibility by gastrointestinal (GI) enzymes or a reduced digestibility due to aggregation. These processes can also lead to different immune responses in the human organism. (Left) Reprinted with permission from Zhao *et al.*, Cell. Mol. Life Sci. **77**, 2681–2699 (2020). Copyright 2020 Springer Nature. (Right) Reprinted from Rodrigues *et al.*, Food Res. Int. **137**, 109709 (2020). Copyright 2020 Elsevier.

in the order of 10 kV/cm are indeed known to inactivate not only micro-organisms but also enzymes.^{280–283} Figure 13 shows how they can affect the three-dimensional protein structure. Next to that, DC and AC fields in the order of 10 V/cm or higher may already result in phase transitions, as illustrated with their use for protein crystallization.²⁸⁴ If such field-induced changes take place in a living organism under plasma treatment, they might obviously have decisive consequences, including different types of cell death. Also in the case of food processing, they may affect the digestion process or the human organism after consumption.²⁸³ Understanding their occurrence and the underlying mechanisms should, therefore, form a crucial part in the investigation of plasma interaction with biological matter.

However, these insights are relevant as well for nanomaterial synthesis and chemistry in the liquid phase or at the plasma-liquid interface. Indeed, also for such applications, the plasma-induced electric field can affect the molecular processes in the solution. Moreover, the movement, accumulation, and clustering of nanoparticles in a solution can be influenced and controlled with an electric field.^{266,286-291} As should be noted, the same remarks count for

magnetic fields (see, e.g., Refs. 292–295). A detailed study of the plasma sheath and its relation to the electric and magnetic fields in the liquid will, therefore, benefit applied research on plasma–liquid interaction in general. In this regard, the sheath dynamics deserves additional attention. It determines the voltage fluctuations over the liquid phase and thus the extent of field penetration, as explained in Sec. II C. Indeed, the amplitude of the penetrating field can only be acquired by means of an accurate sheath model, and to build the latter, more fundamental research needs to be performed.

IV. THE SHEATH AS A MASS TRANSPORT REGULATOR AT LIQUID METAL WALLS IN A NUCLEAR FUSION REACTOR

As already mentioned in Sec. I, the presence of a plasma sheath often leads to undesirable effects, like damage to the solid plasma reactor wall by sputtering or an increased heat flux. In order to improve the reactor lifetime, the solid wall may be replaced with a self-repairing liquid one. This approach is currently considered for future nuclear fusion reactors, where damage to the divertor and main chamber plasma facing components (PFCs) forms one of the major concerns.^{296–298} In addition to the large heat and ion fluxes, PFCs are exposed to edge-localized modes (ELMs), i.e., explosive magnetohydrodynamic instabilities. On the upside, ELMs provide an effective flushing mechanism for impurities that can otherwise lead to a radiative collapse of the plasma discharge.²⁹⁶ On the downside, they can cause cracks, blistering, fuzzy, melting, and bubbles in the case of solid walls, with an impact that scales with the reactor size.^{296–298} Therefore, several ELM control or mitigation techniques have been proposed, including repetitive small pellet injection and resonant 3D magnetic perturbation fields.^{296,299}

Additionally, damage to the reactor can be prevented by the use of liquid metal as PFCs, such as liquid lithium, lead lithium alloy (Pb-16Li), and tin.^{300,301} Among these, liquid Li and Pb-16Li can act as deuterium and tritium breeder blankets, due to their retention properties for hydrogen isotopes.^{300,302,303} As an extra advantage, this results in a diluted Li emission toward the fusion plasma bulk.^{300,304} The plasma sheath over the liquid forms another barrier for the lithium pollution, as displayed in Fig. 14.



Plasma Interface

FIG. 14. Scheme of the plasma–liquid interface at a liquid plasma facing component in a nuclear fusion reactor, according to Andruczyk *et al.*³⁰¹ Released liquid species are presented in white. Various processes involving the ions and neutrals need to be considered, such as sheath formation, sputtering, evaporation, adatom effects, ionization, redeposition, migration, and surface contamination. Note that the thickness of the sheath relative to the one of the vapor cloud is not *a priori* known, and may vary with the operating conditions as well as the stage during an ELM. Reprinted with permission from Andruczyk *et al.*, J. Fusion Energy **39**, 441–447 (2020). Copyright 2020 Springer Nature.

About two-thirds of the sputtered Li particles are, namely, released as ions, which can effectively be accelerated back into the liquid wall by the sheath field.³⁰ ⁶ The Li atoms sputtered as neutrals are readily ionized, as shown in several investigations,³¹ which should further limit the undesired lithium pollution. According to a computational analysis by Brooks et al., the effective redeposition of ejected Li from the surface results in a net erosion rate below 1%.310 However, the simulation of these processes requires advanced modeling methods, because the sheath features vary in time during an ELM. 311 Moreover, the sheath may be influenced by the distinctive properties of the plasma-liquid interface, such as evaporation, surface deformation, droplets, and bubbles. This makes the present Perspective relevant for nuclear fusion research. Table I compares the advantages and disadvantages of solid and liquid PFCs, indicating the need for more investigations on the risks involved with the liquid variant.

As mentioned above, ELMs may be manipulated by means of magnetic fields, and the same is true for the case with liquid walls. Moreover, magnetic fields enable further control of the mass transport in the sheath. For this reason, the study of a magnetized sheath at a liquid surface is of particular interest to nuclear fusion research. Inspiration can be taken from the parallel research line on magnetized sheaths at solid walls. When B is parallel to the wall, in the absence of collisions and turbulence, the incident particle flux

TABLE I. Summary of the advantages and disadvantages of solid and liquid PFCs. The colors indicate the risk, from very low to very high, following the sequence dark green, light green, yellow, orange, and red. Orange and red items could become decisive show stoppers. Reproduced with permission from Rapp, Fusion Sci. Technol. **72**(3), 211–221 (2017). Copyright 2017 Taylor & Francis Ltd (http://www.tandfonline.com).

	Solid (e.g., W)	Liquid
Lifetime of plasma facing components Maximal steady-state heat flux	PFCs need change-outs 5–10 MW/m ²	Liquid can be replenished ~30 MW/m ² or higher
Resilience to transients (ELMs, disruptions)	Crack formation	Thinning of liquid layer
Tritium retention	Most likely acceptable	Huge hydrogen uptake in Li
Low plasma core contamination (Z_{eff} or radiation)	<10-5 demonstrated	Not demonstrated
Chemical compatibility in PFC system	None for He; known for water	Critical issue
Embrittlement of structural materials	Irradiation embrittlement	LM embrittlement
Radioactivity at end of plant lifetime	Moderate to high	Low
Accident tolerance (e.g., leaks, air ingress)	Oxidation, little volatilization	Li is potentially problematic
operation Unknown risks	historically Low	High

will become zero in the steady-state regime.³¹² Such situation is relevant for tokamak or stellarator devices, where most surfaces are almost parallel to the magnetic field.³¹³ The particle-in-cell (PIC) model by Li and Wang predicted such sheath to form with a characteristic time equal to the ion cyclotron time, obtaining a thickness determined by the ion Debye length.³¹⁴ For a certain range of the mean free path, the sheath splits in two layers of opposite space charge, with the positive one near the wall and the negative one near the plasma, according to the PIC simulations by Moritz *et al.*³¹² The width of this electric double layer was found to decrease with the magnetic field strength. Other simulation studies, however, demonstrated an opposite process, where the surface collected a positive charge, to repel ions back toward the plasma.^{315,316}

In the case of an oblique magnetic field, an additional region appears between the pre-sheath and the Debye sheath, called the magnetic pre-sheath or Chodura layer.^{112,312,317,318} Ions from the plasma are first accelerated in the pre-sheath along the magnetic field direction but reorient toward the wall in the Chodura layer in order to satisfy the Bohm criterion. The effect of the magnetic field and the ion temperature on the sheath was investigated in three independent fluid simulation studies, with some conflicting conclusions. Khoramabadi et al. found the sheath width to decrease with the ion temperature,³¹⁹ while Liu et al. reported the opposite relationship.³²⁰ Their models agreed on the predicted sheath size reduction as a function of the magnetic field strength but contradicted with regard to the field orientation. Khoramabadi et al., namely, noticed no effect on the sheath parameters by the field component perpendicular to the wall, in contrast to the sheath thickness decrease seen by Liu et al. for a field turning toward this perpendicular direction. The latter effect was also acquired with the model of Pandey et al.³²¹ Most fluid models conventionally assume the Boltzmann relation for electron density, which induces inaccuracies. By omitting this assumption, Wang et al. found a floating wall potential reduction and, in the low wall bias range, sheath narrowing.³²² Using a kinetic trajectory simulation model, Chalise and Khanal observed a magnetic field dominant region near the sheath entrance and an electric field dominant region at the wall.³² Such effects may be useful to manipulate the mass transport through the sheath, but more research is required to obtain insight into the deviations between the models and the sensitivity of the involved parameters.

The situation at a liquid wall with a magnetic field presents some additional challenges in understanding, as well as unique opportunities to regulate the plasma-wall interaction. In electrospraying and electrospinning, for instance, a magnetic field along the symmetry axis of the Taylor cone on the liquid surface can be used to stabilize the cone or to overcome a bending instability of the spraying jet.³²⁴⁻³²⁷ On the contrary, charged droplet ejection from the liquid surface may be controlled with an oblique or parallel magnetic field. A similar strategy could be applied to suppress Taylor cone formation or other types of surface deformation. For liquid lithium specifically, a magnetic field parallel with the wall has been proposed as a method to make the lithium flow along the reactor boundaries by means of magnetic propulsion, an effect discovered at the end of the previous century.^{328,329} Additionally, lithium can be passively pumped by means of thermocapillary³ and thermoelectric effects.³³¹ Combined, these mechanisms have

motivated the development of thermoelectric magnetohydrodynamics (TE-MHD),³³² which allows us to describe stirring of metallic liquids with a magnetic field and an electron beam, consistent with experiments.^{331,333} Although such a description seems relevant mainly for very specific systems like fusion reactors, magnetic fields are known to have an effect on liquids in general as well. A strong magnetic field perpendicular to a diamagnetic liquid surface, namely, deforms the interface by depressing it, referred to as the Moses effect.^{334,335} Paramagnetic liquids, on the other hand, display the reverse Moses effect, where a bump forms on the surface.^{334,335} Both effects are still poorly understood. In this regard, it is useful to keep in mind that liquid lithium is paramagnetic. Water, as a diamagnetic solvent, can also be deformed by this effect. Therefore, magnetic fields may serve as potential regulators of the sheath and the liquid surface in plasma-liquid interaction for a wide range of applications. The study of magnetized plasma sheaths, therefore, forms an interesting domain for both plasma engineers and scientists. As such, we hope to motivate a collaboration with nuclear fusion scientists and plasma researchers of other fields to further investigate the underlying fundamentals and to develop advanced models for a comprehensive description of magnetized sheaths.

V. THE SHEATH AS A CHEMISTRY REGULATOR IN NANOMATERIAL SYNTHESIS AND OTHER APPLICATIONS

In Sec. II C, we explained how the chemistry at the plasmaliquid interface strongly depends on the sheath properties. An accurate understanding of this dependency will enable the fine-tuning of target reactions for a specific application. A few examples can already be found in investigations on nanomaterial synthesis. Kaneko and Hatakeyama studied, for instance, the chemical modification of the ionic liquid $[C_8H_{15}N_2]^+[BF_4]^-$ as a function of the incident ion energy.³³⁶ As seen in Fig. 15(a), the plasma irradiation of the liquid induced a peak at 297 nm in its UV-Vis absorption spectrum, growing with the ion energy for a fixed treatment time. Consequently, the solution changed from pale to dark yellow. When the ionic liquid was used as an anode instead of a cathode, corresponding with electron instead of ion irradiation, the same effect was not observed [see Fig. 15(b)]. According to the authors, the ion bombardment, therefore, causes dissociation of the liquid molecules, for which the efficiency improved with ion energy. Following this principle, ion irradiation of ionic liquids may be used for material synthesis, through reactions whose performance can be tuned with a plasma sheath.

Although electron bombardment seemed ineffective for this particular experiment, it may be effective in others. In fact, gaseous plasma has been proposed as a versatile cathode for electrochemical reactions that are unpractical or impossible with solid cathodes. Certain electron reactions, namely, require an activation energy inaccessible by conventional electrochemistry. An anode sheath at the liquid surface, in contrast, can accelerate the electrons toward the liquid, giving access to the reaction at its surface. In their review of 2011,³³⁷ Mariotti and Sankaran elegantly describe how plasmas allow us to decouple the reaction kinetics at a liquid surface from the overall system thermodynamics. According to



FIG. 15. UV–Vis absorption spectra of the plasma-treated ionic liquid $[C_8H_{15}N_2]^+[BF_4]^-$ (a) as a liquid cathode for different ion energy E_i and (b) as a liquid anode for electrons with an energy E_e of about 10 eV. The treatment was performed with Ar plasma at a pressure P_{gas} for 2 min. The sheath potential could be controlled by changing P_{gas} at a constant discharge current of 1 mA. From Kaneko and Hatakeyama, *Plasma Processing of Nanomaterials*. Copyright 2012 Taylor & Francis Group. Reproduced with permission from Taylor & Francis Group.

their description, the principles behind electron-induced reactions in a gas phase plasma remain valid at a plasma–liquid interface. In other words, cross-sectional data similar to the gas phase counterpart can be imagined for electron collisions with dissolved species at the liquid surface. As a well-known quantum mechanical effect, excitation, dissociation, or ionization of a particle generally displays resonant regimes around certain electron energies, visible as a local maximum in the cross section. Applying this idea to the plasma– liquid interface, an anode sheath can be used to tune the incident electron energy, in order to stimulate one specific reaction.

To illustrate this, Mariotti and Sankaran elaborated on dissociative electron attachment by means of the model for a hypothetical diatomic system AB in Fig. 16 by Krishnakumar *et al.* The latter authors explained the dissociation process as a sequence of resonant electron attachment to the excited state AB^{-*} and dissociation along its repulsive potential energy curve (purple line).³³⁸ In order to obtain the AB^{-*} state, only energy in a narrow interval can be added to the AB ground state, next to the attachment of the electron. The width of this interval is indicated by the blue peak in Fig. 16. Such resonant electron capture by the molecule can be realized from a vibrationally or electronically excited intermediate AB^* before the electron attachment, or directly from the AB ground state through the appropriate kinetic energy of the colliding electron.^{338,339} In other words, a specific dissociative electron



FIG. 16. Schematic model of dissociative electron attachment of a hypothetical diatomic system AB. The attachment occurs in the Franck–Condon region to form the resonant state AB^{-*} , which has a repulsive potential energy curve indicated by the purple line. The width of this curve represents the finite lifetime of AB^{-*} against auto-detachment, i.e., spontaneous electron ejection, denoted with the arrow **a**. The more likely dissociative path is shown by means of the arrow **d**. If the repulsive state survives against auto-detachment until the internuclear distance R_c , it dissociates to give the stable neutral fragment A and the negative ion B^- . Reprinted with permission from Krishnakumar *et al.*, in XXV International Conference on Photonic, Electronic and Atomic Collisions (2007), Copyright 2007 Author(s), licensed under a Creative Commons Attribution (CC BY) license.

attachment process can be selectively initiated by means of the electron energy. At a liquid anode, this energy can on its turn be tuned with the anode sheath properties. This permits a strategy to selectively synthesize nanomaterials with plasma–liquid interaction.

Nonetheless, we would like to put forward three points of caution about this hypothesis. First of all, reaction mechanisms like the one in Fig. 16 are usually studied in the gas phase, instead of at the liquid surface. Prabhudesai et al., for instance, observed resonant electron capture directly from the AB ground state during the interaction of a molecular beam with a pulsed electron beam.³ In the gas phase, the dissociation process along the repulsive potential curve (arrow d in Fig. 16) mainly competes with the less likely auto-detachment process (arrow a). In the liquid phase, however, several other relaxation channels might become available. This a priori puts into question the mechanism's validity at the liquid surface. Yet, as pointed out by Mariotti and Sankaran, dissociative electron attachment has already been reported for electron beam excitation of various solutions from alcohols to water, demonstrating its validity *a posteriori*.^{337,338,340–342} Even so, such confirmation is required for all other types of reactions, if one wishes to translate a gas phase mechanism to the liquid surface.

As a second point of caution, this still does not prove the mechanism's effectiveness at the plasma-liquid interface because the strong local field may increase the probabilities of the various relaxation channels competing with the reaction. As a third point of caution, even if the reaction proceeds, the electric field may also interfere with its pathway. The field is, namely, expected to reorient the liquid surface species in an anisotropic manner, changing its direction relative to their bond and reaction axes, in agreement with the chemical field effects discussed in Sec. II C. In fact, this could provoke reaction pathways inaccessible in conventional electron beam experiments, adding another dimension of selectivity to the plasma-liquid interfacial chemistry. Using electron energy as a control parameter, Krishnakumar et al. found dissociative electron attachment to selectively break the N-H and O-H bonds in carboxylic acids, without much damage to other bonds.³³⁸ In contrast, the selectivity did not appear as good for C-H bonds. The local field of the sheath may provide a means to modify this pattern, allowing the synthesis of unique nanoparticles. As an important remark, the orientation of the bond to be broken relative to the incoming electron direction is also expected to be an important factor in the chemical control and anisotropy. Krishnakumar et al., for instance, observed this orientation to be decisive for the angular distribution of the ejected product anions, independent of the molecular orientation.³³⁸ They termed this phenomenon bond orientation dependent electron attachment.

The plasma sheath can also influence the chemistry at the liquid surface with non-collisional processes. An example is given by Morishita *et al.* in a reaction route toward nanocarbons realized with bipolar pulsed spark–glow transition plasma in benzene.³⁴³ According to their study, this route starts with the electronic excitation of benzene at the plasma––solution interface by the local field. The π -conjugated bonding and antibonding orbitals, namely, lie close to the Fermi level, giving the molecule a high reactivity. The electrons in the π -orbitals are, therefore, readily excited to π^* orbitals by the plasma sheath potential, which plays a similar role as the

electrical double layer potential in conventional electrochemical reactions. Subsequently, the excited electrons can be ejected by collisions of plasma particles at the interface. This produces benzene radical cations, which serve as important intermediates in the formation of polycyclic aromatic hydrocarbons, i.e., nanocarbons. In comparison to the other organic solvents (hexane, hexadecane, and cyclohexane), benzene displayed the highest synthesis rate. Morishita et al. explained the lower efficiency for the linear molecules with a synthesis process in the gaseous plasma from small molecules such as C2 under heat, similar to pyrolysis. For the saturated ring of cyclohexane, on the other hand, unsaturated ring molecules first needed to be formed through C-H dissociation, adding additional steps in the reaction pathway toward the nanocarbons. These different routes likely also underlie the lower degree of nanocarbon crystallinity obtained for the ring molecules relative to the linear ones. The proposed reaction schemes are in good agreement with the reactivity of the starting materials, as evaluated via ab initio molecular orbital calculations.²

As another example of non-collisional interfacial chemistry that may be controllable by the sheath properties, reactions of solvated electrons are expected to strongly depend on their electronic state. Rumbach et al. investigated the solvation of electrons by a DC atmospheric pressure glow discharge into a water anode, finding an unexpected blueshift of about 50 nm in the measured absorption spectrum relative to the well-known peak of the bulk solvated electron at 720 nm [Fig. 17(a)].¹³¹ They attributed this blueshift to the intense electric field in the interfacial Debye layer, which is closely related to the sheath features. If this is correct, the interfacial solvated electron reaction kinetics may be controllable by the sheath, forming another argument to intensify investigations on this topic. However, the origin of the blueshift is speculative for now because it might instead be an inherent property of the interface, independent of the plasma. Although several computational studies suggest the fully solvated electrons at the air-water interface to be almost or completely indistinguishable from their bulk counterpart (see, e.g., Refs. 54, 55, 58, 344, and 345), their findings do not contradict a possible blueshift of 50 nm (or 0.13 eV) in the absorption spectrum. Figure 17(b) illustrates this with results from mixed quantum mechanics/molecular mechanics simulations combined with time-dependent density functional theory (TD-DFT) calculations, using the same protocol for the interfacial and bulk spectrum.³⁴⁵ A blueshift of about 1 eV can be seen for the interfacial variant, in agreement with a later analysis of the same data⁵⁵ and with the experimental observations by Rumbach et al. Yet, more investigations are required to provide a conclusive assessment about the origin of this blueshift, since contradictive output has been obtained with other simulation methods. A redshift of 0.5 eV and no shift at all in the interfacial absorption peak have been predicted by the respective TB and LGS models, named after their developers Turi and Borgis, and Larsen, Glover, and Schwartz, respectively.^{57,58,346} We also note that Fig. 17(a) seems to be the first experimental absorption spectrum of the interfacial solvated electron reported in the literature. Moreover, none of the mentioned models take into consideration the possible long-range quantum correlations between neighboring solvated electrons and negative ions, which may significantly affect their spectral features and underlie the experimental blueshift as well.



FIG. 17. The optical absorption spectrum of the solvated electron (a) as measured at the plasma–solution interface using laser diodes at different wavelengths and (b) as computed at a gas–water interface using a mixed quantum and classical protocol with time-dependent density functional theory (TD-DFT). The black error bars with capped ends represent the root mean square variance in the raw measured data. The overlaid red error bars additionally account for the systematic uncertainty in the laser–plasma overlap. The simulated curve (in red) is compared with its counterpart in the liquid bulk, obtained with the same computation protocol. Furthermore, the black solid lines in both graphs show the experimental spectrum for the solvated electron in the bulk liquid. (a) Reprinted with permission from Rumbach *et al.*, Nat. Commun. **6**(1), 1–7 (2015). Copyright 2015 Author(s), licensed under a Creative Commons Attribution 4.0 International License. (b) Reprinted with permission from Uhlig *et al.*, J. Phys. Chem. A **118**(35), 7507–7515 (2014). Copyright 2014 American Chemical Society.

In principle, the sheath can also influence the solvated electron chemistry at the liquid surface in more indirect manners, by regulating the penetration depth or the local density of the species. According to Mota-Lima, two additive contributions need to be distinguished in the penetration depth: (i) the thermalization penetration, i.e., the distance due to slowing the kinetic motion of the plasma-injected electrons, and (ii) the diffusion length of the solvated electrons, i.e., the range of the associated mass diffusion within a given time window.³⁴⁷ In the presence of an electric field in the liquid, however, a third contribution needs to be considered as well, namely, (iii) the drift of the solvated electrons along the field. The total penetration depth is, therefore, expected to depend on the sheath properties. As should be noted, the thermalization depth is often called the penetration depth in the literature, so caution is required when interpreting the given values.

In the study by Rumbach *et al.*, the average thermalization depth of the electrons was estimated to be 2.5 ± 1.0 nm, based on the aforementioned absorption measurements and the reaction kinetics.¹³¹ From this value, the authors concluded the electrons to get fully solvated before reacting. Monte Carlo simulations by Meesungnoen *et al.* gave a thermalization penetration of 1–30 nm for electron energies between 1 and 100 eV.³⁴⁸ Diffusion lengths as calculated by Mota-Lima ranged from 269 to 2084 nm.³⁴⁷ Only rapidly changing sheath fields can penetrate the liquid down to such depths (see Sec. III C). Rumbach *et al.* determined a field strength of 10⁴ V/m at the liquid side in the interfacial electrostatic Debye layer, by means of an analytic model.¹²⁸ Using this value, they disregarded the drift component in the solvated electron

transport, finding a penetration depth ranging between 10 and 100 nm over a wide range of electron current densities j_e , inversely scaling with j_e and reaching 28 nm for a typical current density $j_e = 10^4 \text{ Am}^{-2}$.³⁴⁹ According to the model, the interfacial concentration of the solvated electrons increases with j_e , ranging between 0.02 and 1 mM. The increasing density and decreasing penetration depth with j_e was also observed in the model of Keniley and Curreli³⁵⁰ and has recently been confirmed with experiments.³⁵¹ Furthermore, these results are in good agreement with the simulation output from the particle-in-cell Monte Carlo collision (PIC-MCC) model with liquid chemistry developed by Gopalakrishnan et al., which provided an electric field strength in the liquid of 10⁴ V/m, and a solvated electron density profile from almost 1 mM at the surface to around 0.1 mM at a depth of 20 nm, dropping to 10^{-3} mM around 90 nm.¹²⁹ The external electric field was found to only weakly influence the solvated electron density profile.

However, both the models from Gopalakrishnan *et al.* and Rumbach *et al.* have neglected the free electron penetration through thermalization upon impact. Their results, therefore, do not represent the conditions in the first molecular layers of the liquid. For instance, the calculated electric field strengths of 104 V/m at the liquid side cannot explain the aforementioned blueshift in the absorption peak,^{128,352} but stronger fields may still be present near the liquid surface due to such disregarded effects. The possible field-dependency of the observed blueshift thus remains an open question. Next to that, the solvated electron chemistry may be regulated by the sheath in the upper region of the liquid, by means of the varying thermalization depth with the incident

electron energy, as acquired with the Monte Carlo simulations by Meesungnoen et al.³⁴⁸ In this respect, Levko et al. performed another interesting modeling study of streamer penetration into the surface of a de-ionized water anode with the PIC-MCC method.¹³⁰ In contrast to other models, which ignore electron impact reactions, their simulations predict ionization of the water molecules at the surface due to the kinetic electrons from the plasma. Additionally, the simulations revealed an ion-rich sheath with positive space charge in the vicinity of the water surface on the gas side, as already discussed in Sec. II D and Fig. 5. This forced plasma electrons back toward the plasma phase. Further in the plasma, the electric field reversed, strongly accelerating the plasma electrons toward the liquid surface to overcome this repulsion. At the surface, the electrons penetrated into the liquid to a depth of about 20 nm, producing solvated electrons with an average kinetic energy of 0.02 eV,¹³⁰ i.e., thermal energies expected around room temperature. The striking differences with the other models regarding electron solvation form yet another reason to promote more fundamental work on the sheath properties in plasma-liquid interactions. In particular, more accurate information on the solvation dynamics of electrons and other plasma species for the unique conditions at the plasma-liquid interface is highly desirable.

Deeper toward the liquid bulk, below the thermalization depth, the chemistry likely becomes rather independent from the external field. Importantly, the solvated electron chemistry displays a strong selectivity on its own, making it particularly attractive for nanoparticle and chemical synthesis applications. Hawtof et al. recently reported a record-high faradaic efficiency approaching 100% for ammonia synthesis from nitrogen plasma and water, attributed to the selective production of hydrogen radicals from solvated electrons.³⁵³ Rumbach et al. measured a faradaic efficiency close to 10% for CO₂ reduction in an aqueous solution by the solvated electrons injected from an argon plasma and postulated it to reach 100% for an increasing CO₂ concentration.³⁵⁴ Mota-Lima explained the obtained results with a theoretical framework, similarly predicting the reduction efficiency to become 98%, with 97% selectivity to oxalate generation, if a flow cell is used to refill the aqueous CO₂ in the reactor.³⁴⁷ Using a computational model for silver reduction with plasma-produced solvated electrons, Zheng et al. found the relative electron and silver ion concentrations in the liquid phase to be decisive for the type of products being formed.3 An excess of solvated electrons mainly resulted in neutral silver clusters, while ionic silver clusters were dominantly generated in the case of excess argon ions. Various studies have demonstrated the crucial role of the current density, plasma gas, and scavenger concentration on the solvated electron density and chemistry (see, e.g., Refs. 129, 353, and 355-357). In addition to the selection of these parameters, a more profound understanding of the plasma sheath will allow further fine-tuning of the species transport through the interface and thus of the aqueous chemistry accordingly.

If an electrolyte solution is used as a liquid cathode to obtain a plasma-induced liquid chemistry, the system is often referred to as glow discharge electrolysis (GDE).^{144,358–360} This configuration has been intensively investigated for various applications, including chemical and nanomaterial synthesis, water treatment, surface modification, and functional polymer preparation.^{358–360} As we will illustrate in Sec. VI A, the ions bombarding the electrolytic cathode induce several competing reaction pathways in the liquid phase, some of which involve excess electrons. Correspondingly, electron emission may occur, or the electrons react further in the solution, perhaps with additional energy before getting fully solvated. Therefore, the above discussions on dissociative electron attachment and solvated electrons at a liquid anode may also apply to a liquid cathode to a certain extent. It would thus be interesting to investigate in future research the prevalence of solvated electrons at a liquid cathode and to compare the related chemical mechanisms with the opposite electrode polarity.

VI. TOWARD A FUNDAMENTAL UNDERSTANDING OF THE LIQUID-RELATED SHEATH PROPERTIES

A. Electron emission mechanisms for a liquid surface

As indicated already in Fig. 1, one of the most crucial material features affecting the plasma sheath involves its ability to emit electrons. While the electron emission mechanisms from a solid surface are relatively well understood, the situation for a liquid surface remains more obscure. A significant part of our previous review paper has been devoted to this topic,³⁵ so we will only give a short overview here, with a few additions. On the time scale of a single plasma species interaction with the surface, the liquid appears frozen in time to a good approximation. Physical sputtering by an incident ion, for instance, can take place in a few to tens of femtoseconds.^{361,362} Local heating effects due to the transfer of the ion kinetic energy occur on a subpicosecond time scale up to a few ps.^{361,363,364} During this entire event, the liquid can be considered very similar to a solid, which permits us to adopt the electron emission mechanisms for solid electrodes. More precisely, electrons may be released from a liquid surface via the photoelectric effect, or through secondary electron emission by bombardment with ions, hot neutrals, metastables, or electrons, as long as the energetic conditions allow it. In the case of ion bombardment, the electron to be emitted can absorb both the kinetic and potential energy of the ion. As should be noted, insulating dielectric solids are known to display a generally higher secondary electron emission yield in comparison with metals.³⁶⁵ This also counts for water ice, of which the emission yield has been measured to be significantly higher than the one of aluminum.^{35,366} Additionally, a strong local electric field can cause band bending and the shifting of surface levels, aiding the escape of the electron. Thermionic emission, on the other hand, is only expected to be relevant for liquids that do not decompose or evaporate below the high temperatures needed for it.

On the atomic scale, the electron emission mechanism of a liquid surface can, therefore, be identical to the ones described for solids. However, dielectric liquids possess a few characteristics that may counteract these effects. In the first place, the charge transport between their surface and bulk transpires through diffusion, drift, and convection, in contrast to solids. Accordingly, the overall electron emission is likely transport-limited. Such a limitation may explain the relatively low secondary electron emission coefficient frequently measured for electrolyte solutions. For example, Delgado *et al.* recently obtained a value below 10^{-5} from their experiments, meaning that only one electron is emitted by bombardment with more than 100 000 ions.⁵³ In the second place, the electron

solvation dynamics in liquids often involve the rotational or librational reorientation of the composing particles. In principle, these effects do not necessarily prevent the emission of electrons, but they affect the charge organization and microscopic structure of the liquid surface. As a central question, one may ask where emitted electrons from this distinct structure exactly come from.

In this context, several mechanisms have been proposed involving the individual liquid constituents, such as solvated electrons or negative ions residing in the liquid phase. For example, Cserfalvi and Mezei postulated a four-step process for a water surface, where incident ions generate solvated electrons, which react to produce aqueous hydrogen atoms that on their turn diffuse toward the gas phase, where they get ionized and emit secondary electrons.¹⁵⁰ Gaisin and Son instead assumed electrons to be released by negative ions in the gas or liquid side of the interface.³⁶ Polyakov et al. went further by considering the electron emission from the liquid phase to be a competitive process with solvation and scavenging of quasi-free electrons.³⁶⁸ Delgado et al. recently extended this idea with the scheme of Fig. 18 and by specifying the energetic state of the quasi-free electron.53 According to their model, the electron resides at the bottom of the conduction band of the liquid, about 1 eV below the vacuum level, before rapid localization into a pre-solvated state would take place. This is a more favorable state for electron emission than the solvated electron, which has a vertical binding energy of about 3.7 eV in the liquid bulk.^{55,58,369} Delgado et al. suggested that the required emission energy of 1 eV for the conduction band electron may originate from the kinetic energy of the incident ion, although they did not exclude the possible contribution of other mechanisms, such as field emission. $^{\rm 53}$

We support the idea behind this model but propose a further extension and refinement. First of all, Delgado *et al.* assumed the mechanism for incident Ar^+ ions, while electron emission is likely favored for H^+ ions and hot H atoms. As already pointed out by Polyakov *et al.*, protons are the major fragmentation product of water molecules under electron and ion impact.³⁶⁸ Moreover, they have an order of magnitude higher mean free path in water vapor than heavier ions, such as Ar^+ and H_2O^+ . Therefore, they can accelerate to a substantially higher kinetic energy in the sheath before colliding with the liquid surface. Intermediate charge transfer reactions can transform them into hot H atoms, which have an even higher cross section for liquid water ionization.^{368,370,371} Such details are important, considering the low secondary electron emission yield of 10^{-5} measured by Delgado *et al.*⁵³

Second, envisioning a more universal look on plasma–liquid interaction, the time-dependence of the plasma features needs to be taken into consideration as well. Babaeva *et al.*, for example, simulated the interaction of a positive streamer in atmospheric air with dry and wet wounds.¹⁹⁸ During the first few nanoseconds when the plasma filament struck the surface, they found an electric field strength in the sheath significantly surpassing 10^7 V/m. Assuming an ion mean free path of half a micrometer at atmospheric pressure, they deduced incident ion energies in excess of 20–30 eV on dry wounds, and even beyond 60–70 eV on wet wounds with high permittivity.¹⁹⁸ Such a brief pulse of energetic ions likely induces effective secondary electron emission and distinct aqueous reaction pathways.



FIG. 18. Scheme of the ion-induced secondary electron emission mechanism proposed by Delgado *et al.* For *n* argon ions bombarding the surface, $\gamma \times n$ emitted electrons e_g^- are produced. The argon ions interact with a water molecule in the liquid phase near the surface, which may ionize the molecule in competition with other reactions. In the case of ionization, the resulting conduction band electron e_{cb}^- either is emitted if it has sufficient kinetic energy or relaxes into a pre-solvated state e_{pre}^- to subsequently become a solvated electron e_{aq}^- . The electron levels are indicated relative to the vacuum level. Reprinted with permission from Delgado *et al.*, Langmuir **36**(5), 1156–1164 (2020). Copyright 2020 American Chemical Society.

Third, the water surface is expected to be a complex quantum mechanical environment, with a more convoluted electronic structure than the one presented in Fig. 18. As already discussed in Sec. V, the blueshift in the optical absorption peak of the interfacial solvated electron by Rumbach et al. still remains an open question. It seems to imply a larger energy between the ground state and the first excited state of the solvated electron but may also be related to a smaller vertical binding energy of the latter and perhaps significantly longer lifetimes of the excited states. The energy scheme will display local variations due to the presence of other charged species at the interface and surface deformations (see also below). Moreover, the electronic structure of the interface can be further modified by long-range quantum correlations between excess electrons, which are extremely hard to capture even with the most advanced modern ab initio computational quantum mechanical techniques.

Fourth, the ionization and electron emission processes may involve excitation mechanisms characteristic to the condensed phase. For instance, two neighboring electronically excited species or solvated electrons may transfer energy between each other to generate an Auger or Auger-like electron emission event. Alternatively, the ensemble of such species at the interface may acquire excitations of a more collective nature. It is worth noting that Polyakov et al. already suggested the possible contribution of pre-existing collective excitations of water molecules in electron emission at the liquid surface.³⁶⁸ However, they did not further specify the nature and mechanisms behind these phenomena. Collective excitations and their interactions are well-known in condensed matter physics, often expressed in terms of quasi-particles. They might, therefore, play a crucial role at the plasma-liquid interface too. In theory, electronic excitations of individual interfacial aqueous species can form plasmonic waves. If the energy of such surface plasmons exceeds the binding energy of an electron, electron emission may occur. To our knowledge, such quasi-particle-based electron emission mechanism has not been proposed before in the scientific literature. It can be more generally described for any plasma-liquid interface by means of the multiplasma model, a quasi-particle-based theoretical framework that we recently introduced for the excitation and thermalization processes in laser-excited matter.⁷⁷ Similarly, the multi-plasma model could serve as a useful toolbox to describe excitation and relaxation mechanisms at a plasma-liquid or plasma-solid interface in general.

Nevertheless, the applicability of these models and mechanisms to plasma-liquid interactions is still speculative, because several other processes complicate the interfacial structure. The surface of volatile liquids is continuously covered by a vapor layer, which may effectively shield the surface from incident ions. Taking into account the relatively low latent energy of 0.4 eV to evaporate a water molecule on average from the bulk liquid, the heat flux caused by the ion bombardment may even enhance this effect, counteracting the ion-induced electron emission. This invokes another question, whether electron emission predominantly occurs at the main liquid surface or in the plasma sheath itself. Indeed, negative charge can also be transferred from the liquid to the gas phase in the form of negative ions, clusters, or droplets. Strong local field enhancement at such clusters and droplets, as well as modifications in the solvated electron state, perhaps permit a more favorable electron emission process in comparison to at the main surface in contact with the bulk liquid (see also Sec. VI B). Additionally, droplets adjacent to the main liquid surface can enhance the local electric field there too.³⁷² Closely related is the explosive electron emission mechanism proposed by Mesyats, where electrons are released in an explosive event at the sharp tip of Taylor cones formed on the surface under influence of the sheath field and local field enhancement.^{373,374} Note in this regard that electron emission may transpire as discrete events, limited in time by surface deformation and droplet formation, rather than through stochastics in the individual interactions of ions with the surface. Accordingly, each of the processes depicted in Fig. 1 is relevant to the discussion of electron emission from a liquid surface. Which of these mechanisms dominates the electron emission remains an open question, requiring more fundamental experimental and computational studies.

B. Origin of droplets in the plasma sheath

In principle, droplets over a liquid surface can originate from either droplet ejection or nucleation in the vapor phase. At the plasma-liquid interface, several mechanisms of droplet ejection can be thought of. Electrospray ionization serves as a famous example with a rich research history, where charged droplets are emitted from a Taylor cone, under influence of the local electric field.³⁷⁵ In general, droplet ejection may be expected as a product of extreme deformations of the liquid surface. Fuchs et al., for instance, proposed field-induced electrospray processes and the breakup of microjets by capillary waves to explain microdroplet formation during the operation of a floating water bridge.³⁷⁶ Similar effects may be at work at a plasma-liquid interface, where conditions are expected to be even more violent. Plasma can even penetrate through the surface into the liquid bulk, as observed in experiments.^{377,378} Next to that, boiling and electrolysis enable the generation and collapse of microbubbles at the liquid surface, also leading to possible microdroplet ejection.³⁵ When the charged droplets enter the sheath, they can reduce in size by evaporation, fission processes, and sputtering, similar to the mechanisms in electrospray ionization.³⁷⁵ Still, droplets ejected from the liquid have the potential to be comparable in size to the sheath thickness. Since a sheath also forms around them, they can significantly alter the sheath properties.

Nucleation in the vapor phase, on the other hand, results in molecular clusters and droplets of a much smaller size. Many useful insights into this phenomenon have been reported in aerosol science, for the study of the atmosphere,^{379,380} nanoparticle synthesis,³⁸¹ and various industrial processes. These insights often seem to directly apply to the plasma sheath at a volatile liquid, but will likely need to get revised to the conditions specific to the considered interface, such as the field strength and ion densities. This forms a challenging task, considering the experimental and computational difficulties encountered in research on vapor nucleation outside a plasma environment. Detection of nucleating clusters requires highly sensitive instrumentation that minimizes cluster fragmentation during measurement.³⁸² The transient nature of the nucleation poses another challenge, especially when rapid

nucleation rates demand a high time-resolution of the measuring device. Next to that, nucleation often occurs in complex chemical environments with numerous species as possible participants. In a plasma sheath, the presence of the liquid surface further complicates the cluster detection. Still, the detection technology has advanced tremendously in the past few decades, currently allowing the observation of nucleation on the molecular level, e.g., by means of mass spectrometry. A complementary source of information is provided by modeling techniques. For this purpose, the most commonly applied atomistic methods are quantum chemistry calculations, Monte Carlo, and molecular dynamics simulations.³⁸² The former relies on first principles of quantum mechanics, by which cluster energy is obtained with the highest level of accuracy, but at a high computational cost. The latter two, in contrast, are mostly based on atomic force fields and enable the simulation of larger clusters with decreased accuracy. Despite the advancement of these methods and the large research efforts in this domain, finding agreement between experimental and simulation output regarding the nucleation rates remains problematic.

To the best of our knowledge, investigations on vapor nucleation at the plasma-liquid interface have not been performed yet in situ on the molecular level. In this sense, the mechanism remains speculative for now in this system. However, the wide interest of plasma-liquid interaction for nanomaterial synthesis implies that this hypothesis is not new. Moreover, vapor nucleation in laser ablation is a well-known effect with a clear resemblance.³⁸¹ At the plasma-liquid interface, its occurrence is expected to depend on various local factors, such as the temperature, pressure, and their spatial and temporal variation; the oversaturation degree of the vapor; and the presence of nucleation precursors. As should be noted, ions serve as effective initiators of nucleation,^{379,381} strengthening the hypothesis. For an atmospheric air plasma containing humidity, for instance, H₂O molecules attach to O₂⁻ through cascade reactions to form $O_2^-(H_2O)_3$ as the most probable cluster.³⁸⁶ An analogous process is observed for positive ions but in a less pronounced manner.³⁸⁷ Another open question is the subsequent growth of the clusters into microdroplets and how the electric field influences this process. According to the classical thermodynamic nucleation theory, clustering of vapor molecules needs to overcome an energy barrier in order to obtain a cluster size above which further growth is spontaneous (see Fig. 19).³ This energy barrier depends on the vapor saturation ratio S. If S is less than 1, the Gibbs free energy keeps rising with cluster size, and no spontaneous growth can be reached. If it is much higher than 1, the energy barrier disappears and spontaneous clustering is immediate.

However, classical thermodynamics is known to break down at the quantum scale, so this picture is likely oversimplified. We refer here to the analogy with nanobubbles in the liquid phase, which were thought for a long time to be thermodynamically impossible but still turned out to exist with a remarkable stability.^{35,388–390} Likewise, various subtle quantum mechanical effects may need to be taken into account for an accurate calculation of the cluster free energy. A strongly related point to consider is the local electric field at a microdroplet surface and the effect of an external field on the stability and growth rate. As the state-of-the-art in aerosol science indicates, vapor nucleation in the



FIG. 19. The Gibbs free energy ΔG_k of cluster formation as a function of cluster size for three examples of the vapor saturation ratio S. Reprinted with permission from Li and Signorell, J. Aerosol Sci. **153**, 105676 (2020). Copyright 2020 Elsevier.

plasma sheath will likely remain a topic plagued with persistent uncertainties in the first years to come. New fundamental experimental and computational investigations will likely not only increase our understanding on this process but also provide insight into how to optimize its effect for specific applications, especially with regard to cluster and microdroplet chemistry. As an interesting motivation for such research, Lee *et al.* recently observed spontaneous H_2O_2 generation on aqueous microdroplets.³⁹¹ They attributed this phenomenon to autoionization at the air–water interface, causing a strong electric field that subsequently generates an intermediate solvated electron.

VII. SUMMARY AND OUTLOOK

In this Perspective, we gave multiple arguments on why investigating the plasma sheath at the plasma-liquid interface is not only recommended but also essential, both for an accurate understanding of plasma-liquid interactions and for making progress in the related applications. On a fundamental level, the sheath plays an active role in the fluid dynamics continuity equations and the electrical coupling between the plasma and the liquid phase (see Sec. II A). The sheath models developed for the plasma-solid interface must not be applied at a liquid surface without taking into account several liquid-specific aspects. These additional effects include fluid dynamical processes, such as evaporation, surface deformations, and droplet ejection, as well as electrical factors, such as the formation of an electric double layer, an ion drift-mediated liquid resistivity, and the yet unclear mechanisms behind secondary electron emission. More basic research is required to investigate these processes on a microscopic level in order to assess their influence on the sheath properties. As a possible experimental strategy, different types of liquids can be compared in their effect on the

plasma properties and the liquid surface charging for fixed reactor conditions. Ionic liquids and molten salts, for instance, display a negligible evaporation, which makes them a useful reference when investigating the effect of vapor in the sheath. Metallic liquids form an interesting reference with regard to the influence of the electrical liquid properties.

Detailed knowledge on the sheath is crucial to understand the bidirectional mass transfer across the plasma-liquid interface (Sec. II B), which is of prime importance to most applications. Throughout the scientific literature, the focus heavily lies on the injection of reactive species from the plasma into the liquid phase. However, also for applications mainly relying on this principle, the emission of liquid species into the gas phase affects the sheath and plasma properties and thus the entire plasma treatment process. Accordingly, the corresponding desorption, extraction, and sputter mechanisms need to be included into the fundamental study of the plasma sheath. With a deeper understanding of such mechanisms, the sheath can be employed as a selective filter for plasma and liquid species, as illustrated in Sec. IV for the liquid walls in a fusion reactor. Next to that, the bidirectional mass transfer across the plasma-liquid interface is not simply expected to be influenced by the chemistry in the sheath but largely based on it for many plasma-liquid systems. The dominance of the sheath chemistry in the species transfer depends on the sheath size, the species lifetimes, and mean free paths, but there are strong reasons to deem it high even in collisionless or relatively thin sheaths, as discussed in Sec. II C. The number of publications on sheath chemistry is remarkably scarce, also for plasma-solid interactions. Therefore, we want to stimulate a higher awareness and more intense research on this topic, as one of the main purposes of this Perspective. Accordingly, Sec. V illustrated how the sheath can be used to tune specific chemical reactions for nanomaterial and chemical synthesis. Section VI discussed electron emission mechanisms and droplet formation at the plasma-liquid interface, which are also expected to contribute to the interfacial chemistry. Another crucial aspect is the type of sheath formed at the liquid surface, in particular, at a liquid anode, as we explained in Sec. II D.

A great part of this work deals with field-induced effects in the condensed phase, as we also believe this aspect deserves more attention. We selected biological materials as an example because a large body of knowledge already exists about their stimulation by electric fields and because the related applications in plasma medicine, plasma agriculture, and food processing make up some of the strongest drivers in the plasma-liquid research domain. On a cellular level, electroporation and electrostatic disruption of the cell membrane are often considered possible plasma-induced effects, which can underlie immediate cell death. According to a few recent experimental studies, endocytosis has been identified as the main transfection mechanism, indicating that the fields penetrating the condensed phase may be less intense than the threshold value for electroporation. For an accurate estimation of these fields for various plasma sources, a more profound insight into the sheath properties is required, both in terms of structure and dynamics. The rate of voltage fluctuations over the condensed phase relative to the charging times in the liquid, namely, determines the extent to which the field can penetrate. In physiological tissue, this charging time lies around 1 µs, so sub-microsecond fluctuations are

required for effective field penetration. Based on this knowledge and an accurate sheath model, specialized plasma sources can be engineered to obtain a desired effect, such as electroporation or electro-endocytosis. As should be emphasized, however, this principle also counts for applications of plasma-liquid systems in general. For example, the plasma-induced fields can regulate key processes in the liquid phase for nanomaterial synthesis. For this purpose, the field-induced effects on a cellular level can serve as an inspiration for mechanisms on a nanoparticle level. Additionally, the field also influences the liquid on a molecular level, which is relevant to all applications. In this way, it can regulate in-liquid phase transitions or chemistry, with field intensity and frequency as control parameters, tuned by means of the sheath. The study of the plasma sheath at a liquid surface is, therefore, tightly linked to the investigation of electromagnetic field effects in the liquid phase.

AUTHORS' CONTRIBUTIONS

P.V. contributed to the conceptualization, methodology, investigation, writing of the original draft, and visualization of the article. A.B. contributed to the reviewing, editing, and supervision of the article.

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DATA AVAILABILITY

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

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