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Roadmap

The 2022 Plasma Roadmap: low temperature plasma science and technology

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Abstract

The 2022 Roadmap is the next update in the series of Plasma Roadmaps published by *Journal of Physics* D with the intent to identify important outstanding challenges in the field of low-temperature plasma (LTP) physics and technology. The format of the Roadmap is the same as the previous Roadmaps representing the visions of 41 leading experts representing 21 countries and five continents in the various sub-fields of LTP science and technology. In recognition of the evolution in the field, several new topics have been introduced or given more prominence. These new topics and emphasis highlight increased interests in plasma-enabled additive manufacturing, soft materials, electrification of chemical conversions, plasma propulsion, extreme plasma regimes, plasmas in hypersonics, data-driven plasma science and technology and the contribution of LTP to combat COVID-19. In the last few decades, LTP science and technology has made a tremendously positive impact on our society. It is our hope that this roadmap will help continue this excellent track record over the next 5–10 years.

Keywords: low temperature plasma, roadmap, plasma science and technology, plasma diagnostics, plasma modeling, plasma material processing, plasma applications

(Some figures may appear in color only in the online journal)

Contents

Introduction

The *Journal of Physics D: Applied Physics* published the first and second Plasma Roadmap in 2012 and 2017, respectively [1, 2]. The 2022 Roadmap is the next update in the series of Plasma Roadmaps and consists of a series of short, formalized sections representing the visions of 41 leading experts representing 21 countries and five continents in the various subfields of low-temperature plasma (LTP) science and technology. The intention of the roadmap series is to identify outstanding challenges and provide guidance to the field of LTP physics and technology for colleagues, funding agencies, and government institutions and hopefully contribute to the field a more solid base for identifying needs in resources. The format of the 2022 Roadmap remains similar to the 2017 edition with two authors per section, as identified in each section, enabling a broad perspective for each subtopic. While each section is authored by different experts, one of the editors last minute contributed as a co-author to a second section that was originally assigned to a colleague who was unfortunately unable to contribute. Finally, as in the previous edition, author names are listed in alphabetical order.

In this roadmap, the focus is on LTPs. Even if some common basic phenomena exist between all types of plasmas, specific topics related to fusion plasmas, laser-induced plasmas, high energy density plasmas, beam-produced plasmas or space plasmas, while potentially touched upon in the context of LTPs, are not part of this roadmap. LTPs are usually generated by applying a voltage difference across electrodes to a gas or liquid. The resulting plasma is a quasi-neutral medium composed of positive and negative ions, electrons, photons and neutral (reactive) species. LTPs can be obtained at various pressures, usually from near vacuum to atmospheric pressure although higher density gasses are also studied. The ionization degree of LTPs is usually rather small but can reach up to 100% in thermal arc discharges, pulsed magnetron discharges, plasma thrusters or nanosecond pulsed plasmas in dense gasses or liquids. Interestingly, even at typical ionization degrees of 10^{-6}–10^{-4}, LTP properties differ substantially from those of a neutral gas. The name 'low-temperature plasma' finds its origin in the usually low gas temperature, i.e. the temperature of heavy species (ions and neutrals), which is much less than the electron temperature. This thermal non-equilibrium is a key parameter of LTPs as energetic electrons colliding with neutral species efficiently produce radicals and excited species. The obtained chemical reactivity at low gas temperatures is one of the main characteristics of LTPs and is of great interest for different applications. Nonetheless, the gas temperature and the level of thermal non-equilibrium of LTPs may vary. For example, thermal plasmas, which are typically also considered to be LTPs, operate usually close to thermal and chemical equilibrium with a gas and electron temperature of a few tens of thousands of Kelvin. A second key characteristic of LTPs is related to the charged species of different masses and energies present in these plasmas. In particular, close to surfaces, non-neutral sheaths are formed and the acceleration of ions in these sheaths can deliver fluxes of energetic ions to substrates. The tailoring and control of the production of ions and their energy upon arrival at a substrate augmented with reactive neutral chemistry enables a large diversity of surface etching and deposition applications. Finally, magnetic fields can be used to confine LTPs. The resulting dynamics of low-temperature magnetized plasmas is often very complex with various instabilities, mostly because electrons are magnetized whereas ions are often not or only partially magnetized.

In the last few decades, LTP science and technology has made a tremendous impact on our society. For example, the entire microelectronics industry is enabled by plasma–surface interactions which deposit and remove materials up to nanometer resolutions in the fabrication of microprocessors. More recently, electric propulsion systems are gaining importance for motion control of satellites orbiting Earth enabling our global communication and navigation (GPS) network. These are just two of the many possible examples illustrating the diversity of applications of LTPs at reduced pressure. At atmospheric pressure, thermal plasmas are widely applied in industry for welding and material processing. Dielectric barrier discharge plasmas have been used for several decades for ozone generation in water treatment plants. With the continued development in the generation of low-temperature non-equilibrium plasmas at atmospheric pressure a broad range of new application areas has emerged in the last decade including the establishment of new multidisciplinary research fields such as plasma medicine and plasma agriculture which are highlighted in this roadmap. We want to highlight that most current impactful LTP applications in industry have no alternative. When alternative methods exist, plasma processes are often considered, at first, as expensive either in equipment, energy consumption or due to the need of skilled operators. Therefore, most LTP research focuses on conditions not accessible by alternative technologies, where the unique properties of plasma processes are beneficial for the targeted applications or provide a green alternative. For example, LTPs provide significant opportunities for decarbonizing industrial processes. In this context, benchmarking plasma technologies with competing alternatives remains exceedingly important.

Low temperatures plasmas can be seen as a very complex system involving many often mutually interacting processes studied in the fields of electrodynamics, fluid mechanics, thermodynamics, chemistry, atomic and molecular physics, heat and radiation transfer, material and surface science, chemical engineering, electrical engineering and recently even biology and medicine. To understand and control non-equilibrium plasma processes, the bottleneck is usually to correctly identify the key phenomena involved. The study of LTPs needs to take into account spatial and temporal scales that span several orders of magnitude imposing many challenges for both modeling and diagnostics of which recent advances and remaining challenges are addressed in several sections of this roadmap.

While the format of the 2022 Roadmap remained identical as the 2017 Roadmap, in recognition of the evolution of our research field in the last 5 years, several new section topics have been introduced and the focus has changed in sections already included in the previous roadmap. In view of the increasing interest in additive manufacturing (AM) and plasma processing of soft materials including biomaterials we included two new sections on these topics. The LTP field has also actively responded to the challenges introduced by the COVID-19 pandemic due to the ability of plasmas to inactivate virus but also its long-term potential for medical treatments including contributions to vaccine development as discussed in a new dedicated section on this topic. In addition, plasmas in hypersonics have gained significant interest in view of their applications in planetary entry and cruise vehicles, as well as the demise of man-made space debris and are addressed in a dedicated section combined with plasma assisted combustion.

Motivated by recent scientific developments we also included specific sections on hot topics on 'diagnostics and modeling of plasma–surface interactions' and 'data-driven plasma science and technology'. Dusty plasmas, electrification of chemical conversions, plasma propulsion (PP) and extreme plasma regimes, while already part of the previous roadmap, have now been included as separate sections in recognition of the growing or continued extensive efforts in these topical areas in our research community. The inclusion of these new sections led to the reorganization of several topics covered in the 2017 Plasma Roadmap. This led for example to the inclusion of validation and particle transport in the modeling and atomic and molecular data section. The 2022 Roadmap does not have separate sections on flow control, plasmas in analytical chemistry and plasma metamaterials anymore. The descriptions on these topics in the 2017 Roadmap remain aligned with current research activities and new developments have been touched upon in other sections of the Roadmap.

The recent achievements of our community highlighted in the Roadmap define the LTP community as a highly innovative field with many advances in a broad range of applications. The exceedingly broad range of societal impact areas from space exploration to health care and sustainability and energy applications provides our community with opportunities to continue to diversify our research field while recognizing that targeted new efforts and initiatives for diversifying the researcher demographics would be welcome. While more opportunities for interdisciplinary collaborations will without doubt enhance the societal impact from our field, there remains, however, a continued need to invest in fundamental plasma science to enable the development of the next generation of technologies that can address grand societal challenges related to sustainability, energy and health.

The success of many innovations in plasma science for a broader range of applications, as indicated for several applications in the 2022 Roadmap, requires plasma process optimization and scale up to enable a smooth translation from the laboratory scale research to industry and society. The development of fully predictive computational models that are physics and chemistry based, but also have the robustness to be used for design and optimization of devices remains a key priority. This requires a community wide effort involving code verification and validation and atomic and molecular data generation, curation, and validation. Recent international benchmark studies of codes used to model low-pressure magnetized plasmas and atmospheric pressure streamers illustrate that our community is ready to embrace the introduction of much needed community-wide developed reference benchmark cases involving complex phenomena as instabilities or wave propagation. In the last decade, the development of open-access databases with standardized atomic and molecular input data has been very beneficial for our community. The next step includes a joint effort of the atomic, molecular, and optical physics (AMO) and the plasma communities to measure or calculate missing data required to describe key elementary processes, and propose recommendations of reaction mechanisms to be used. Finally, due to the multiscale and multi-physics nature of LTPs, the comparison of experiments and simulations remains challenging.

Our community could benefit from more intense collaborations between experts working on plasma source development, diagnostics, and modeling and include more systematically sensitivity analysis and uncertainty quantification approaches. Developing such frameworks and more accessible computational and experimental capabilities would also enable us to more effectively train a new generation of scientists in fundamental LTP science that would be able to tackle many societal challenges in the coming decades and would be well placed to take on leadership roles in academia, research institutes and private R&D.

Anne Bourdon and Peter Bruggeman
Editors of the 2022 Plasma Roadmap

1. New plasma excitation and generation approaches

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Status

The development of novel approaches to excite and generate plasma discharges has been motivated by the unique needs of the increasingly large amount of application areas being tackled by plasma technology. New plasma generation approaches are often required to generate plasmas in dense media including high pressure gases or liquids and pulsed generation of plasmas by ultra-high electric fields with durations as small as hundreds of picoseconds [3, 4].

In recent years, several combined discharge-laser approaches have been proposed for the fabrication of composite nanomaterials with specified parameters such as hybrid, doped and alloyed nanostructures [5]. Most approaches are based on the generation of discharges in and in contact with liquids (see section 3) as well as laser-induced plasmas in liquids [6]. Another nice example of a plasma source innovation based on a new theoretical concept is the low pressure inductively coupled array (INCA) source as shown in figure 1, where collisionless electron heating is enabled by periodically structured vortex fields, which produce certain electron resonances in velocity space [7]. A key advantage of the source is that the array can be scaled up to arbitrary dimensions while keeping its electrical characteristics.

In spite that low pressure plasma sources are being developed for semiconductor processing for decades and atmospheric pressure micro-plasmas became a corner stone of the LTP research field, there continue to be innovative developments in plasma excitation with as goal to control reactive species generation through pulse modulation and waveform tailoring techniques [8]. Ongoing efforts to optimize plasma excitation and sources are being pursued for a variety of applications including thruster source design for electric propulsion [9], plasma chemistry for nitrogen fixation [10], surface discharge reactors for efficient water treatment [11], gliding arc (GA) discharges with innovative electrode configurations for CO_2 conversion [12], a novel pin-hole plasma source in liquid for production of chemically active species [13], or atmospheric pressure glow discharges (APGDs) for inactivation of microorganisms [14]. In addition to plasma source design motivated by applications, new plasma generation approaches have also been motivated by fundamental plasma physics. There has been, for example, substantial progress in magnetized dusty plasma experiments (MDPXs) with as goal to understand the impact of the magnetic field on the coupling between the plasma and the charged dust particles which is of critical importance in space physics but also laboratory plasmas [15] (see also section 4). A summary of different plasma generation approaches is given in figure 2.

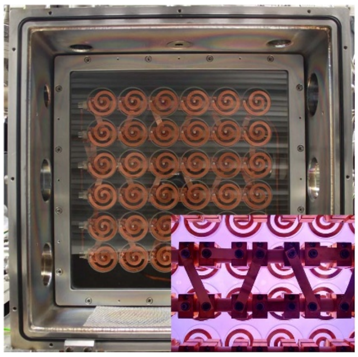

Figure 1. Photograph of the INCA source during operation (insert) and front view of the coils used to excite the plasma. Reproduced from [7]. © IOP Publishing Ltd. All rights reserved.

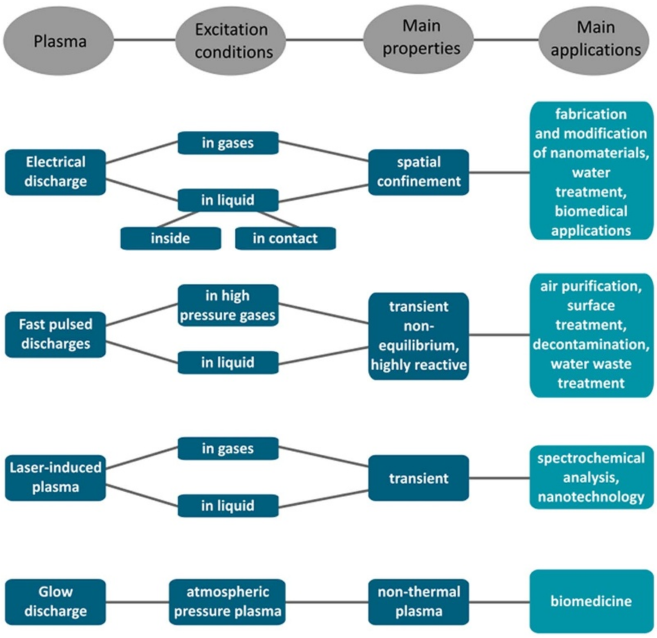

Figure 2. Overview of plasma excitation and generation approaches currently being explored.

Current and future challenges

Despite the particular interest from an application perspective in a broad range of plasma sources, the often unique properties of the larger variety of plasma sources lead to many interesting unsolved questions. For example, many mechanisms underlying the breakdown processes and plasma formation in a complex molecular gas composition or even multiphase environment, especially with novel excitation approaches, remain to be explored. Many processes at atmospheric pressure or in dense media occur on sub-nanosecond up to microsecond timescales, which make the control of the breakdown process and resulting plasma parameters an exceedingly complex task.

Our understanding of the initial ionization processes in dense media remains incomplete and we have insufficient collisional cross section data to describe the breakdown process or the process might not be fully described by the conventional Paschen or Meek breakdown criteria.

Recent studies explained the ability to create near full ionization on nanosecond timescales in pulsed nanosecond plasmas [16] and ultrafast gas heating in air but many aspects of such processes remain unclear particularly in more complex gas mixtures and dense media. Streamer formation and propagation has been studied for decades but their often-random nature remains an exceptional challenge for experimental studies and many efforts recently have focused on the development of plasma sources that enable the production of guided streamers in plasmas jets or smart multiple streamer experiments that enable the stabilization of a single streamer [17]. However, our understanding of surface ionization waves (SIWs) and streamer discharges on dielectric surfaces is just emerging. The strong interaction with surfaces can lead to self-organizing behavior, most likely resulting from memory effects associated with surface charge patterns or streamer–streamer interactions. Control of such behavior to enable homogeneous surface treatment or exploit advantages of self-organized patterns for deliberate inhomogeneous treatments remain out of reach. This self-organization behavior and plasma instabilities at elevated pressures lead also to challenges for plasma source scale-up at atmospheric pressure as required for many emerging applications.

Different plasma generation approaches lead to an equally broad range of chemical reaction conditions and products that can be formed even if the discharge is initiated in the same liquid/gas environment. While it is well established that desired plasma reactions can be initiated by channeling the electron energy into desired excitations that can be favored by the application of specific discharge excitation approaches, currently available predictive capabilities are not able to optimize plasma applications. Many applications require unique plasma excitation properties with high demands on power supplies. A smoother translation from research in the lab to industry put significant demand on plasma sources from a perspective of portability, scale up ability, energy efficiency and reliability.

Advances in science and technology to meet challenges

The further development of stabilized plasma sources allowing reproducible plasma formation in space and time would significantly enhance the capability for detailed mapping of temporal and spatial evolution of the plasma generation. To study the inception, propagation, and dynamics of streamers in the volume or along the dielectric surfaces their guiding by a weak laser-induced pre-ionization can be applied. Both electrical and optical measurements with ns or even sub-ns temporal resolution can be applied to deduce a broad range of relevant plasma parameters. The further development and a more widespread implementation of three-dimensional plasma codes might be helpful to model the generation of filamentary plasmas and self-organization.

To meet the challenges related to achieving desired plasma processing conditions for specific applications, a detailed control of the plasma parameters might be needed and can be attained by voltage waveform tailoring requiring modifications and advances in power supply and delivery circuits. The threshold of translating technologies from the research lab to industry can possibly be lowered for low pressure plasmas by a continued focus on power supply development compatible with existing industrial equipment such as explored for voltage waveform tailoring and high power impulse magnetron sputtering (HiPIMS). Plasma processes and parameters are strongly linked to plasma generation and might benefit from more extensive datasets correlating plasma excitation and plasma properties which could be enabled by new development in diagnostics (see section 17). All these challenges would benefit of the further development of predictive modeling capabilities to overcome the often trial and error approach used for the development of novel plasma generation approaches.

Several applications such as electric propulsion and medical applications require miniaturization or portability of the plasma sources. While many low-pressure plasma material processing have been scaled-up successfully, scale up of plasma sources at high pressures for large scale applications becomes an increasingly important and deciding factor in the future success of novel plasma applications explored to date (see for example sections 11–13). As plasma instabilities put inherent limitations on power density and plasmas dimensions, this will require dedicated plasma source and process design allowing for easy parallelization of plasma sources as successfully achieved for AC excitation used in corona treatment and ozonizers but needs to be extended to a broader range of different excitation sources. As energy efficiency is often a key challenge for plasma technology, an efficient coupling of the electrical energy into the plasma is crucial.

Concluding remarks

The continued expansion of plasma-enabled applications, including interdisciplinary research areas require the development of new and unique plasma generation approaches. Plasma source design will undoubtedly remain a hot topic in the field of plasma technologies in the foreseeable future. Significant effort is needed to further optimize and extend plasma excitation approaches by detailed studies of the physical and chemical processes particularly at high pressure and in/near dense media. The complexity and variety of the accompanying processes requires further progress in diagnostic techniques as well as plasma modeling. In addition, progress in the design of power sources towards the miniaturization and portability of plasma generation systems as well as source and reactor designs that enable easy scale up will facilitate new plasma-based technological applications.

2. Extreme plasma regimes

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Status

Advances in plasma science and technology are often preceded by the introduction of sources that enable access to new regimes. Historically, vacuum pumps allowed pioneers of the discipline to create low density plasma sources with modest dc energy supplies, which led to the development of efficient lighting and eventually dramatic improvements in microelectronics processing. The 2017 Plasma Roadmap summarized how the development of pulsed plasmas (with sub 50 ns electrical or optical excitation) and microplasmas (scales from 1 to 1000 μm) have opened new areas of research by enabling generation of plasmas in previously unexplored media, including liquids, supercritical fluids (SCFs), and dense plasmas at interfaces. In the past 5 years this field has advanced significantly through the creation of plasmas in an expanding multitude of phases of matter [18], including high-pressure sparks [19], laser breakdown of high-pressure gases [20], plasma–liquid interfaces [21], and cavitating bubbles [22], as well as by advancing the ability to diagnose and model these plasmas. This research has changed the concept of what constitutes a ‘plasma’, expanding it beyond the traditional notion of an ionized gas into ionized states of liquids, SCFs, and multiphase media.

This section focuses on two active directions for exploring extreme states of LTPs (extreme LTP): low temperature (cryogenic plasmas from 300 K down to a few K), and high density (above atmospheric pressure in the gas phase or produced from condensed media) [18]; as illustrated in figure 3. Both examples illustrate how pulsed sources enable the production of plasmas in regimes that are traditionally condensed matter states. Although recombination occurs, rapid pulsation generates an essentially steady-state plasma at density and temperature conditions that would be liquids, solids, or SCFs at thermal equilibrium. The fundamental physics of such novel non-equilibrium plasmas is not well understood and should be advanced to explore their potentially promising properties. At the same time, these novel plasmas are being applied to industrial processes, such as etching [18], materials processing [18, 23], and chemical synthesis [18] with applications in biotechnology and medicine. It is also expected to be applied as a new frontier space environment simulator, such as that for ice planets in the outer solar system [24].

Current and future challenges

Extremes of low temperature and high density pose new challenges in diagnostics and modeling (see also sections 17–21). One of the largest current experimental challenges is that the sizes of such extreme plasmas are very small, typically to microspaces (<1 mm) (microplasma) and nanospaces (<1 μm) (nanoplasma). Therefore, improved spatial resolution is required for plasma diagnostics. In addition, the damage to the reactors and walls caused by these plasmas and the impurities caused by them are serious problems. These current issues will continue to be serious also in the future.

An essential challenge in modeling is that interactions between some species (particularly ions) are strongly correlated. The strength of correlations can be estimated from the coupling strength parameter, $\Gamma_{\alpha\beta} = \phi_{\alpha\beta}(a_{\alpha\beta})/k_{\mathrm{B}}T$, where $\phi_{\alpha\beta}(a_{\alpha\beta})$ is the interaction potential evaluated at the average distance between particles of species α and β. Interactions are strongly correlated when $\Gamma_{\alpha\beta} > 1$; liquids are typically characterized by coupling parameters in the 10 s and solids in the 100 s. Plasma theory, modeling and experimental techniques have largely been developed from the perspective that plasmas are weakly correlated. For instance, the common kinetic and fluid equations (such as the Boltzmann equation) are based on the expansion parameter: $\Gamma_{\alpha\beta} \ll 1$. Such methods are the basis for transport models and how we interpret many diagnostic measurements. The ability to model and measure extreme LTPs will require significant developments to these foundational concepts.

Advances in strongly coupled plasmas have been made outside of the traditional LTP field, primarily in the context of dense plasmas that arise in inertial confinement fusion, or in ultracold and non-neutral plasmas [25]. Although some of these developments can be applied to extreme LTPs, there are also important differences that limit the connection. When strong ion coupling is encountered in fusion contexts, electrons are often in a Fermi degenerate state. Another important distinction is the prominent role of neutrals in extreme LTPs. For instance, recent work by Hagelaar *et al* [26] has shown that electron–electron collisions in plasmas above atmospheric pressure are significantly influenced by the presence of neutrals. The same physics would also be expected to influence ion–ion collisions when the ion-neutral mean free path is less than approximately a Debye length; see figure 4. This defines a strong charge-neutral coupling regime where charge particle interactions are altered by neutrals.

Advances in science and technology to meet challenges

As mentioned in the section above, in general, these novel extreme plasmas have (a) a very small size of the plasma reaction field, (b) most of the plasmas are pulsed plasmas, which are transient phenomena in time, and (c) the energy density of the plasma is often large. As a result, plasma diagnostics and plasma process applications face significant difficulties in the present and the future. To solve problem (a), large-scale integration of small plasmas is expected. Through the development of plasma televisions, we have already acquired sufficient expertize in the technology of large-scale integration of plasmas, and future developments are expected. Regarding issues (a) and (b), improvement of spatial and temporal resolution of various plasma diagnostic methods, especially spectroscopic methods, is expected, and steady efforts are being made. As

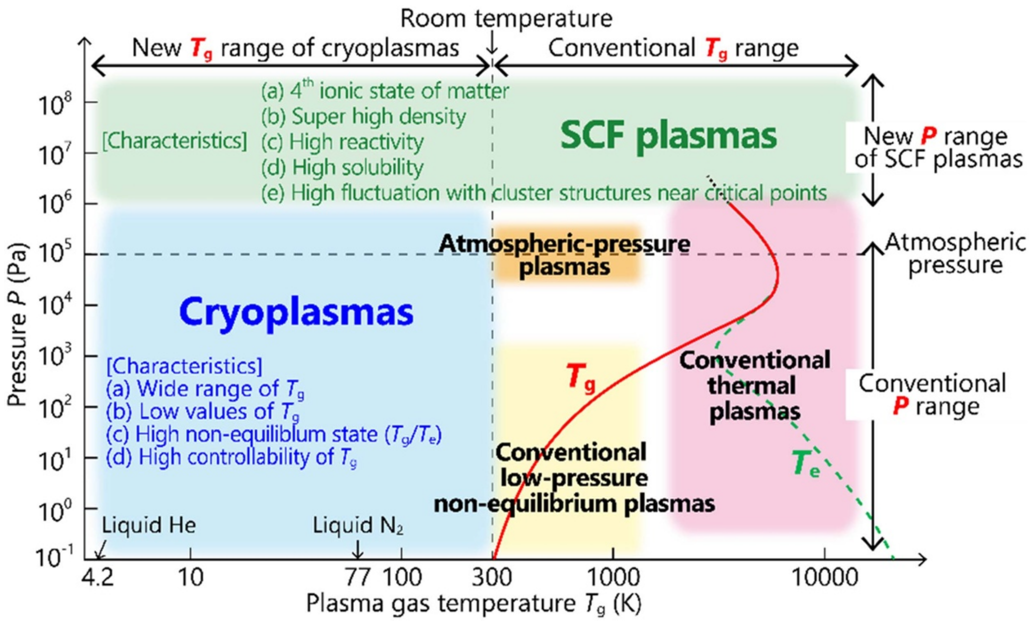

Figure 3. Two promising extreme plasma regimes: plasmas in high-pressure conditions above atmospheric pressure including SCFs plasmas and plasmas in cryogenic temperature conditions below room temperatures including cryoplasmas.

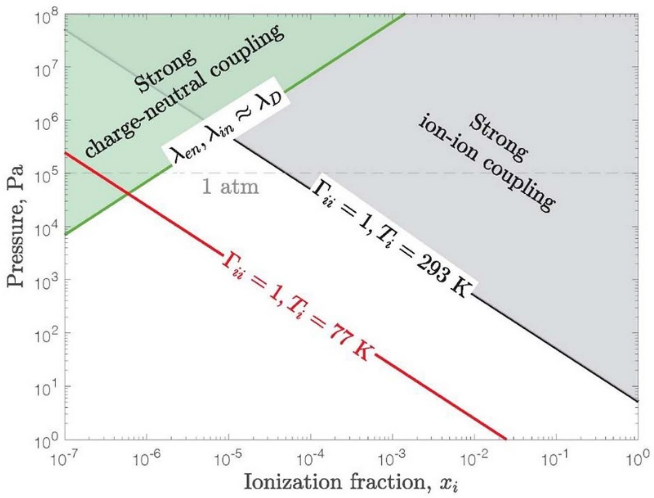

Figure 4. Parameter space of strong ion-ion coupling at room temperature (gray shaded region), and strong charge-neutral coupling (green shaded region). Both regimes are encountered in cryoplasmas and high-pressure plasmas, including SCF plasmas. Here, the electron and ion neutral mean free path was estimated using a constant cross section value of $\sigma \approx 2 \times 10^{-19}$ m^{-3}.

for issue (c), the development of alloys and ceramic materials with high resistance to plasma damage is desired. In addition, ideas for new material selection, such as the use of superconducting materials as electrode materials, are also desired.

Because of the difficulty of diagnostic access, modeling is likely to be especially important for progress. Although microscopic physics, such as interactions, can be modeled by adapting the molecular dynamics (MD) techniques used in analytical chemistry and dense plasmas, modeling the macroscopic scale of experiments will require significant developments in numerical methods and kinetic theory. Particle-in-cell (PIC) techniques are perhaps the most common method used in LTPs. These solve a Boltzmann equation that applies only when the plasma is weakly coupled, and the numerical methods make assumptions, such as assigning large macroparticle weights and setting spatial resolution to a Debye length, that also only apply at weak coupling. Macroscopic scale simulations might be achieved by combining aspects of MD and PIC in a hybrid format. Alternatively, advances in plasma theory are providing accurate kinetic equations that can model strong correlation physics relevant to extreme LTP states [27, 28]. New approaches to kinetic simulations may follow if efficient algorithms can be developed to numerically solve these equations. It is also important to note that extreme LTP states interact strongly with boundaries [29, 30], and that photoionization and radiation transport can be significant [31, 32]. Accounting for these provides further challenges for theory and simulations.

Concluding remarks

Plasmas generated in extremes of low temperature or high density represent fundamentally new states that exhibit novel physical properties that can be utilized in applications. This research field is currently in an early exploratory stage but is already yielding beneficial applications in materials synthesis and materials processing. Advances in foundational science and modeling will be required to realize the full potential of this developing research field.

3. Plasma–liquid interactions

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Status

Plasmas sustained directly in liquids or interacting with liquids are being intensively investigated to address fundamental properties (e.g. plasma-to-liquid transport of reactive species, electron solvation), synthesis of novel nanomaterials and a growing use of plasma activated liquids in medicine, agriculture and environmental applications. These activities address both polar (e.g. water, ethanol, methanol) and non-polar (e.g. hydrocarbons with only C–C and C–H bonds, N_2/Ar/He) liquids under conditions ranging from ambient to cryogenic. However, research during the past 5 years has been dominated by plasmas interacting with water, aerosols or aqueous solutions motivated, in part, by the rapid development of plasma medicine and agriculture, and synthesis of materials.

Nanosecond discharges in cryogenic liquid nitrogen were used to synthesize new materials, such as an energetic non-molecular form of nitrogen-rich materials [33]. High-resolution imaging (down to one micron and tens of picoseconds) and spectrometric diagnostics have enabled new insights into the coupled phenomena that control the initiation of ns discharges in liquid water [34]. A new mechanism for the multiplication of electrons inside electric-field-stretched nanovoids in water was proposed and computationally investigated, emphasizing the key role of secondary electron emission inside the cavity [35].

Progress has also been made in understanding plasma-chemical processes at the plasma–liquid interface. This progress includes predictive modeling of the interfacial behavior of hydroxyl radicals and solvated electrons delivered to and created at the boundary of aqueous solutions [36], experimental measurements of oxygen atoms produced above the water surface and penetrating into the bulk liquid [37], studies of reactive oxygen species induced oxychlorine chemistry in saline solutions [38], evidence of modification of dissolved biomarkers in complex liquid media [39], role of ultrafast photochemistry at the gas–liquid interface [40], and production of nitrogen compounds such as ammonia and nitrate ions from active nitrogen species impinging on the water surface [41].

The synthesis of new materials, and nanomaterials in particular, from plasma-driven solution electrolysis (PDSE) has emerged as a new research area [42]. PDSE augments conventional electrochemistry by replacing one (or both) electrodes with a plasma in contact with the liquid. This configuration enables large fluxes of electrons (or ions) to impinge on the surface to produce, for example, a highly-reducing environment. Plasma produced radicals or stable species that hydrolyze in solution are also introduced. PDSE is being investigated for synthesis of nanoparticles and chemical conversion [43]. Much of the focus of research in PDSE is on creating non-equilibrium conditions at the plasma–liquid interface, and on the disposition of solvated electrons [44].

The investigation of plasma-self-organization of SIWs on liquid surfaces has contributed to improved understanding of mechanisms and transport processes of these unique structures [21]. The investigation of plasma activation of aerosols and droplets has produced advanced in our understanding of plasma–liquid interfacial transport and methods to customize the chemical reactivity of the droplets for applications such as high-nitrate liquid fertilizer [45] and ammonia production [46] (see also section 12).

Current and future challenges

Considerable uncertainty remains about processes underlying formation of microfilaments from electric field-stretched nanovoids during breakdown of discharges in polar liquids. Modeling of electron acceleration and multiplication in the cavitation-controlled environment remains to be a challenge of fundamental importance. Novel diagnostic approaches performed with sub-ns and micron resolution are required to identify signatures differentiating the direct breakdown from bubble-assisted breakdown. It is also important to clarify the dynamics of formation of sub-micron sized bubbles in periodic discharges which may impact successive discharges. Micro-bubbles have long charge-stabilized lifetimes and may form suspensions that would decrease potential barriers to breakdown (eventually leading to changes in the discharge mechanism). A related challenge is understanding the mechanisms of pulsed discharges in immiscible liquids composed of layers of polar and non-polar fluids.

Optimizing plasmas in contact with liquids for applications requires a better understanding of the transport of plasma-produced species into the liquid, while accounting for the dynamics of the gas–liquid and plasma–liquid interfaces. These dynamics include deformation of the liquid surface, plasma induced convection in the liquid, heating of the liquid and subsequent change in the saturated vapor layer, temperature dependence of Henry's laws constants, the consequences of photoionizing and photo-dissociating radiation and processes involving solvated electrons. The role of adsorption on transport into the liquid of plasma-produced species is poorly understood in spite of analogues of adsorption on aerosols studied in atmospheric chemistry. Understanding this transport will require deconstructing complex interface interactions into elementary processes (e.g. photon-driven processes) influencing charge transfer, interfacial instabilities, fluid flows and chemical activation. Experimental and theoretical efforts should include not only simple liquids (such as deionized/distilled water or saline), but also liquids with complex organic and inorganic content (such as nutrition media, solutions containing lipids/proteins).

There are many potential applications of these fundamental plasma–liquid processes, particularly in research related to electrification of the chemical industry and synthesis of nanomaterials. Each have their own challenges. For example, plasma-assisted wastewater treatment to remove pharmaceutical pollutants is challenged by low energy efficiency. Except for niche applications or production of high value materials, scaleup of plasma–liquid systems to municipal or industrial scales require significant improvements in efficiency, ranging from optimized impedance matching of pulsed power delivered to the plasma–liquid system, to optimizing transport of plasma produced species to the liquid interface. The latter may be achieved by leveraging plasma-to-liquid systems having large surface-to-volume ratios such as thin films or droplets, or systems with high rates of mixing.

Advances in science and technology to meet challenges

Due to the complex multi-phase nature of plasmas in liquids or plasmas interacting with liquids, a major experimental challenge is improving reproducibility of measurements, to capture single-shot events or devising better statistical methods to analyze the data. This challenge results from the filamentary nature of the micro-discharges, instability of plasma–liquid interface, uncontrolled plasma-produced convection in the liquid, drift during long-duration experiments (temperature, liquid conductivity and composition, liquid pH). Standard noise-reduction techniques will likely not address this complexity. Progress may be made by applying machine learning analysis and techniques constrained by the known physics.

New *in-situ*, real-time techniques are required to determine absolute densities of transient species in the liquid phase and in the saturated vapor layer with a time and spatial resolution that are compatible with characteristic plasma scales. These measurements may utilize short pulse (fs/ps/ns) laser-based techniques to overcome high rates of collisional broadening and quenching. Although developing, for example, in-liquid laser diagnostics for real-time measurements will be extremely challenging, there are few alternatives to obtain measurements of transient and short-lived species. The need for these diagnostics is particularly great in PDSE and plasma-touching conditions where electron solvation occurs, and where the accompanying reactive boundary layers may be only tens of nm thick. In-liquid dissociative processes at the plasma–liquid interface (due to charge exchange, photolysis and energetic particle bombardment) likely lead to Franck–Condon heated fragments, in analogy to gas phase hot-atom chemistry. The possible in-liquid non-equilibrium resulting from these events should be investigated and quantified. The roles of photolysis and photoionization, and possible in-liquid hot-electron production, by vacuum ultraviolet (VUV) photons incident from surface-touching plasmas are poorly understood. The use of second harmonic generation (SHG) and sum frequency generation (SFG) to interrogate plasma–solid interactions is a burgeoning field, techniques which can also be applied to the liquid surface. These techniques would also aid investigation of self-organization.

A great challenge in the modeling of the plasma–liquid boundary and in-liquid discharges is the lack of fundamental reaction rate and cross-section data developed specifically for the liquid phase. Models now typically rely on gas-phase data whose extrapolation to the condensed phase is questionable. The equivalent of classical swarm and scattering experiments and generalized theoretical expressions would advance plasma–liquid modeling. A focus on modeling transport from the gas phase into the liquid is required while accounting for adsorbed layers, energetic particles, testing the validity of equilibrium assumptions (such as Henry's law limits at the surface) and atomistic processes. In addition to modeling of plasma, leveraging high-performance-computing for MD and quantum chemical simulations may be necessary to obtain atomistic data (e.g. accommodation coefficients, rates of solvation) (see figure 5). The onset of convection in the liquid by plasma generated forces is poorly understood from both modeling and experimental perspectives.

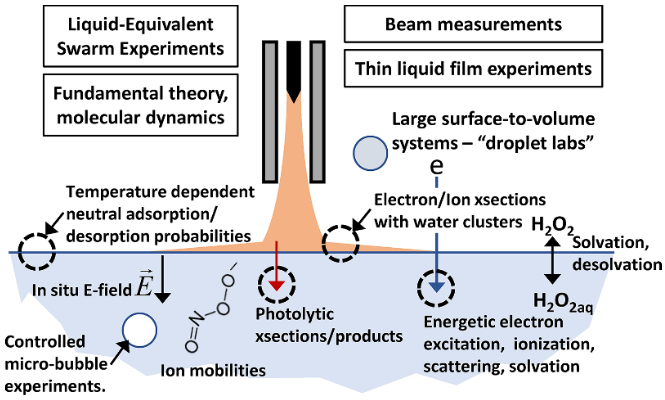

Figure 5. Rapid progress in understanding plasma liquid interactions requires significant improvements in fundamental data, ranging from adsorption probabilities to ion mobilities. The complexity of current systems makes such measurements difficult. Deconstructing complex experiments into *unit-operations* akin to swarm and beam experiments will be required to make unambiguous measurements of fundamental parameters. These efforts must be augmented by theory and computations (e.g. MD).

Concluding remarks

The complexity of plasmas in liquids or in contact with liquids, difficulties with reproducibility and the inter-related fundamental processes ask for a more deliberate systematic approach to the investigation of these phenomena. The LTP field has greatly benefited from standard plasma sources to enable lab-to-lab comparisons and to establish well characterized baselines. A similar set of standard configurations for plasma–liquid studies would serve the field well. Investigation of gas phase plasmas has advanced by decomposing the system into a set of relatively independent fundamental processes that can be individually studied. Plasma–liquid interactions would similarly benefit from such a deconstruction. Doing so might require specialized experiments and modeling to isolate the fundamental process for study. Widespread applications require technology advances in scaling plasma treatment of liquids to industrially interesting flow rates with high efficiency. Diagnostic-based control will be needed to address the synergy between the plasma-activated species and in-liquid components (e.g. organics, cells).

4. Dusty plasmas

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Status

Dusty (complex) plasmas are four-component systems in which charged, solid particulate matter (i.e. 'dust' particles) joins the background of electrons, ions, and neutral atoms. The dust particles are typically nanometers to micrometers in diameter and become charged due to the direct collection of electrons and ions or a variety of other energetic processes, e.g. thermionic emission or photocharging. Irrespective of the charging mechanism, the net charge on the dust particles, from tens of charges for nm-sized particles up to thousands of charges for micron-sized particles, combined with the resultant low charge-to-mass ratio couples the dust to the plasma. Dusty plasma research originated in attempts to understand dust formation and transport in the solar system [47, 48]. Upon the discovery of dust generation in reactive plasmas, the field rapidly evolved into a distinct sub-discipline that has both fundamental scientific interest and important impacts for plasma applications [49, 50]. One can distinguish between studies using larger particles (micrometers), where fundamental understanding has been able to mature longer, and studies of small particles (nanometers), where fundamental understanding has only recently begun to develop. Figure 6 shows an example of a dusty plasma of micrometer-sized particles in a laboratory experiment.

The large size and low charge-to-mass ratio of the dust particles, means that dusty plasmas can exist from weakly to strongly coupled regimes, while being directly imaged using conventional high-speed camera technologies. Consequently, dusty plasmas not only enable kinetic-level measurements of plasma phenomena, the access to a wide range of coupling regimes allow these systems to serve as analogues for fluid and soft-matter systems and a platform to investigate problems in statistical physics [51, 52].

Dust particles can form from the gas phase in reactive plasmas and remain a critical source of contamination. Furthermore, in plasma processing equipment, dust particles are generated by wear and tear, charged negatively by free electrons, and then trapped in the plasma glow. However, the ability to selectively form and process nanodust (sizes less than 100 nm) to enhance the structural, electrical, or mechanical properties of materials is a rapidly emerging industry [53–55]. With the shrinking feature sizes in the semiconductor industry, the 'killer' particle size has decreased from microns to nanometers (see sections 5 and 6). This implies that the electrical charging mechanisms have to be revisited because, at these sizes, particles may exhibit positive and negative charges.

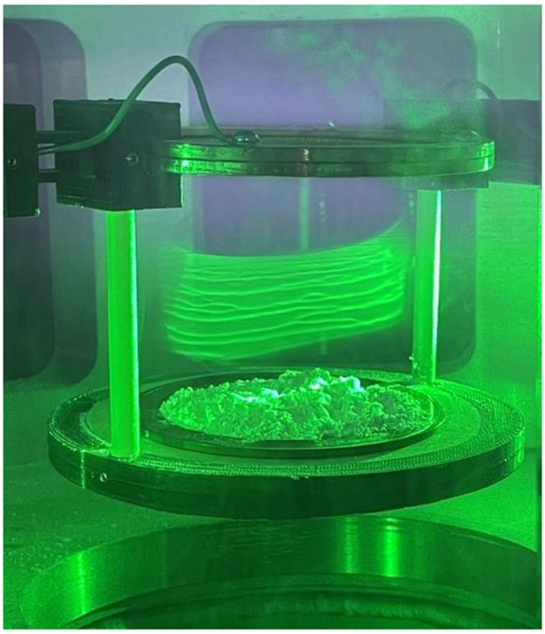

Figure 6. Photograph of dust waves in an argon plasma in the MDPX device. This illustrates the fluid-like properties that can be investigated using dusty/complex plasmas. Photo: Wittenberg University and Auburn University.

Current and future challenges

Dusty/complex research has made significant advances in both the ability to manipulate the particles in laboratory and industrial settings as well as achieving a degree of predictive capabilities to understand particle formation and dynamics. While the study of dusty plasmas consisting of micrometer-sized particles is well-advanced, much work remains to be done on plasmas containing nanoparticles. Ongoing and future work is needed in areas such as:

Controlling particle synthesis and morphology. One of the most exciting and challenging areas of research is the synthesis of nanoparticles in reactive plasmas. This provides insight to questions ranging from the initial processes in solar system formation to improvements in the structural strength of microelectronics. These problems involve detailed understanding of dynamics of free electrons and ions as well as the hundreds of underlying chemical pathways that drive particle formation. In most studies, the particles form spherical particles or agglomerates of spherical particles. Developing new processes that could lead to controlling the particle morphology (e.g. nanorods or other complex shapes) has the potential to create new applications for nanodusty plasmas and is explored in greater detail in section 6.

Determination of particle charge. The real-time, *in-situ* determination of the particle charge has been a challenge. For example, figure 7 shows an example of an experimental

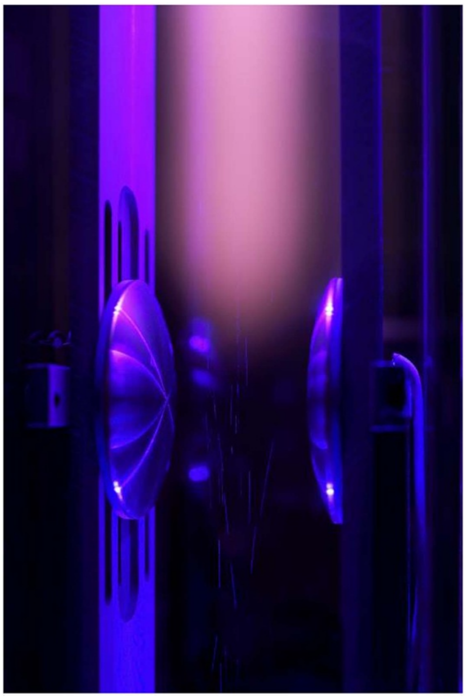

Figure 7. Dust particles falling in a plasma afterglow. The electrodes on the sides induce a static electrical field, which allows the study of charging, de-charging and drift of dust particles. This knowledge is used for the prediction of particle behavior in lithography-related plasmas. Photo: Eindhoven University of Technology. Reproduced with the permission of Bart van Overbeeke Fotografie.

setup to determine particle charge from electrostatic deflection [56]. While there are numerous advanced models for estimating the particle charge, complementary experimental investigations with sufficiently small error bars to definitively distinguish among the models remain elusive. Moreover, as research extends into new regimes, e.g. nanoparticles, magnetized plasmas, high pressure/atmospheric pressure plasmas, where orbit motion limited based models are no longer valid, new experimental and theoretical techniques must be developed.

Beyond electrostatic levitation and confinement. The majority of ground-based, laboratory dusty plasma studies are based on a 'zero-order' force model in which the gravitational force on the micron-sized dust particles is balanced by an electrostatic levitation force. As research interests expand to focus on smaller (nm) particles, microgravity systems [57], magnetized plasmas [15], and/or strong ion-flow dominated systems where ion-dust or dust–dust forces are comparable in strength to electrostatic forces, it is critical to develop a more complete understanding of these forces.

Advances in science and technology to meet challenges

In order to address the challenges identified above, new advances in theoretical, computational, and experimental techniques are required. Some of the most critical needs are in the three areas identified below.

Self-consistent, multi-scale modeling. A critical challenge in the study of the dusty/complex plasmas is the lack of fully self-consistent models. Whether considering either mass ($m_{\mathrm{dust}} \sim 10^{15}\ m_{\mathrm{electron}}$) or charge-to-mass ($q_{\mathrm{dust}}/m_{\mathrm{dust}} \sim 10^{-11}\ q_{\mathrm{e}}/m_{\mathrm{e}}$) ratios, these wide differences challenge the ability to create models that can describe these systems. Developing new open-source computational tools, coupled with new theoretical approaches that also include modules that incorporate chemical pathways for particle growth studies, is an important need for the research community.

Diagnostic developments. As in all parts of plasma physics, the development of new diagnostic tools is a constant need. For dusty/complex plasmas, there are two particular needs. First, for nanoparticle systems, the development of real-time, submicron imaging diagnostics will be of great value. Possibly based on pulsed ultraviolet (UV) light sources, in order to minimize photocharging of the particles, such tools may provide new insights into the coupling between the dust particles and the plasma. Second, the development of new techniques that allow experimenters to non-perturbatively determine the charge on the dust grains is critical to differentiate among the various charging models.

Extending dusty plasmas. As the types of LTP systems expand to new regimes, this provides opportunities to extend the application of the dusty plasma concept, tools, and analysis techniques to these systems. The formation of so-called 'misty' plasmas that involve charged liquid-droplets [58], 'dust' particles consisting of active matter [59], and beyond, inorganic materials, controlling and trapping micron-sized, airborne bioaerosols and pathogens [60] offer new opportunities to leverage the advances made in dusty plasma research to other physical systems.

Concluding remarks

The study and application of dusty/complex plasmas remains a vibrant area of scientific research. As the field has grown over the past three decades, there has been somewhat of a self-separation among the various subtopics, i.e. dusty plasmas in space and astrophysical systems, complex plasmas as analogues for soft-matter systems, and nanodust as an industrial commodity in plasma manufacturing. Each of these areas relies on a basic understanding of the coupling between charged, solid particulate matter and the surrounding plasma and future efforts need to be made for these different communities of researchers to re-engage with each other. For a robust future of dusty/complex plasma research and applications, we believe researchers will need to form collaborative networks that unite experimental, theoretical, and computational tools to solve the challenging, multi-scale problems that arise this in work.

5. Atomic layer etching (ALE) and deposition

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Status

Realizing manufacturing of 7 nm advanced semiconductor technology has been enabled by revolutionary advances in patterning, the emergence of 3D devices and integration. Now, logic device roadmaps predict significant change in the form and nature for 3 and 2 nm generation devices referred to as 3/2 nm (e.g. III–V's, SiGe, Ge, nanowires, nanosheets and heterogeneous complementary-field effect transistor (FET)) and discussion of novel memory with a host of novel materials is commonplace. Even with these changes, fabrication technology will need to address ultrahigh aspect ratios (ARs), damage-free processing and the maintenance of complex profiles through many process steps. During the last decade, a great deal of efforts have focused on achieving atomic-scale etching and deposition processes in semiconductor fabrication, i.e. ALE [61, 62] and atomic layer deposition (ALD) [63, 64]. The major challenges associated with these techniques are related to smaller dimensions, higher ARs, and a larger set of materials. Another major theme in semiconductor processing that is coming to the forefront is manufacturing of increasingly 3D structures as lateral features are approaching dimensions that are just a few nanometers for scaled down devices (see also section 6).

The 2017 Roadmap pointed out many essential challenges in the area of plasma etching and deposition. As we will see from the description below, most of the challenges articulated in the 2017 Roadmap still apply, and in fact have increased, e.g. driven by higher AR, more materials against which etching selectivity is required, or need for area-selective deposition. The achievement of atomically abrupt material selectivity in ALE using novel chemical precursors, isotropic ALE processes for a number of important materials, along with impressive demonstrations of area (material) selective deposition for a significant number of materials are important advances.

Current and future challenges

As indicated, interest in ALE has increased considerably in the last decade [61–64]. Although some of the recent work can more accurately be termed nano-scale layer-by-layer etching, it is undeniable that the nanoelectronics industry is seeking etch solutions that remove materials with atomic precision, high selectivity between materials, and leaving the unetched material atomically pristine. With respect to plasma-enhanced ALE, these techniques can be classified into ion energy assisted etch methods to directionally etch Si, SiO_2, Si_3N_4, and organic polymers. Neutral-beam-enhanced ALE (NBALE) has attracted attention as one method to address the challenges of atomic precision plasma processing because of eliminating the incidence of charged particles and UV photons on the substrate [65, 66]. These attributes enable precise nano-processing, while suppressing the formation of defects at the atomic layer level. Sub 6 nm Fin-FETs produced in this way are shown in figure 8(a) and for a 3/2 nm heterogeneous complementary-FET in figure 8(b) [65, 66]. Especially, 3 and 2 nm generation devices require bonding of heterogeneous channel materials (for example, Si/Ge, Si/GaN). Then, atomic layer neutral beam thinning and bonding technology for channel materials are required [66].

Area selective deposition (ASD) is an enabling technology that because of its substrate sensitivity has advantages relative to traditional ALD processes [67, 68]. Many enhanced processing challenges are made difficult by the highly heterogeneous chemical make-up of the surfaces of complex substrates that are required for advanced devices. For these situations, material selective deposition enabled by ASD, is a key advantage. While selective deposition processes have long been used in the semiconductor industry, such high-temperature reactions are not suitable for many materials. Low substrate temperature processes can be realized using plasma excitation and achieve high materials sensitivity of growth. An example of the performance of area-selective deposition of TiN is illustrated in figure 9 [69]. The process consists of several cycles that include dosing with inhibitor molecules at the start of every ALD cycle—in their case aromatic molecules which gave good metal/dielectric selectivity because of their strong and selective adsorption on transition metal surfaces [63].

Advances in science and technology to meet challenges

With plasma processing increasingly requiring atomic level precision, future developments will greatly benefit from research in several areas. The fundamentals of material-plasma interaction at the atomic scale (in particular during ALE and ASD) are not well understood. Surface analytical techniques for ALE and ASD, can help in this regard. The ion energy in many industrial plasma sources may be too high for atomic-precision materials processing. The ion energy can be reduced by pulsing the radiofrequency (RF) sources. Irrespective of the plasma source, better control over ion energy and angular distribution (IEAD) and the electron energy distribution is needed [70]. One of the key issues in processing of high AR structures is the lack of knowledge of key factors which limit processing as a function of AR. This is related to the lack of knowledge of both neutral and ionic (neutral beam) species fluxes, and their composition and energies within such structures as a function of AR, and the surface-chemical mechanisms that are operative and limit processing. One of the challenges is the development of physical/chemical characterizations of these parameters as a function of AR for increasingly diverse material sets and structures. An additional complication is that these effects are highly sensitive to the exact layout and material design of the microscopic structures that are

Advanced CMOS Technology

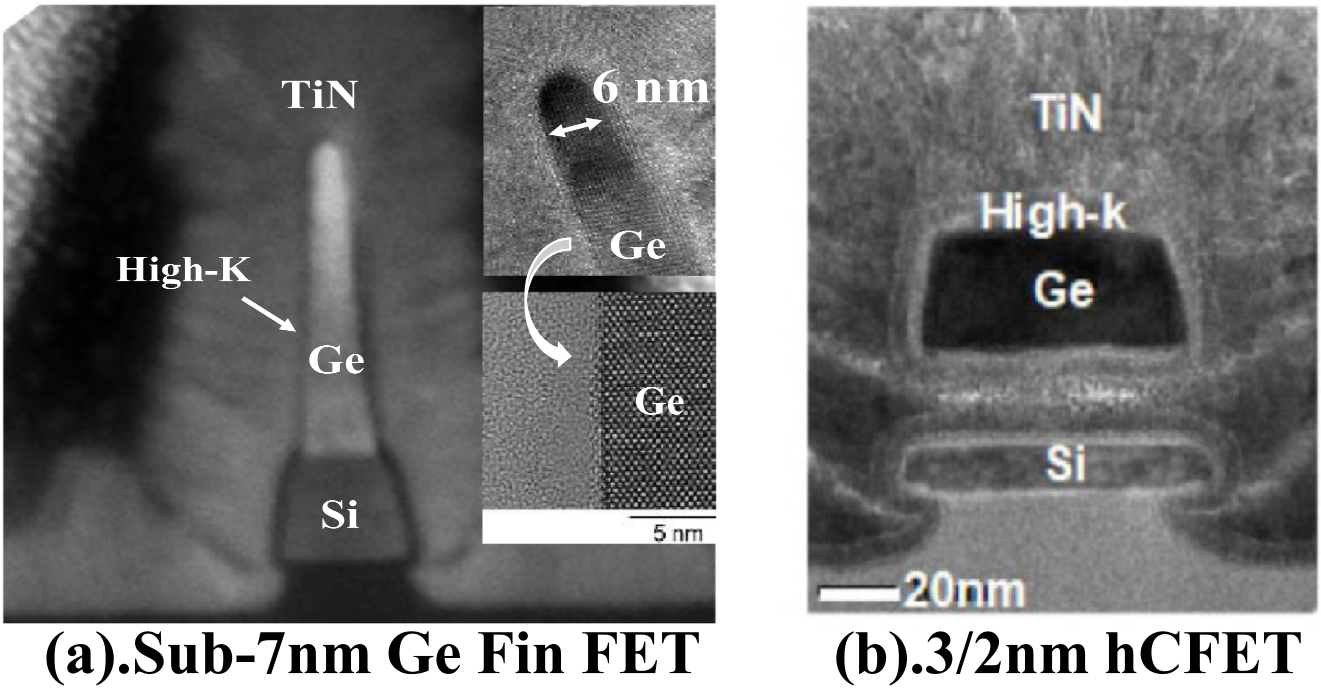

Figure 8. Advanced complementary metal-oxide-semiconductor (CMOS) devices fabricated by NBALE. © 2007 IEEE. Reprinted, with permission, from [65]. © 2004 IEEE. Reprinted, with permission, from [66].

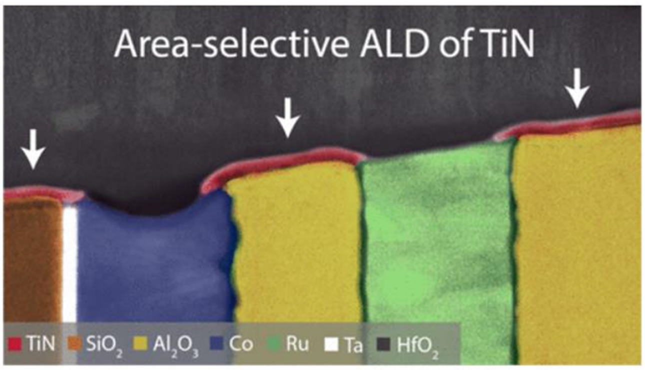

Figure 9. Demonstration of selective deposition ∼6 nm TiN on SiO_2 and Al_2O_3 areas of a nanoscale pattern with Co and Ru non-growth areas. Reproduced with permission from [69]. CC BY-NC 4.0.

being produced. Comprehensive computational simulations of such processes are producing important insights, and validation of these approaches will be required [71] (see also section 19). Atomistic modeling of ALE processes can leverage significant advances that have been achieved in the application of computational modeling methods to ALD processes. For an example of this to thermal ALE of aluminum oxide thin films, the reader is referred to the work by Yun *et al* [72]. They describe for this problem the application of density functional theory (DFT) -based electronic structure calculations and evaluate possible reaction pathways and kinetic parameters using kinetic Monte Carlo methods. This appears prototypical, and extensions to energy-driven directional ALE approaches may be possible.

Concluding remarks

Plasma materials processing remains one of the vital technologies for nanoelectronics fabrication. The need for atomic-level precision for many plasma etching and deposition processes has been accepted by industry, and has prompted the development and exploration of techniques that enable better control of the ion/neutral-beam energy and angular distribution, electron energy distribution, reactive neutral to ion flux ratio, e.g. by using novel precursors for more effective surface functionalization [73], and the UV photon flux [65, 66]. Future advances in the field will benefit from good fundamental understanding of low energy synergistic (<20 eV) ion-radical interactions with materials. Although the emphasis here has been on ALE and ASD that are controlled by plasma pulsing, other techniques to achieve atomic scale control, such as self-assembled structures, also show promise. One of the key enablers of advanced etching and deposition processes is the use of self-limited surface reactions. The computational work [71] mentioned in the last section can be viewed as exemplary for the general value and opportunity of simulation approaches to investigate many issues connected with advanced etching and deposition approaches that may be impossible or impractical to examine directly experimentally, and impact future scientific and technological advances.

6. Nanostructures and nanomaterials

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Status

As noted in the 2017 Roadmap [74], plasma nanomaterial synthesis complements methods such as solution, vapor phase and aerosol processing. The interest in nanostructures and nanomaterials has only grown in recent years due to applications ranging from advanced electronics to sensors and health-related applications. Plasma for nanomaterial processing has many potentially powerful roles for both organic and inorganic materials. Plasma can be created and maintained in an enormous number of ways and the corresponding set of effects on nanostructured surfaces and particles is equally large. For example, the degree of gas and surface heating can range from negligible to large. Plasma-generated ions and reactive radical alter both gas phase precursor formation as well as directly alter surface conditions. Plasma creates photons, typically from the visible to the vacuum UV. There are widely documented effects of synergies in plasma materials processing. But in addition, the types of plasma and the conditions under which plasma is generated can vary dramatically as well. Plasma can be maintained in a steady- or quasi-steady state or it can be pulsed and transient. It can be relatively homogeneous and uniform, or it can form filaments or jets. Particles and surfaces in contact with plasma can be solid or liquid. The net result is a virtually limitless set of conditions to explore to find some approximately optimal set of design and operating parameters for the nanomaterial synthesis or processing task at hand.

One set of approaches to use plasma for nanostructured materials is referred to as 'atomic layer processing'. Atomic scale etching of a surface with plasma can be performed (see section 5), but the use of plasma for approximate atomic layer addition or deposition is better developed and will be stressed here [63]. Another set of approaches discussed in this article focuses on the formation and transport of nanostructured materials directly in the plasma environment, with the aim to produce 0D (nanoparticles), 1D (nanotubes), 2D (nanosheets and flakes) and 3D nanomaterials. The challenge of creating nanostructured materials is now emerging as a key theme in the semiconductor industry as new, post-silicon materials, sculpted with atomic scale precision, are increasingly in demand. The need for plasma processes for fabricating defect-free nanostructured materials is a cross-cutting demand in multiple fields. Plasma synthesis of nanostructured materials enables current and near-future technological materials, but we also discuss how our insatiable needs for performance and increased emphasis on sustainability drive new developments in the field.

Current and future challenges

In the burgeoning area of plasma-assisted ALD (PALD), important advances in understanding how to minimize damage from energetic ions and the unwanted redeposition of ALD reaction species have been made [63, 75]. One promising recent development exploits the ability of gentle plasmas to chemically activate otherwise chemically inert surfaces. This has been shown for 2D van der Waals materials through the plasma-generation of reactive sites at surfaces, but little is known about these effects in other systems [76]. Further, recent studies in plasma etching have shown the importance of plasma-generated UV and VUV photons in surface chemistry but this effect has not been extensively explored to date in PALD [77]. The role of the energy flux density of species impacting the surface in controlling nanostructure has begun to be explored but much work remains [78, 79].

Nanomaterial synthesis in thermal plasma reactors is studied since the 1990s, with an initial focus on refractory materials [80]. The thermal plasma was initially used as a source of heat and momentum and conditions for nuclei formation and growth, but gradually more for complex high-temperature chemistry. Non-equilibrium, cold plasmas provide milder heating conditions that permit the synthesis of organic nanomaterials and core–shell nanostructures of vastly different materials, and a finer control of the surface chemistry which is essential for stabilization and compatibilization with a host matrix [81]. Precursors include solid targets, micron-sized particles, aerosols, slurries, liquids and gases. Pulsed laser ablation of solid targets in gases and liquids (another plasma-based approach) [82] provides additional versatile environments for nanomaterial synthesis, and deposition of nanoparticles over nanomaterials [83]. One particular area of fast-growing interest is the synthesis of 2D nanomaterials. Such novel materials which consist of thin layers—thickness possibly down to one atomic layer with nanometers extent in the other two dimensions offer high surface atoms-to-bulk atom ratios, adaptable surface chemistry and quantum effects of interest to quantum information science and catalysis, to name a few promising applications.

A corollary of the above-mentioned wide range of processing conditions and associated parameter sensitivity is the need to maintain tight control of the plasma. This can be challenging since plasma is a highly non-linear state of matter and small changes in conditions or seemingly minor external perturbations can alter plasma dynamics significantly and ultimately, the properties of the nanostructured materials. Automation, machine learning and artificial intelligence [84] are today's tools to integrate with plasma processing and online diagnostic equipment. But our ability to characterize the produced nanomaterials *in-situ*, for rapid screening purposes at the very least, often becomes a bottleneck.

Advances in science and technology to meet challenges

Plasma synthesis of nanostructures and nanomaterials involves understanding and controlling the bidirectional

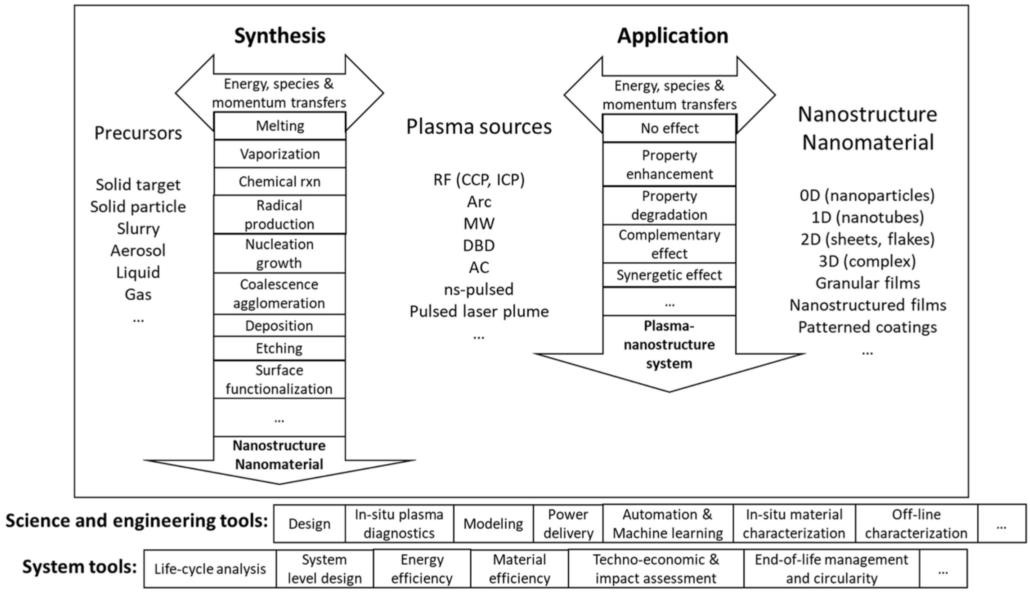

Figure 10. Schematic view of the vast realm of plasma source-precursor combinations for nanostructure/nanomaterial synthesis (left) and possible outcomes of plasma-nanostructure/nanomaterial interactions in an application context (right). Non-exhaustive list of science, engineering and system tools required for the development of a sustainable plasma-based nanostructure/nanomaterial technology.

interactions between at least two states of matter (solid and plasma) and sometimes, all four. A vast realm of complex nanostructures and nanomaterials can be produced and stabilized under equilibrium and non-equilibrium conditions. Recent research has shown that the intrinsic properties and performances of materials may be altered when placed in contact with the plasma (e.g. plasma-catalysis [85], see also sections 19). This leads to the important new caveat that the plasma-material interactions require a system view, to optimize both the synthesis and utilization conditions. This nourishes the perpetual need for more complex multi-phase modeling and *in-situ* diagnostics under very challenging conditions (sections 17 and 18). Furthermore, the synthesis of nanostructures and nanomaterials may not be possible with a unique plasma source, even when the densities and fluxes of species, and electron and heavy species temperatures are carefully designed, thus requiring combinations of plasma sources. The design of the next generation of plasma processes requires a system's view where the plasma reactor is also used to evaluate the early performance of the produced nanostructures and nanomaterials (figure 10, see also section 1). Plasma-catalysis is an active research and development area where *in-situ* diagnostics of the plasma-catalyst interactions and catalyst material evolution have begun to be reported (e.g. *operando* Diffuse Reflectance Infrared Fourier Transform spectroscopy (DRIFTS) [86]). A necessary next step to accelerate material discovery in this field will be the integration of the plasma synthesis and plasma-catalysis reactors.

Though most nanostructures/materials produced through plasma processing aim for high energy, material, device and/or system efficiencies, little attention has been paid thus far to the sustainability of the raw materials, products and plasma processes. As new opportunities for plasma processing arise with the electrification of the chemical processing and manufacturing industries, there is a need to rapidly adopt a life cycle view on the energy and material flows, as well as transformation steps [87]. A paradigm shift is required so that concepts such as design-for-no-waste and maximum resource utilization efficiency become hard-coded design criteria. Similar to the emerging field of plasma medicine, a field that was enabled through collaborative work amongst physicists, engineers, biologists and physicians, sustainable plasma processing for nanostructure/materials will thrive by reaching out to researchers that focus on system design, life cycle analysis and socio-economic impact.

Concluding remarks

The synthesis of nanomaterials and nanostructures continues to be a vector of innovation in plasma source and reactor design. Notable commercial-scale successes have arisen since the birth of microelectronics to today's nanomaterials production facilities, but numerous challenges remain to unlock the full potential of plasma processing. The understanding and control of plasma chemistry as well as plasma–solid and plasma–liquid interactions with extreme fluxes of energy and reactive species, often under non-equilibrium conditions and with multiple states of matter present, remains a cornerstone for the successful development of applications. There is a need to integrate automation, learning and decision-making tools capable of handling numerous operating parameters with fewer but more sophisticated measurements to guide accelerated material discovery. A system's view is required, notably to meet the increasingly coupled synthesis and material performance requirements, and overall sustainability of the material journey. The transition from fossil fuels to renewable electricity provides new opportunities to plasma processing for nanostructures and nanomaterials.

7. Additive manufacturing (AM) and coatings

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Status

Plasmas are widely applied to produce thin-film coatings on surfaces. Low-pressure plasmas are employed in industrial processes such as magnetron sputtering, filtered arc deposition, plasma-enhanced chemical vapor deposition, and ALD to deposit metals, ceramics, diamond-like carbon, polymers, and many other materials [88]. Innovation continues; for example, HiPIMS [89] allows the production of higher density films, and section 5 addresses recent advances in ALD. Thermal plasmas are routinely implemented in plasma spraying to deposit thicker (up to mm) coatings [90]. Non-thermal, atmospheric-pressure plasmas are increasingly being used to avoid the need for a vacuum vessel, but material quality and large-area, uniform deposition remain challenging [91].

The recent emergence of AM has stimulated interest in plasma-assisted coating processes that would follow the American Society for Testing and Materials definition of AM, i.e. 'joining materials to make objects from 3D model data, usually layer upon layer, as opposed to subtractive manufacturing methodologies, such as traditional machining' [92]. In traditional coating processes, the precursor is generated in the gas phase, and only a small fraction is ultimately deposited on the substrate. In addition, the deposition is not typically controlled spatially, and any shape or pattern that may be desired in the fabricated material requires additional process steps to remove the undesired regions. Benefits of AM include minimized material waste and the production of customized parts and structures that are intricate and complex, often not attainable by more traditional subtractive techniques. AM has rapidly expanded from creating smaller prototypes, usually from polymeric materials to larger parts and other materials such as metals. Commercial opportunities have emerged in, for example, electronics, automotive, aerospace, and medical industries.

Both non-thermal and thermal plasmas are applied in AM strategies [93, 94]. Non-thermal plasmas play a diverse range of roles that can be organized by their position in the process flow (figure 11). Prior to deposition of a layer, non-thermal plasmas enable surface modification of temperature-sensitive substrates such as polymers through processes including surface cleaning, chemical functionalization, surface coatings, and changes to the surface energy. Most of these processes are aimed at improving adhesion to avoid delamination of materials in subsequent deposition steps. Several companies, such as Reylon Plasma, Essentium, and Innophysics, now incorporate non-thermal plasmas for this purpose, towards the ultimate goal of 3D printing polymers. More recently, non-thermal plasmas have been applied during deposition, to treat the liquid or aerosol feed, droplets generated from a nozzle [95], or

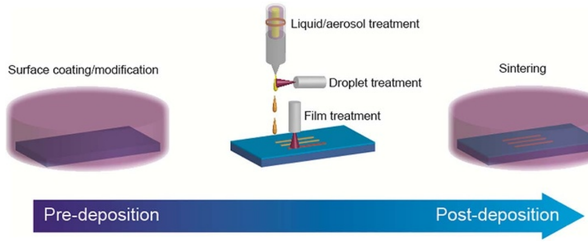

Figure 11. Current and emerging schemes for incorporating non-thermal plasmas in AM. Large-volume plasmas can apply a coating or modify a surface before deposition, or sinter a film after deposition. Spatially localized plasmas can be applied to treat and modify, for example, liquid or aerosol precursors, in-flight droplets, or a deposited film.

the film immediately upon deposition. In addition to enhancing adhesion, in this case, the plasma can drive physical processes, such as charging, evaporation, and heating, or chemical processes, such as reduction/oxidation, degradation, and etching. Following deposition, non-thermal plasmas can replace thermal processes for sintering films to remove organic constituents and crystallize the material.

The application of thermal plasmas in AM, as also noted in section 16, includes the production of metal powders by spheroidization of particles in an rf plasma [96] or break-up of a wire by a plasma jet. The metal powders are then printed as part of an AM process, such as laser powder-bed fusion. Thermal plasmas are now directly implemented in the layer-by-layer fabrication of metal parts by wire-arc AM, a process that is closely related to arc welding. Wire-arc AM is relatively well-established, and commercial systems are available from, for example, Norsk Titanium, MX3DAM, and AML3D.

Current and future challenges

Despite the recent emergence of commercial applications of plasmas in AM, several challenges remain. Non-thermal plasmas have been limited to the deposition of films or pre- or post-treatment of layers deposited by non-plasma methods. There are very few, if any, examples of layer-by-layer assembly to build 3D structures. Deposition rates are often low, making 3D fabrication time-consuming. More broadly, there is a need for AM to expand to more metals, alloys, and other materials such as ceramics and composites. While thermal plasma processes such as wire-arc AM have made substantial inroads with metals, control of microstructure and the deposition of graded structures remain challenging. The combination of hard and soft materials is also of interest, but because of temperature considerations, would be better addressed by non-thermal plasmas. Finally, spatial resolution is typically limited to the size of the plasma source, which at best is usually in the sub-mm range for non-thermal plasmas and of order 1 mm for thermal plasmas.

At a more fundamental level, plasma processes are very complex, especially when they involve multiple phases such as aerosol particles (solid) or droplets (liquid) in a gas flow or a solid wire evaporating into the gas phase and depositing onto

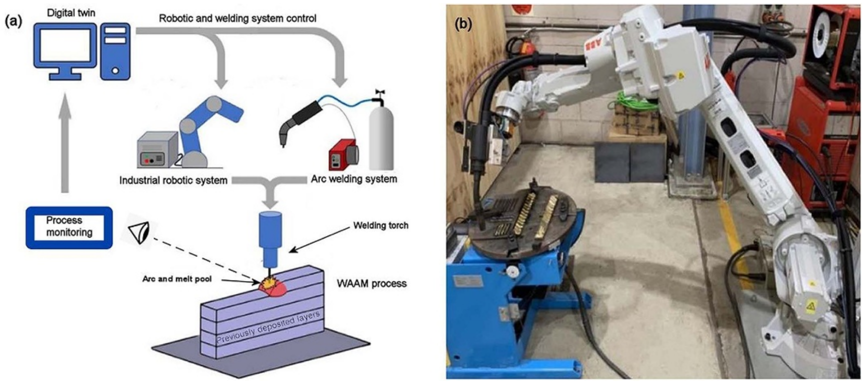

Figure 12. (a) Schematic diagram and (b) photo of a wire-arc AM system, with the diagram showing the elements of a digital twin. A machine-learning-based model (the digital twin) runs in parallel with the physical process, receives input from process diagnostics and controls and corrects the process in real-time. Modified from [97].

a solid part. The interactions can be two-way; for example, the plasma species react with the aerosol or the solid wire to cause evaporation, and the generated vapor affects the plasma and species production. Challenges in plasma–liquid and plasma–particle interactions are considered in more detail in sections 3 and 6, respectively. In wire-arc AM, there are several challenges associated with the production of complex metal structures, which accentuate the interactions between the arc and metal [97]. The structure geometry alters, for example, the flow of shielding gas, the magnetic field induced by the current flow, and the current density at the arc–metal interface, which in turn affect the heat transfer to the structure. Such plasma–metal interactions reduce the value of standard approaches to modeling arc welding that approximate the arc by estimated heat flux distributions and instead favor models that explicitly include the arc and its interactions with the metal. Computational models of the AM processes are thus needed to address the interaction of the plasma with the surface, phase changes, large spatial gradients, and rapid time variation.

Advances in science and technology to meet challenges

Two important directions are being pursued to address the complexity of plasma processes in AM. The first is real-time diagnostics. The diagnostics must be non-invasive because of the confined geometries and lack of access that usually apply, and thus, spectroscopic methods have been the most common. However, interpretation of the spectra to provide information about complex multi-phase phenomena is often based on correlations rather than physical understanding. For example, in laser-induced-plasma-based AM, data-driven machine-learning approaches are required to link the composition of mixed-material deposits to optical emission spectra [98]. The incorporation of a detailed physical understanding in machine learning (i.e. physics-informed modeling [99] rather than data-driven modeling) will improve reliability and broaden the applicability of such methods.

The second is computational modeling. Improvements in handling of the coupling of the physical and chemical phenomena occurring during deposition with different time and length scales are needed to improve predictive capabilities and help optimize the process. Beyond this goal, models will be an important component in real-time process control. Here, machine learning will be a critical factor.

Wire-arc AM provides a good example. The large differences in length and time scales between the arc and molten metal (sub-millimeter and millisecond) and the part (meter and minute) processes mean that a full computational simulation of the building of a part is beyond current capabilities. In any case, sophisticated physics-based models do not run in real-time. A potential approach is to use simulations to teach or provide constraints to a machine-learning model (physics-informed modeling [99]). A long-term goal is an integration of machine-learning-based models and process diagnostics to produce a digital twin of the process (figure 12) [100].

In the specific case of non-thermal plasmas, the challenges for 3D structures include how to improve deposition rates and the spatial resolution of the deposited material. These issues are being addressed by combining printing approaches with plasmas. For example, plasmas have been used to sinter printed films of nanoparticles. Alternatively, particle-free inks have elicited interest to avoid organic stabilizers that must be removed after printing, and plasmas are uniquely capable of converting them after printing at low temperature (<150 °C), which is compatible with a wide range of substrates, including polymers that have low glass transition temperatures (T_g) [101, 102].

Concluding remarks

Progressing from single-layer deposition processes to AM of 3D structures is a challenging task. Wire-arc AM has achieved this goal for large-scale metal structures. For non-thermal plasmas, multiple layer deposition is possible, but 3D structures are more challenging. Advances in process design, process control (including diagnostics and modeling), materials, and spatial resolution are all required. In the meantime, hybrid processes in which the plasma is used, for example, to post- or pre-process materials deposited by other means, will continue to dominate.

8. Plasma engineering of soft materials and biomaterials

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Status

The interactions of the plasma gas-phase with soft matter include penetration of energetic ions, electrons and photons in the material, as well as bond breaking, collision cascades near the surface, and diffusion and extend beyond the characteristic plasma-hard material interfacial region [2], encompassing larger penetration and diffusion depths.

Soft matter refers to organic materials with complex structural and dynamic properties between those of rigid solids and fluids. Materials in this category are polymers, colloids, gels, and include biomacromolecules such as polypeptides, all being often employed as biomaterials. Such soft materials are aimed to augment or replace partially or totally any tissue, organ or function of the body, in order to maintain or improve the quality of life of the individual.

Due to the relatively weak intermolecular interaction, thermal fluctuations, external fields and boundary effects strongly influence the structure and properties of soft matter, and thus, soft matter must have special consideration when exploring their interaction with a complex system such as non-equilibrium LTPS, also requiring efficient plasma diagnostics and modeling (see sections 17–19). This section considers essentially the family of polymeric soft biomaterials that are plasma-engineered to support the interaction with biological systems for therapeutic or diagnostic medical purposes. These include hydrogels, scaffolds or microfluidic devices for wound care, tissue engineering and implants, to name a few. Expected advancement in the field relies on the improved understanding of direct plasma–soft matter interaction as well as on the controlled surface functionalization by plasma deposition.

Current and future challenges

Surface modification of biopolymers by LTP has traditionally focused on improving wettability and introducing surface functionalities fostering interaction with cells [103]. The development of plasma sources at atmospheric pressure (see section 1) has allowed the treatment of liquids (see section 3) and soft materials, paving the way for new medical applications, i.e. wound healing or cancer treatment (see also section 9) [104–106]. In plasma treatment of soft materials, the interaction with water is highly relevant [107]. Plasma engineering is a well-suited and versatile tool to adjust biomaterial properties and the related water interaction regarding wettability, water layering/structuring, absorption/swelling/uptake, and stability/degradation, to provide the medium for the transport of active substances (RONS, drugs) and biomolecules. In this sense, two main areas are of interest that associate critical challenges:

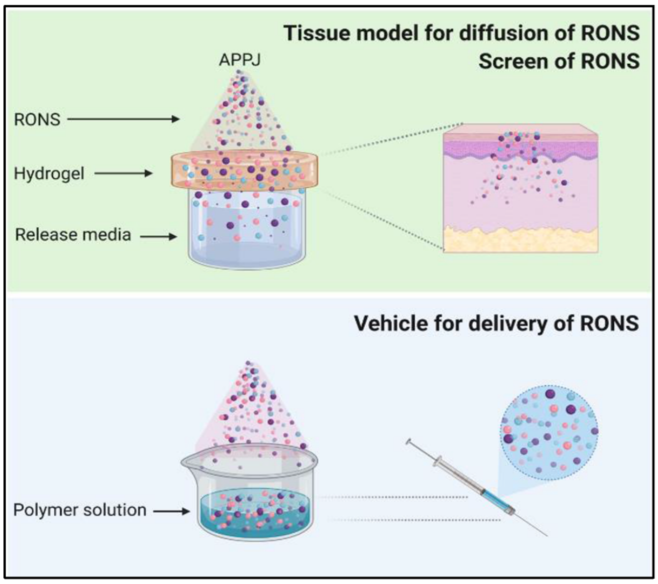

Figure 13. Current strategies related to treatment of hydrogels for applications in plasma medicine: (top) hydrogels are used as surrogates of tissues to investigate the penetration depth of plasmas, as screens for certain reactive oxygen and nitrogen species (RONS) during plasma treatment, or (bottom) in liquid solution with ability to crosslink, they are employed to generate and deliver RONS locally to the diseased site.

(a) Plasma treatment of hydrated polymer networks (hydrogels) is an emerging area that requires increasing the understanding on fundamental mechanisms underlying the chemistry in the interaction with plasmas–liquid biopolymers. So far, plasma treatment of hydrogels (figure 13) has focused on: (1) model systems for the living tissues; or (2) as vehicles for the delivery of reactive species, both for medical applications [108] (see also section 9). The penetration depth of plasmas during treatment of biological tissues has been modeled with different natural biopolymer thin films as skin surrogates [108], revealing non-uniform distribution of reactive oxygen and nitrogen species (RONS) from plasmas in the films. Relatively high penetration depths are observed together with delayed formation of secondary species within the hydrogel. In another approach, plasma treatment of biopolymers in solution with the ability to crosslink in the body is envisaged as a method of delivering RONS to the diseased site by injection (see section 9). Plasma jet treatment of diluted solutions of natural polymers [109] can generate RONS within them superior to water or conventional saline solutions. The release of RONS generated by plasmas in liquid polymer solutions and their crosslinking ability is still in its infancy and can be of interest in different biomedical applications such as for anticancer therapies.

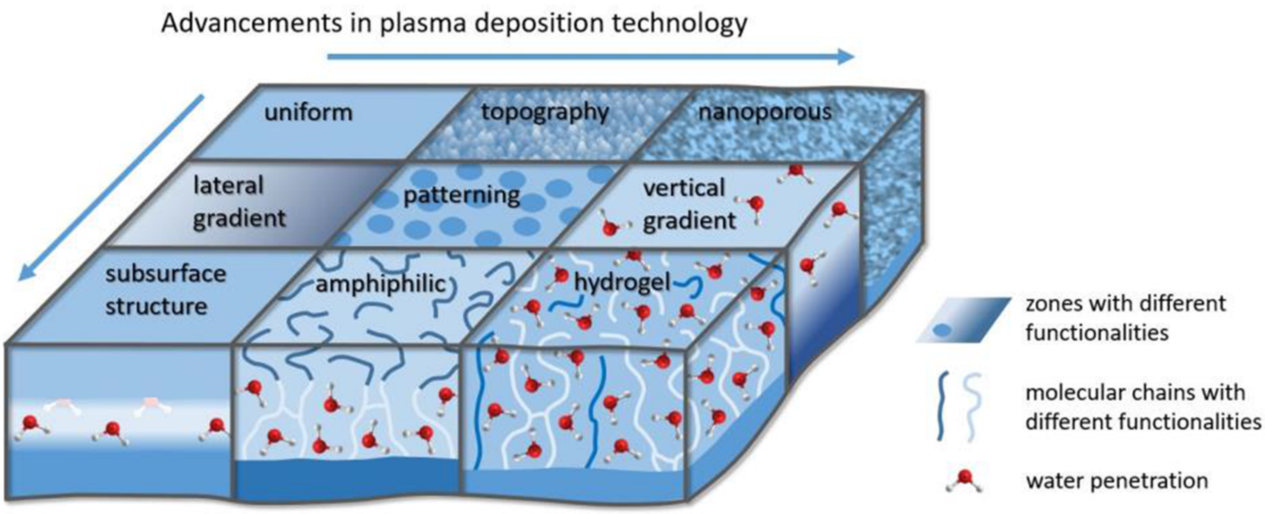

Figure 14. Representation of advanced surface functionalities important for biomaterials. While surface modifications are well studied, the controlled structuring of the near-surface region enables novel surface characteristics based on the combination of different functionalities and related water interaction.

(b) Advanced plasma polymer film architectures (see also section 6) deposited on soft materials are to be further developed that combine different functionalities at the nanoscale as well as providing strategies to enhance their stability to meet today's challenges for a healthy life [2, 110–112].

Advances in science and technology to meet challenges

In plasma engineering of hydrogels, technological advances need to associate compact and mild sources allowing the treatment of relatively large volumes (up to 100 ml) in short times to produce high amounts of RONS without damaging the polymer structure and designed to operate in a surgical room.

Besides, advancements in the deposition of plasma polymer films towards multifunctional surfaces are pursued (figure 14). While uniformly functionalized surfaces, variations in topography, and lateral gradients in functional group density represent established technologies, novel nanopatterning techniques allow the deposition of dual plasma polymer films yielding chemical differences, e.g. carboxyl and amine groups, in patterned polymeric features with dimensions down to about 20–30 nm in height [113]. Such sub-micron patterns match specific sub-cellular structures and might control the presentation of proteins to single cell arrays. Most of all, the controlled structuring of the near-surface region adds another dimension to be exploited for novel surface characteristics. Nanoporous films provide a high functional surface area, e.g. for lubricant-infused slippery surfaces [114]. Furthermore, the ordering of water molecules at the surface has a direct influence on the interaction with biological systems. Modulating the interfacial water structure by a deliberate plasma polymer film architecture, as an example, enhances the control over the initial protein adsorption [115]. To this end, vertical gradients to stabilize functional groups and thus the outermost water-interacting layer, buried interfaces in the subsurface for the nanoconfinement of water molecules, amphiphilic, zwitterionic, and hydrogel-like layers are investigated using nanoscale control over plasma deposition processes and co-polymerization [112]. Such plasma coatings with retained chemical functionalities can be combined with biodegradable, drug-releasing and/or antimicrobial substrates, when water is allowed to reach their interface. Advances in anti-biofouling, controlled protein adsorption, and cell growth can thus be expected requiring further investigations into water interaction and water structure.

Concluding remarks

The emergence and increasing applications of biopolymers, and novel applications arising from their engineering with LTP is opening a novel field with many challenges ahead. Plasma-engineered hydrogels treated to deliver the right amount of RONS in the right place have great potential to support medical therapies. Together with the advances in nanostructuring of soft materials using plasma deposition technologies to yield multifunctional surfaces great prospects can be expected in the field.

9. Medical plasma applications

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Status

Based on comprehensive physical and biological research as well as advanced technical development, the first cold atmospheric plasma (CAP, LTPs operating near room temperature) devices are CE-certified as medical devices since 2013. In chronic wound healing, CAP application is now on its way to clinical routine. Acceleration of wound healing by CAP treatment was proven *in vitro* and *in vivo*, which is based not only on antisepsis, but mainly on direct stimulation of tissue regeneration. This huge effort in clinical plasma application was accompanied by a deeper understanding of molecular mechanisms of plasma–tissue interaction [116]. Plasma devices are also used to treat infective and/or inflammatory skin diseases like herpes zoster, atopic eczema, acne, or athlete's foot and actinic keratosis, a precancerous skin disease. These applications remain rather sporadic to date. More preclinical and clinical research will enable the extension of clinical applications of plasma medicine as well as enhance the adaptation and/or extend certifications of respective plasma devices. The insight of the essential role of RONS for biological plasma effects makes it possible to name plasma medicine as a field of applied redox biology [117]. Water and biological molecules inside the cells or tissues could be excited and—directly by plasma-produced UV radiation [118] or via secondary reactions—converted to OH, H_2O_2, NO and NO_2^- and other RONS (see also section 3). These plasma-induced reactions are the fastest processes occurring during the plasma exposure of cells. Additionally, the plasma-produced RONS are transported inside the cells or tissues by diffusion processes, which occur on a much larger time scale. In general, both processes are very important in the interaction of plasma with biological cells or tissues. According to the concept of oxidative eustress and distress, the intensity of CAP application and, consequently, impact of RONS is decisive for inducing stimulating or inactivation effects on cells and tissue (figure 15). The concentration as well as the rate of RONS-induced reactions can be influenced by plasma parameters and might be enhanced by physical parameters like electrical fields and UV radiation, but depends also on the type of cells and the cellular environment. Plasma-induced cell inactivation is of particular importance because CAP can inactivate cancer cells in a redox dependent manner. The application of plasma in oncology is a highly promising and growing field currently in the stage of preclinical and clinical research [119].

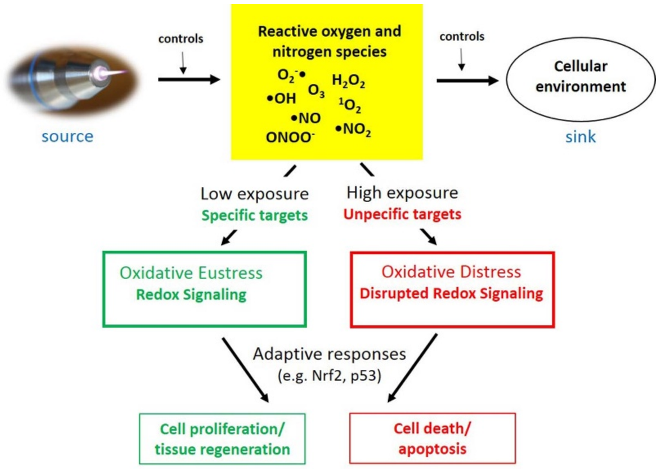

Figure 15. Plasma medicine as applied redox biology following the concept of oxidative eustress and distress. The intensity of reactive oxygen and nitrogen impact can be determined by plasma source characteristics, but also depends on cellular characteristics and the cellular environment. Reproduced with permission from [117]. © 2019 The Author(s).

Current and future challenges

The standardization of medical CAP devices has been started in IEC TC62D by identifying characteristics that are critical for safe usage: plasma gas temperature, ozone level, nitrogen oxide level, H_2O_2 level, UV level, electrical current, electrical leakage, electrical insulation, usage error, electromagnetic compatibility (EMC), electrostatic discharge potential and inspection of device prior to use. In general, dosing and control of plasma application in medical applications might be the most important outstanding challenge as already identified in the 2017 Plasma Roadmap [2]. In the last 5 years, more insight was gained into the dependence of RONS composition, plasma density and electron temperatures on target characteristics and plasma–target interactions [120]. A continuous real time *in situ* plasma monitoring with feedback control of device input could be the key for stable and constant plasma and treatment conditions. Following the increasing establishment of clinical CAP applications, plasma devices will have to be adapted to specific application fields with laparoscopic and endoscopic applications potentially the most challenging because of the specific environmental conditions [121].

As it was pointed out in the 2017 Plasma Roadmap [2], effects of CAP causing cancer cell death are accompanied by influences on immune cells leading to systemic tumor-specific immunity [122]. This has not only consequences with regard to possible systemic effects of local CAP application leading to so-called abscopal plasma effects. It could open up new strategies for CAP-based vaccination in oncology [123]. It is reported that orally administered plasma treated liquids (PTLs) are able to inhibit progressive tumor growth without reduction in body weight, although showing tumor size and weights reduction in the chemo-resistant lung cancer

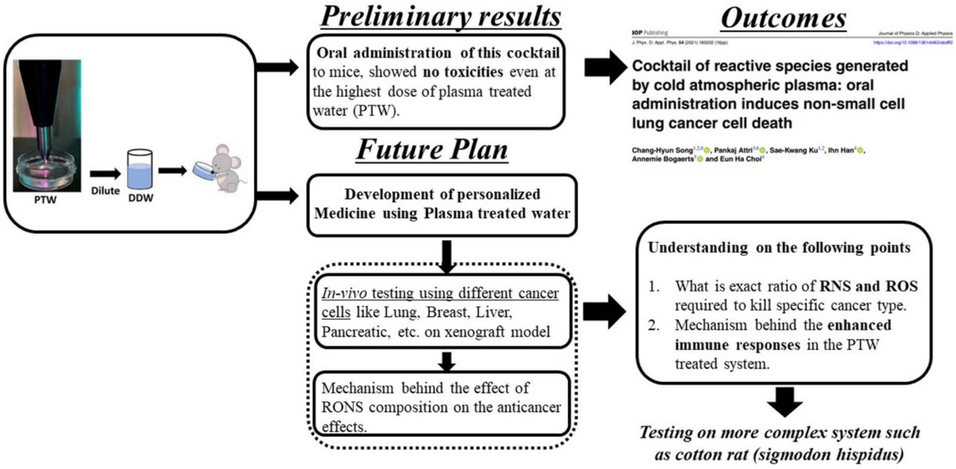

Figure 16. Cocktail of NAP reactive species for oral administration of cancer therapy. Reproduced from [124].

xenograft mice model [124]. To date, orally administrated PTL has been only tested for non-small cell lung cancer and using fixed concentrations of RONS like H_2O_2, NO_2^- and NO_3^-. Moving forward, we need to focus on assessing the impact of different RONS concentrations in PTL and study its effect on patient-derived xenograft mouse models for promising plasma cancer therapy (figure 16). Nonetheless, the potential of PTL as a possible novel and self-contained therapeutic principle has been shown with many promising applications including the treatment of disseminated abdominal tumors to be explored [125]. Our understanding of plasma–liquid interactions made an enormous progress in the last 5 years [2] (see also section 3), but it remains necessary to further substantiate the application conditions and the main challenge to overcome is the classification of PTL from a regulatory point of view.

Advances in science and technology to meet challenges

Future challenges include standardization of plasma sources and treatment doses for biological and medical applications since these are one of the most important topics in plasma medicine. This would be expected to guide and guarantee safety and effectiveness of CAP application to health and hygiene. The physical and technical challenges in plasma device adaptation and optimization are in the development of compact and miniaturized tools not only for plasma treatment but also for monitoring varying plasma and target characteristics during treatment. Based on both plasma and target monitoring the aim must be a more 'dynamic' adaptation of plasma parameters to actual (short-term) characteristics of the target considering specific therapeutic goals. Here, the dependence of specific biological effects on specific plasma characteristics have to be further investigated with specific regard to short-term variations of plasma parameters and its consequences for (long-term) biological effects. Nowadays, there are different modeling approaches available that are very useful to simulate direct interaction of plasma components with single biomolecules up to complex biological tissue models [126]. Combining these modeling approaches with laboratory experiments *in vitro* and—if possible—*in vivo* research will give much more insight into details of plasma interaction with biological systems. For effective data processing and device control, innovative methods of robotics, machine learning and artificial intelligence have to be made available for plasma medicine [127, 128]. To get closer toward a solution of the 'dose' challenge it has to be kept in mind that according to the actual stage of knowledge biological plasma effects are indeed mainly based on plasma-generated RONS but it is not clarified yet whether or to what extent single RONS are specifically responsible for distinct biological effects. It could be useful to establish whether biological effects could be correlated with a general redox potential hence depending not on individual RONS but on their reactivity. Here, current developments in redox sensors [129] might be helpful to detect plasma-caused oxidative stress *in situ* and correlate such data both with plasma parameters and resulting biological effects.

Concluding remarks

CAP application in medicine has developed from an idea, driven by plasma physicists, to an interdisciplinary research field with growing acceptance in the medical community. To fully understand the interrelationship between plasma and biological cells and tissues, preclinical and clinical trials should be conducted and evaluated. For this, standards as well as comprehensible test protocols should be established. As one of the next steps, international standardization of CAP sources for medical application with regard both to its technical parameters (beyond the general regulations for medical devices) and to its biological performance will be crucial for harmonization of research efforts and for a sound transfer of medical CAP technology to industry and, finally, to the patients. To expand the plasma medicine field more, the community must focus on nurturing and supporting the new generation of researchers and engineers related to plasma science.

10. Contribution of plasma to combat COVID-19

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Status

In late 2019, coronavirus disease 2019 (COVID-19), the pandemic caused by the severe acute respiratory syndrome coronavirus 2 (SARS-CoV-2), emerged as a new global health emergency. It has affected every country in the world, shutting down economies, and causing greater than 200 million infections and more than 4.3 million deaths [130]. The virus is transmitted between people through inhalation of virus-laden respiratory droplets. The clinical course of a person infected with SARS-CoV-2 is highly variable, ranging from asymptomatic infection to mild upper respiratory tract illnesses to respiratory failure and death [131]. Rapidly emerging genetic variants are also contributing to its ongoing high transmissibility, even causing breakthrough infections in the vaccinated, and keeping scientists, clinicians and governments on their toes in search of urgent solutions to combat this pandemic. The medical community is focusing its efforts on improving the safety and efficacy of vaccines and developing new therapeutics.

Investigations are also ongoing to identify novel methods to mitigate the virus in the environment to break the transmission cycle and thereby prevent infections. Since the discovery of the plasma-type ozone generator by Werner von Siemens in 1857, ozone has been used in many countries to purify and disinfect water supplies (see also section 12). In 1968, a prototype of a sterilizer for surgical instruments by RF plasma under low pressure using hydrogen peroxide was developed, which is now commonly used in medical practice [132] (see also section 9). With advancements in science and technology, plasma has shown efficacy in inactivating viruses and even prions, which are the cause of the dangerous mad cow disease (bovine spongiform encephalopathy) [133, 134]. Therefore, research that expands the use of LTP for the inactivation of SARS-CoV-2 is important for systematizing the effects of plasma on pathogenic microorganisms and furthering the academic development of the field of plasma biotechnology. It would also contribute toward elucidating the mechanism of action of LTP for other medical applications (section 9). Recently, the immunomodulatory effects of LTP have also been described, stimulating investigations for uses in immunotherapy of many diseases [123]. We believe LTP can play a vital role in both preventative and therapeutic strategies against COVID-19 because of its synergistic anti-microbial and immunomodulatory effects.

Current and future challenges

Viruses are essentially particles consisting of nucleic acids and proteins without cytoplasm or other structures. Most viruses have a capsid that surrounds the nucleic acid with (as in SARS-CoV-2) or without an outer envelope derived from the host cell membrane which is composed mainly of phospholipids. They use the host cellular machinery to replicate therefore are hard to treat.

The scientific community mobilized in response to SARS-CoV-2, publishing its genetic sequence in 4 months and developing vaccines within 12 months which have reduced hospitalizations and deaths; however, the pathogenesis of COVID and immune responses against this virus are still not fully understood. A huge logistical challenge for working with this virus is that it is a highly infectious, biosafety level 3 pathogen requiring specialized containment facilities to work with in the laboratory. This precludes investigations that test the efficacy of disinfection strategies against the free virus in aerosols. There are few animal models of this disease (with some limitations), further constraining disease progression and therapeutic efficacy studies. These challenges offer the LTP community exciting new opportunities to work toward novel approaches to combat this disease.

For LTP technology to be accepted as a viable solution for viral inactivation and as a therapeutic alternative to other, better accepted technologies, several questions must be resolved. Crucial among them is the issue of key effector(s) and their mechanism(s) of action. How do electrons, ions, radicals, and light generated by plasma affect viruses (direct exposure)? Are plasma-conditioned inorganic and organic solutions effective in inactivating viruses (indirect exposure)? To what extent is there a difference in response between capsid structures and envelope-free structures to plasma? Since LTP composition from different devices is vastly different, lack of this knowledge serves as a source of confusion among non-plasma communities. The secondary outcome of this ignorance is the difficulty in defining dose required for a specific effect, the common lingo for most biomedical devices. Furthermore, it impedes the identification of safe operating parameters necessary for approvals by regulatory agencies.

The unanswered questions offer new opportunities to apply LTP for inactivation of different viruses (figure 17).

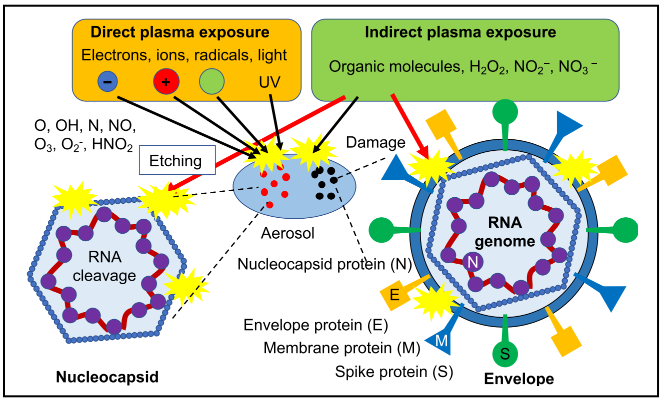

Figure 17. Approach for SARS-CoV-2 inactivation by LTP.

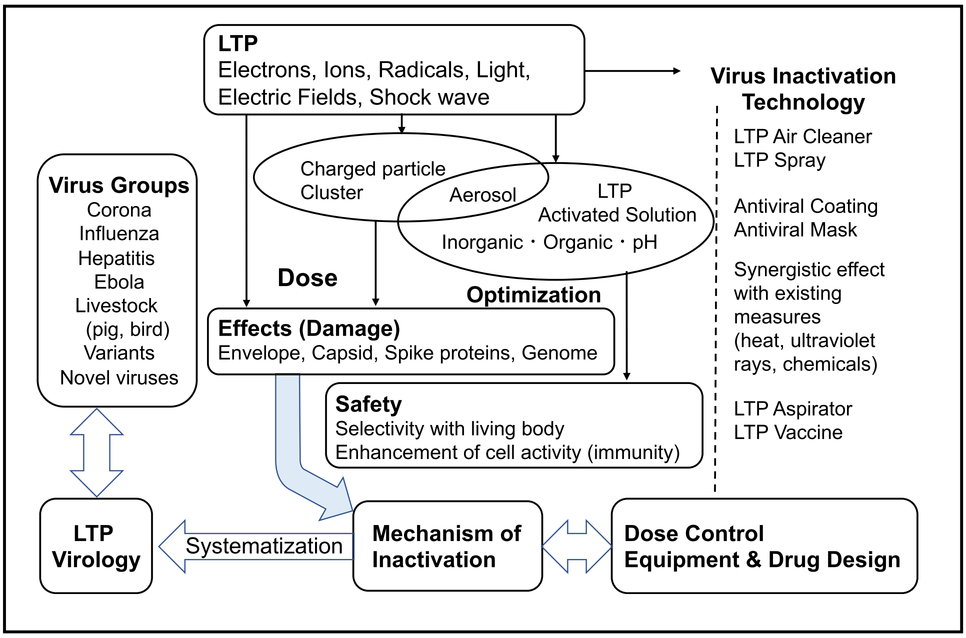

Figure 18. Use of LTP for mitigation of epidemics and pandemics by viruses and scientific areas for further exploration.

Advances in science and technology to meet challenges

A key mode of intervention for reducing the societal impact of SARS-CoV-2 infection remains epidemiological i.e. prevention of spread. Here, the path for incorporation of LTP technology into existing infrastructure is relatively easy. Inactivation of SARS-CoV-2 on surfaces was recently demonstrated by Chen *et al* [135]. While not tested on intact virus, Bisag *et al* show the susceptibility of naked SARS-CoV-2 RNA genome [136]. What is exciting is that the anti-viral properties of LTP in aerosols against the porcine reproductive and respiratory syndrome virus are already demonstrated [137], suggesting that rapid inactivation of other viruses in air is possible. Thus, integration of LTP into existing heating, ventilation and air-conditioning systems is conceivable. A few studies have suggested that genome degradation and protein modifications may be responsible for viral inactivation (reviewed in [138]). Better understanding of LTP effectors and their targets would allow for device improvements for environmental mitigation of the virus. Figure 18 shows the scheme of the LTP for virus pandemic prevention.

Conceptually, developments in LTP science would also facilitate its adoption into biological prophylactic and therapeutic strategies for COVID. Further understanding of how LTP alters SARS-CoV-2 specifically would allow explorations into enhanced antigenicity of the modified viral particles as a vaccine candidate. Better definition of the 'dose' required for direct anti-viral effects may permit device development for a safe therapeutic whereby virus in the upper respiratory tract may be targeted. As our knowledge of the disease and its resolution improves and the immunomodulatory effects of LTP against viruses are better understood, LTP application in patients may serve the dual purpose of reducing the viral burden, simultaneously stimulating protective immune responses—in essence serving as an autologous vaccine [138]. This would also address the continued challenge of mutational variants of SARS-CoV-2. For safe delivery of LTP effectors, of course, demonstration of short- and long-term safety would be a vital step. Hence, LTP could become the simplest form of personalized precision medicine against COVID. Eventually, as the systematized science of plasma–virus interactions develops, it is expected to revolutionize not only medicine but also the livestock industry, for the inactivation of SARS-CoV-2, the swine flu virus and bird flu viruses among them.

Concluding remarks

The COVID-19 pandemic has exposed numerous deficiencies in our knowledge of and ability to handle infections by novel pathogens. The LTP group has risen to the challenge and has presented unique solutions to many of the practical problems that populations are facing worldwide. Numerous laboratories started investigating the most effective use of LTP-chemical-free, rapid disinfection of masks and other fomites. Device development for disinfection of different environments and even for treatment of patients became another area of active development. Lessons learned from work in cancer are being explored for application in SARS-CoV-2 disease. The international LTP community also responded by increasing collaborative work among interdisciplinary investigators. Together, these efforts will contribute to improving the fundamental understanding of LTP and its interaction with biological molecules, cells and tissues that would translate into clinical applications in many diseases.

11. Plasma agriculture and innovative food cycles

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Status

Research on the application of plasma in agriculture emerged in the last two decades using LTPs operating at low pressure. While these low-pressure plasmas are still successfully used for the treatment of various types of seeds to increase germination [139–141], the majority of the applications nowadays rely on the atmospheric pressure plasmas [141–143]. Significant momentum was gained with the development of a large range of non-equilibrium atmospheric pressure discharge devices for applications in plasma medicine (section 9) [2, 117, 144]. The established important role of RONS in plasma medicine (section 9) [144] was transferred and forms the foundation of the new discipline of plasma agriculture [117]. To date, more than 2000 papers per year are being published in the field of plasma agriculture.

The field of plasma agriculture is highly multidisciplinary and complex including the use of plasmas to treat seeds (figure 19) to enhance germination, enable decontamination or coat seeds. In addition, plasmas enable plant and plant tissue treatments including biotechnology applications in the realm of plant originated pharmaceutical and cosmetic compounds or are being used to treat liquids leading the generation of plasma activated water (PAW) [145, 146] (section 3) which enables pathogen control and nitrogen fixation. Lately, research into utilizing plasmas for tackling foodborne bacteria and specific viruses is also gaining momentum for food preservation and decontamination [147, 148]. These activities are already extensive and every day new research is added.

The importance of the field of plasma agriculture continues to increase due to the increasing demand for food caused by population growth and further enhanced by reduced agricultural production due to climate change. In fact, to recover the food production reduction in a conventional way, the Food and Agriculture Organization predicts the requirement of an additional synthetic nitrogen fertilizer, whose synthesis leads to an increase of 1.6 billion tons CO_2 emission further increasing the impact on society. Plasma technology has the potential to be a green alternative and bring added value to the conventional agricultural processes by improving the sustainability of agriculture and reducing adverse effects on the environment.

Current and future challenges

Recently reported results in plasma treatments of seeds, plants, PAW production and food and packaging processing show great promise. Nonetheless, many experiments were (and continue to be) conducted with very different plasma systems, different treatment protocols and a wide range of processing conditions, making the comparison and consequently systematic progress in the field difficult. It has been shown that seeds of different plants might require a unique set of treatment parameters to be effective and that not the same plasma systems and operation conditions can be used for treatments of seeds, plant tissue, decontamination/activation of water and food processing. This leads to yet further challenge in atmospheric pressure plasma source design (section 1). The major challenge remains the development of scaled up energy efficient processing based on atmospheric pressure plasma technology (section 1). We can define several remaining scientific challenges that need to be addressed to enable progress in the field. The fundamental mechanisms responsible for the desired plasma-induced effects on seeds and plants remain elusive. Figure 20 shows an example of plasma-induced stress on plants and potential resulting genetic and epigenetic changes. Whether unique properties of different varieties of seeds/plants produce different responses to the same set of plasma treatment parameters remain to be determined. The next important step is to assess whether these similarities and differences in response to plasma parameters can be used to define standard procedures and protocols that can be broadly implemented in agriculture. At the same time, we need to identify economic and environmental benefits and drawbacks of the LTP technologies in comparison with established technologies such as chemical fertilizers and pesticides by detailed comparative studies. The theoretical limit of energy consumption of non-thermal plasma nitrogen fixation is less than half of energy efficiency of the Haber–Bosch process, whereas the realized NO_x production efficiency based on plasma-dissipated power is recently found to be comparable with that of the current the Haber–Bosch process [149, 150]. It also significantly reduces the CO_2 footprint of the process. Furthermore, the most important challenge for LTPs to penetrate the food industry is to meet the required standards for the quality and safety of plasma treated foods [148].

Advances in science and technology to meet challenges

The existing and future challenges in the field of plasma agriculture demand significant advances in fundamental research and technological development. The optimization of LTPs parameters used for direct plasma application or indirect through the application of PAW is important. The chemically active environment (gas or liquid) containing RONS interact with cell membranes, signaling pathways and mechanisms that lead to the plasma-induced effects aiming to speed up and increase plant growth and resulting in better yields, while protecting plants from bacteria, fungus and animal pests. LTP offers alterations of DNA methylation of seeds [151], which indicates that LTP can be developed as a novel method

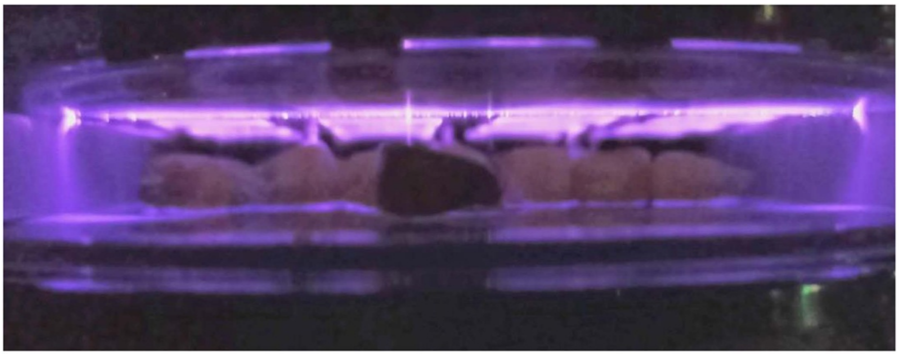
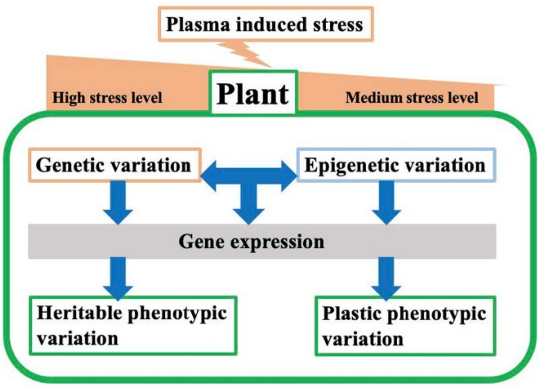


Figure 19. Atmospheric pressure DBD for corn seed treatment.

(a)



(b)

Figure 20. (a) 5 years old Plumeria from seed (left) without and (right) with plasma irradiation, and (b) Potential interaction between genetic and epigenetic variation in plants under plasma induced stress.

of epigenetic control. Therefore, in fundamental research the development of complex models and extensive diagnostics to characterize LTP systems will be a paramount in the determination of the LTP interactions with seeds, plants and food products (sections 17 and 18). Unlike in the case of plasma medicine (sections 9), where plasma sources do not need to be scaled up, we need to work on more suitable configurations and geometries of LTP sources together with the development of power supplies in order to meet technological demands at the scale of future markets. These prototypes will need procedures and protocols defined for the end user. The applications of LPTs in food and packaging processing require significant advances in the research of the quality and safety characteristics of plasma treated foods. It is important to identify in the food chain where plasma technology could have the largest potential for translation to the industrial scale. All this needs to be developed within the existing regulatory framework while delivering on energy consumption with food safety and quality in mind. Detailed comparisons of LTPs with competing technologies, both established and innovative processes, to assess plasma strengths and weaknesses are crucially important.

Concluding remarks

Plasma Agriculture is a developing research field with several important challenges that need to be addressed. These challenges encompass both scientific and technological aspects and require a concerted effort of the multidisciplinary research community. Process optimization and scale up remain a significant technological challenge. The scientific challenges include the determination of roles of plasma originated RONS in signaling pathways and mechanisms for better plant yield or protection from pathogens, especially in food processing where off target effects such as food oxidation is undesired. The nutritional value of plant food products obtained when LTPs were used before or during the growth process must be carefully studied. Therefore, the development of new plasma sources, their detailed characterization, complemented with detailed models will be a paramount in meeting the scientific and technological challenges. The LTP community, together with colleagues from agriculture, life sciences, food industry and regulatory agencies are needed to add LTP technology to the new standards of agricultural and food processing.

12. Plasma pollution control

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Status

Electrical discharge plasma, and LTP in particular, has been playing a critical role in pollution control for over a century with electrostatic precipitation (ESP) and ozone generation remaining the dominant environmental applications of LTPs. Electrostatic precipitators remove dust from flue gases at large volumetric flowrates and continue to do so with unparalleled efficiency. Recent modernization efforts of these devices that included implementation of many new methods significantly increased their efficiency for cleaning particulate matter in the sub-micron range [152]. The COVID-19 pandemic has prompted renewed interest in ESP for indoor air control, in particular collection and inactivation of harmful respiratory nanoparticles and biocontaminants such as bioaerosols and viruses [153] (see also section 10).

Ozone is an important oxidative species for the removal of pollutants and microorganisms in gaseous and aqueous streams. For most commercial applications ozone is generated in a dielectric barrier discharge without additional byproducts. The size of the ozone market has been steadily increasing which has focused the research on improving the efficiency and lowering the cost of ozone production [154]. Other established and emerging areas of gaseous pollution control include removal of ppm levels of acid gases (nitrogen oxides (NO_x), sulfur oxides (SO_x), etc), greenhouse gases such as perfluorocarbons, volatile organic compounds (toluene, TCA, TCE), ozone-depletion substances including freons and halons, toxic gases (mercury, dioxins, etc), and microorganisms. Highly efficient processes combine LTP with a catalyst, and those are driven by a large amount of research in the area of plasma catalysis which is currently experiencing an unprecedented growth and has become the mainstream plasma process for gaseous pollution control [155]. Since 1990, over a dozen pilot scale and full-scale plasma reactor systems have been demonstrated for flue gas cleaning, NO_x and SO_x abatement and deodorization of malodorous gases. Figure 21 shows two examples of industrial-scale plasma facilities for deodorization of odorant concentrations below 10 ppm.

A renewed interest into the application of LTPs for the treatment of drinking and wastewater to either remove toxic contaminants or inactivate microorganisms has resulted in the development of highly efficient bench- and pilot-scale plasma reactor systems [156]. Today, plasma-based water treatment is considered the leading technology for the destruction of toxic per- and polyfluoroalkyl substances in groundwater [11].

Figure 21. Large-scale application of plasma deodorization facilities in Japan: (a) pulsed plasma chemical process with 30 000 nm^3 h^{-1} processing capacity (b) surface plasma chemical process with 9500 nm^3 h^{-1} capacity. Reproduced with permission from Dr Hosokawa of Masuda Research Co.

Current and future challenges

Industries are facing increasingly stringent environmental regulations and demand improved technologies for effluent cleanup. Coincidentally, LTP research efforts for nearly all applications remain focused on improving the process efficiency and selectivity and lowering the cost of the treatment through power supply and plasma reactor optimization.

The future of ESP is highly dependent on the energy policy and the size of the ESP market is expected to decrease with transition from fossil fuels to green renewable resources. Increasing the efficiency of ozone generation in both small- and large-scale plasma reactors has been an ongoing research effort. Both models and experiments have been used to optimize the operation of dielectric barrier discharge (DBD) reactors for ozone production including the electrode geometry, dielectric properties, operating pressure, gas temperature, and power modulation [157, 158]. Ozone production efficiency is also strongly dependent on the purity of the starting O_2. While increasing the O_2 concentration in air generally increases O_3 production, for very small (lower ppm) levels of nitrogen in the feed gas and in ultra-pure O_2, the O_3 generation efficiency either significantly decreases or drops to zero giving rise to the 'ozone-zero' phenomenon [159].

Large-scale application of LTP for the treatment of gaseous contaminants remains limited by the density and the selectivity of plasma-generated radicals and the process efficiency. While some of these challenges can be overcome by combining the plasma with additional processes (e.g. presence of a catalyst), those add to the overall system complexity and require additional research. Many LTP reactors generate RONS in the 10^1–10^2 ppm level and these concentrations are sufficiently high for oxidizing similar concentration levels of pollutants in both air and water. The transition from laboratory to industrial scale is expected to be closely linked with this 'flux matching', which may be especially challenging for contaminant concentrations exceeding 10^2 ppm [160].

The plasma reactor development for water purification purposes has been and still is largely trial and error driven, due to the lack of knowledge regarding the key physicochemical processes and reactor design elements that control the contaminant removal. As a result, the most effective and efficient bench-scale reactors that are concurrently scalable largely remain unidentified.

Advances in science and technology to meet challenges

Further research directions targeted at overcoming the scientific challenges all necessitate interdisciplinary collaborations among plasma scientists, material scientists, chemists, and engineers, and closing of the gap between fundamental discoveries and engineering solutions. The competitive global market concurrently requires that any new standalone or integrated process, including the plasma, be better, faster and cheaper than any of the existing processes and also scalable.

The development of *in situ* or *operando* measurement techniques to trace the dynamic changes on solid surfaces and liquid interfaces where plasma is impinging will be critical for improving the process efficiency (see also sections 3, 18 and 19). Similar approaches are required to identify, quantify, and differentiate among different plasma agents responsible for various chemical transformations. While some advances have been made in the last decade and pertain mainly to the identification of long-lived species or products, elementary processes that occur on short time scales remain elusive. For gas–liquid applications, visualizing and quantifying the dynamic changes that take place in the bulk liquid will be important for plasma reactor design and scaleup. The final level of process understanding and optimization includes treatment of environmentally relevant streams, identification of the byproducts formed and, where applicable, determination of their toxicity.

The development of cheap, reliable and scalable power supply systems is crucial for nearly all plasma applications (see also section 1). The controlled RONS flux matching required to remove contaminants in gas and liquid phases could be largely achieved with a pulsed power supply capable of delivering narrow pulses (<50 ns) with a high repetition frequency (up to 50 kHz).

The progress in the design, optimization and scaleup of highly efficient plasma reactors could be greatly accelerated if the community collaborated more efficiently to achieve these common goals. To calibrate multiple concurrent research efforts in fundamental science, reactor design and scaleup, the community should agree on using and characterizing a reference plasma treatment system specific for a particular application. The outcomes of fundamental investigations performed on these systems would assist in determining the limitations and the advantages of the technology, its level of performance with respect to the existing technologies, and the key technical challenges that must be overcome before the process can be upscaled.

Concluding remarks

Results of bench-scale investigations confirm that LTP is a promising technology for a wide range of environmental applications. In fact, for some of those, electrical discharge plasma is the most effective and efficient solution available. Recent scaleup efforts for gas and liquid treatments are encouraging and are a testament that the field is progressing in the right direction. To position LTP at the forefront of environmental remediation, the technology cannot be simply as good as the existing processes but significantly better, faster and cheaper. Concurrently, the process must be scalable.

Plasma research is inherently multidisciplinary and taking the technology to the next level will involve contributions from a range of scientific and engineering disciplines and finding an effective way for the community to work together. Aside from the need for fundamental investigations which are likely identical for all LTP applications, development of highly specialized power supplies and the reactor scaling laws will be critical for the successful scaleup of the technology.

13. Electrification of chemical conversions

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Status

Electrification of the (petro)chemical industry is one of the greatest challenges of this century. Plasma technology is gaining increasing interest for this, because it is a turnkey process, hence suitable for combination with (fluctuating) renewable electricity. In the 2017 Plasma Roadmap, the focus was mainly on CO_2 splitting, and the role of vibrational excitation. In recent years, we obtained important insights that other aspects are equally important for performance improvement, addressed in this contribution below. Furthermore, the main focus is no longer only CO_2, but also on CH_4 and N_2 conversion [161–166]. CO_2 splitting leads to CO feedstock that can be combined with H_2 for Fischer–Tropsch synthesis of hydrocarbons or for other chemical feedstocks. CH_4 conversion is of great interest for both H_2 and olefin (mainly ethylene, C_2H_4) production, because nowadays H_2 is still mainly formed by steam methane reforming, causing a lot of CO_2 emission, and C_2H_4 production is also one of the major CO_2 emitters in industry. N_2 fixation is being studied for both NH_3 and NO_x production, as alternatives for the energy-intensive Haber–Bosch and Ostwald processes. While pioneering work took place in previous century in the Soviet Union [167], renewed interest in the last decade led to significant progress [161–166]. Many types of plasma reactors are being investigated, but most work is performed with DBDs, microwave (MW) and GA plasmas, ns-pulsed plasmas, APGDs and spark plasmas [161–166]. DBDs are characterized by reasonable conversion, but low energy efficiency. The latter is much better in the other plasma types, so-called warm plasmas (operating at several 1000 K). However, there might be advantages for DBD where direct integration with catalysts is more straightforward. In principle, the most energy-efficient conversion proceeds by vibrational excitation of the molecules [167], followed by vibrational ladder climbing up to the dissociation limit, but probably at the cost of conversion efficiency. However, in practice, the conversion proceeds mainly by electron impact dissociation in DBD, and by thermal chemistry in warm plasmas at atmospheric pressure, where it might be possible to obtain 70% conversion efficiency, if so-called super-ideal quenching might be obtained [167, 168]. Only at low pressures, there is significant vibrational overpopulation, i.e. vibrational-translational non-equilibrium.

Figure 22 summarizes the state-of-the-art for CO_2 splitting and N_2/O_2 conversion into NO_x, for various plasma types, in terms of conversion and energy efficiency [162, 166].

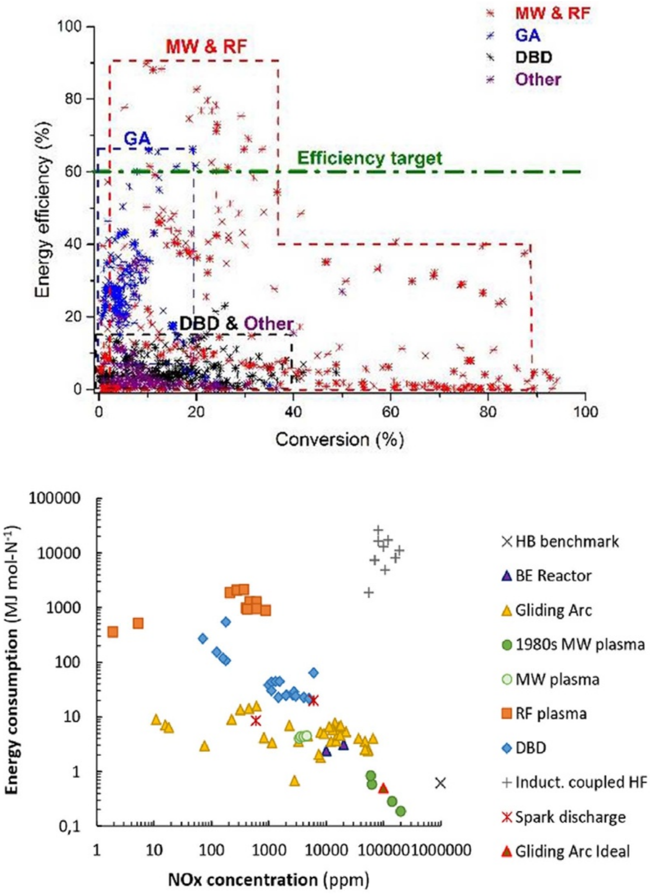

Figure 22. State-of-the-art for CO_2 and N_2/O_2 conversion for various type of plasmas. Reproduced from [162]. CC BY 3.0. Reproduced from [166]. CC BY 3.0.

Current and future challenges

Challenges are to further enhance the (a) conversion, (b) energy efficiency (which is defined by the conversion obtained at a certain energy input), and (c) product selectivity, to make plasma technology of practical interest for the chemical industry. In terms of improving energy and conversion efficiency, most efforts so far were devoted to exploiting the vibrational-translational non-equilibrium, albeit with limited success. Novel approaches to reach non-equilibrium, which might promote the vibrational stimulation route, involve pulsed plasma generation or rapid expansion of the plasma-treated gas to freeze the chemical composition. It has been established that the conversion and also energy efficiency are limited by the fraction of gas passing through the plasma in some reactors, and especially by recombination of the products (back-reactions) after the reactor due to the unfavorable temperature trajectory. As it became apparent that thermal processes are often dominant, the challenge is to further enhance the performance above the thermal equilibrium, e.g. by fast quenching and in parallel promote the radicals formed in the high temperature region (e.g. O and N atoms for the case of CO_2 and N_2/O_2) to react with unconverted gas, possibly further stimulated by internal excitation of the parent molecules [167, 168]. Hence, efforts are needed for reactor design improvements, with major focus on gas flow dynamics, to make sure that unreacted feed gas is treated by the (hot) plasma (filament) and products are quickly removed and/or cooled directly outside the plasma (or after the reactor) to avoid back-reactions.

Product selectivity is a challenge due to the high reactivity of plasma, producing a plethora of products, and separation would add a major cost. Combination with catalysts should provide this selectivity, but this is not yet so successful. Plasma catalysis is indeed very complicated and far from understood. Studies on simple reactions, such as NH_3 synthesis, have revealed novel insights, e.g. on the role of (vibrationally) excited N_2 and plasma-produced radicals, making other catalysts potentially more interesting than in thermal catalysis [169, 170], and also CO_2 hydrogenation to CH_3OH or CH_4 (methanation) have received attention [171]. However, when studying dry reforming of methane (DRM), the focus is still mainly on syngas production (CO/H_2), using similar catalysts as in thermal catalysis.

Advances in science and technology to meet challenges

Clearly more insight is needed to increase the performance of plasma chemical conversion processes in terms of conversion, energy efficiency and product selectivity, not only in the case of plasma catalysis, but also for plasma reactor design improvements. The complexity of using multiple input gases, leading to unwanted side reactions and worse process selectivity, might be circumvented by spatially separating the optimization of radical or internally excited molecule production from the desired product formation. In effect this can be realized in a two-chamber configuration connected by an expanding nozzle (facilitating the rapid quenching), or by a plasma-membrane configuration where the membrane selectively doses the other reactant gas [172] to let them react with a reactive surface which selectively removes one of the reactive products [173] or to use the plasma as an electrode in contact with a liquid surface [174]. The novel electrically stimulated gas conversion routes can be further improved in terms of selectivity by the use of catalysts to steer the desired products [174]. However, designing specific catalysts tailored to the plasma conditions for the selective (one-step) production of the desired products is a holy grail in plasma catalysis.

To guide the plasma reactor design and advance our understanding, detailed space- and time-resolved diagnostics (*in-situ* and *operando*, both for plasma phase and at catalyst surface) are required, as well as improved chemical kinetics and fluid dynamics modeling, cf figure 23. Since high temperatures, steep gradients and highly turbulent conditions in some of the reactors are present, direct numerical simulation

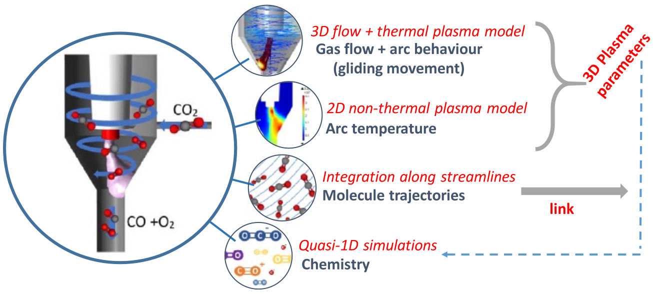

Figure 23. Multiscale aspects of reactor modeling for plasma-chemical conversion, here illustrated for CO_2 conversion in a GA plasma reactor.

of the plasma chemical flow, similar to the efforts in combustion science, need to be explored. Predictive and detailed modeling in this case needs accurate reaction rate constants, often for high temperature regimes and pressure dependences, and including the effects of internal excitation of the reagents (like vibrational modes). In addition, reaction set validation is crucial for predictive modeling. More discussion on reactor design, diagnostics and modeling can be found in sections 1, 17 and 18. If catalyst beds are used to steer selectivity and conversion efficiency, the interaction of excited species, ions and radicals with the catalysts need to be understood in detail (see section 19), for which also rate coefficients (or activation and reaction energies) are needed, as well as the effects of surface charges and local electromagnetic (EM) fields on the catalytic efficacy. Hence, detailed studies need to be executed, possibly exploiting novel catalytic effects.

Concluding remarks

The role of plasma (catalysis) in the electrification of chemical conversions will depend critically on whether the performance has benefits in terms of conversion, energy efficiency and product selectivity. The plasma should only be a reactor component in the total system for a chemical plant. Therefore, e.g. heat recovery of the hot gas streams might provide easy pathways to increase energy efficiencies.

So far, success stories are ozone production and to a lower extent plasma pyrolysis of methane to produce CO_2-neutral H_2. We expect also other processes can become competitive in terms of energy efficiency, with good heat recovery schemes, such as NO_x production from air, CO_2 conversion and DRM, in GA, MW and APGD plasmas. To have a successful entry, plasma should prove that it can provide the scale needed to replace processes with a high CO_2 footprint in the present chemical industry. Plasma-chemical conversion has obvious advantages compared with electrochemical conversion in terms of adapting to the intermittent nature of renewable energy and the possible smaller footprint, due to the higher power density. However, whether this will be the key determining factor remains to be seen.

14. Plasma propulsion (PP)

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Status

In the last decade, PP has taken the lead over chemical propulsion for in-space propulsion and has been used on many satellites and space probes. Currently, the research in PP is extremely active to address three very promising trends. Firstly, onboard electric power on large telecommunication satellites has increased to 25–30 kW, fostering the development of high-power thrusters for full propulsion tasks. Secondly, large plasma thrusters, either in single or clustered configurations, are also envisaged for the Lunar Gateway orbit station and Mars-transfer vehicles. Finally, low power (1–500 W) propulsion systems are needed for the exploding and disruptive market of small-to-nano satellites.

Many PP technologies exist, differing in main physical principles, suitable power range, or development status [1, 2]. The most advanced ones, already with a solid flight heritage since the 1960s, are the gridded ion thruster (GIT) and the Hall effect thruster (HET). GITs may have better performance figures than HETs, but they require more complex and expensive power processing and control subsystems. Thus, except for interplanetary probes, HETs tend to be cost-optimal and cope most of the in-space propulsion market.

Both GITs and HETs use electrodes to establish an energetic plasma discharge and rely on imperfect electrostatic and magnetic confinement of the plasma, thus suffering from material sputtering (limiting their lifetime) and large energy deposition at the walls (affecting their propulsive efficiency). In addition, both include an external hollow cathode to neutralize electrically the high-energy ion beam from the thruster, which adds complexity and criticality to the whole device [175].

As an alternative to GITs and HETs, electrodeless plasma thrusters (EPTs) are under investigation. An EPT is a novel version of electrothermal thrusters, where EM wave energy from an external 'antenna' is absorbed inside a plasma source and a magnetic nozzle guide and accelerates supersonically the plasma beam [176]. EM waves are also used in the operational RF ion thruster.

Finally, as the down-scaling of GIT and HET below 50 W is inefficient, a variety of alternative, simpler devices are being investigated for micropropulsion [177].

Current and future challenges

The main challenges on PP were already identified in the previous Plasma Roadmaps [1, 2] which can be summarized as follows: improvement of plasma-related performances, wider envelopes of operation (in power and specific impulse), reduction of manufacturing and operation costs, improvements on system complexity and compactness, and drastic reduction in development and certification of new thrusters.

Since the 1960s, extensive experimental and theoretical research has provided much insight in the physics of plasma thrusters. Still, their design and development rely on a semi-empirical approach, combined with very long and expensive flight-qualifying tests on endurance, lifetime, and multi-mode characterization. Physics-based predictive engineering models would greatly aid in reducing the costly testing in vacuum chambers and, furthermore, predicting the thruster behavior in space.

The main challenge of understanding the physics of plasma thrusters is the interplay of multiple nonlinear phenomena (ionization, heating, interaction with walls, magnetic confinement, low-divergence acceleration, instabilities, …) and the associated temporal and spatial scales [178]. In most devices, plasmas are weakly collisional and magnetized, which lead easily to the appearance of (a) non-Maxwellian features and (b) multiple instabilities, both phenomena affecting largely the plasma transport and the thruster performances, and both lacking of well-established models. This is the case of the leading HET, where research on mastering instabilities driving the anomalous electron cross-field transport is the main setback for reaching a predictive model [178].

Two-dimensional or 3D kinetic numerical models (generally based on PIC plus Monte Carlo methods) are necessary to tackle the whole set of coupled phenomena, but they are extremely computationally expensive and, to date, only apt for fundamental studies. Fluid approaches are more suitable for a global understanding of physical phenomena and for engineering purposes, but they require phenomenological closure laws. In between, hybrid approaches solving kinetically the heavy species are used nowadays as a computationally affordable compromise [179, 180].

EPTs present the additional challenges of understanding, first, plasma–wave interaction in a highly inhomogeneous environment, the resulting energy absorption, and the coupling with plasma transport processes, and second, the beam acceleration and detachment in the magnetic nozzle [178].

Advances in science and technology to meet challenges

The expensive xenon is becoming resource-critical for the large PP implementation, fostering the search of alternative propellants. A close and viable choice is krypton (figure 24). More challenging scientifically and technologically are iodine [181] or atmospheric gases [182], bearing more complex plasma chemistry and transport.

Micropropulsion is a fertile area for testing miniaturization and widening the niche of possible space applications [177]. Thruster supplies for mega-constellations require more compact designs and cost-effective manufacturing.

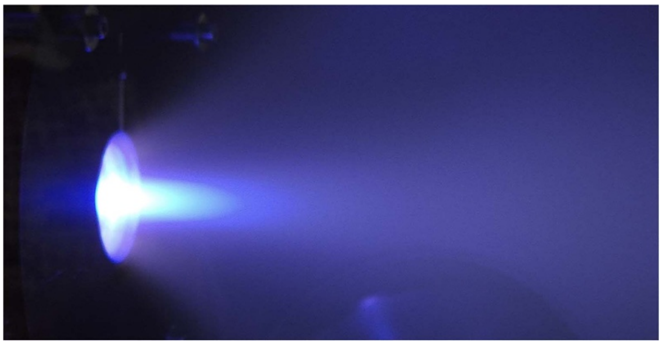

Figure 24. Helicon Thruster breadboard model at 450W, with Krypton (Courtesy of UC3M-SENER).

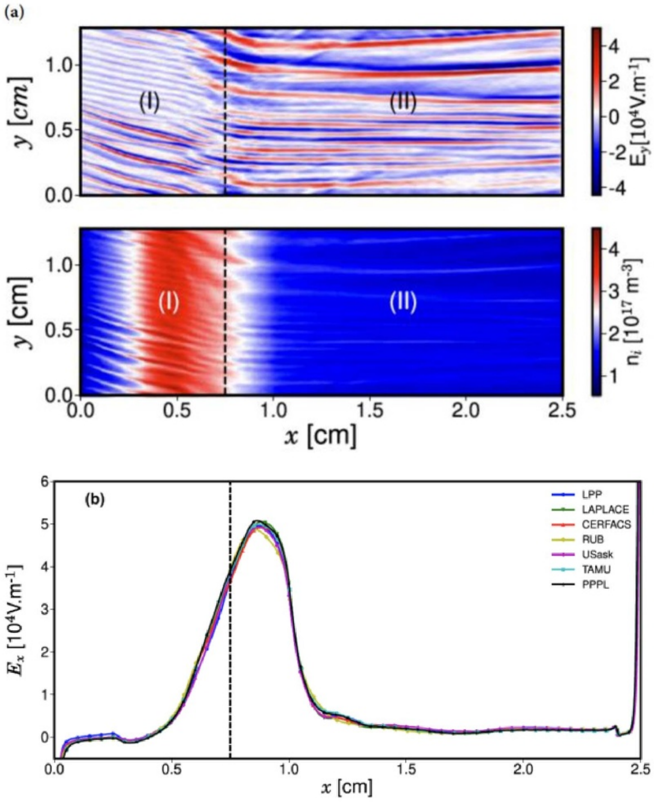

Figure 25. (a) Two-dimensional axial-azimuthal maps of the azimuthal electric field (top) and ion density (bottom) obtained with the PIC code developed at LPP at $t = 20$ μs. Dashed line corresponds to the position of maximum magnetic field that separates zone (I) and zone (II). Reproduced from [185]. (b) Azimuthally and time (between 16 and 20 μs) averaged axial profiles of axial electric field obtained by the different 2D PIC codes developed by the international groups who participated to the benchmark with 300 particles per cell at initialization. Reproduced from [185].

Magnetically shielded HET designs seem promising in improving plasma confinement and reducing erosion [178]. Nested HETs are being tested for high-power applications [2]. LaB_6 hollow cathodes, less sensitive to oxygen contamination, are being implemented [175]. Direct-drive technologies are meant to simplify the power processing and control subsystem of HETs [183].

Efforts in experiments and diagnostics (section 17) coupled to simulations and theories (section 18) have to be pursued to better understand plasmas in thrusters. Lastly, this has allowed to better characterize the high-frequency (>1 MHz) electron cyclotron drift instability [178, 184], a key mechanism in the anomalous electron transport in HETs.

Two international benchmarks of 2D PIC codes have been successfully carried out for $E \times B$ discharges [185, 186], providing confidence on the reproducibility of identified instabilities (figure 25). Similar initiatives, adding physical processes and more realistic thruster configurations, are needed along with the development of massively parallel 3D PIC codes.

Fluid and hybrid codes have to be benchmarked with kinetic ones. This includes the derivation from kinetic solutions, of fluid models for low-collisionality, in particular parametric laws for collisional terms, the pressure tensor, the heat flux and the interaction with walls.

The definitive goal is validating simulations with experiments, for phenomena such as anomalous transport, wall losses, and the whole spatial-temporal plasma response. This is the main bottleneck for achieving predictive engineering tools for plasma thrusters. At the same time obtaining accurate space-and-time-resolved quantitative measurements remain challenging. The development of non-intrusive diagnostics including emission spectroscopy [187], laser induced fluorescence and Thomson scattering [178] should be pursued. Finally, data-driven approaches [188] seem promising for thruster optimization (section 21).

For EPTs, advances on the consistent coupling of wave absorption and plasma transport phenomena are in progress [189]. This must be combined with an increased experimental effort to understand heating mechanisms better and assess the role of turbulent transport.

Concluding remarks

Electric propulsion is an extremely active research field which is considered by all space actors as a key and revolutionary technology for the new generations of commercial and scientific satellites and space probes. Currently, engineering developments are still constrained due to the lack of a complete understanding of the plasma physics of thrusters. In coming years, additional efforts on (PIC, fluid and hybrid) code development and benchmarking are needed, together with comparison with dedicated experiments, combining several diagnostics, to reach a better description of plasma properties. This will pave the way to the development of robust engineering models, which can help to improve existing thrusters and design new concepts.

15. Plasma assisted combustion and hypersonics

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Status

Plasma assisted ignition, combustion, and fuel reforming is a promising approach to expanding the efficient performance envelope of jet engines, gas turbines, and internal combustion engines. Over the last two decades, remarkable progress has been made in the fundamental and applied studies of these processes [190]. Measurements of the plasma parameters (electric field, electron density, and electron temperature (see also section 17)), as well as key parameters of the reacting mixtures (gas temperature; concentrations of excited species, atoms, and radicals; ignition delay time; and flame blow-off velocity [190]), have formed an extensive database. These data are complemented by kinetic modeling analyses [190, 191], which improved our understanding of the dominant kinetic mechanisms. Most of these measurements and modeling predictions have been made in premixed fuel-oxidizer flows and laminar diffusion flames. More applied studies, focused on the plasma-assisted ignition and flame holding in non-premixed turbulent flows and supersonic flows, highlighted the critical importance of fuel injection dynamics and fuel-air mixing, along with the kinetics of plasma chemical reactions.

Hypersonic flight is generally understood as flight within a planetary atmosphere at speed of Mach 5 and beyond. Plasma generation in high-enthalpy flows, such as behind strong shock waves during atmospheric entry, is well-known to result in radiative heating and communication blackouts. The effect of the plasma enveloping a hypersonic vehicle on the EM wave propagation, as well as means of control using external electric and magnetic fields, has been studied using kinetic modeling but experimental data remain rather scarce. Plasma-surface interactions (also addressed in section 19), such as catalytic recombination of atoms at the wall as well as ablation of thermal protection materials (see figure 26), are key drivers for the heatshield design ensuring the integrity of spacecraft. To date, coupled simulations of hypersonic flow, radiation, and material fields are not predictive yet, while testing in ground facilities can only partially reproduce flight conditions. Beside, blackout and heat management, additional hypersonic applications are the signature of cruise vehicles, re-entry and demise of man-made space debris, and meteors.

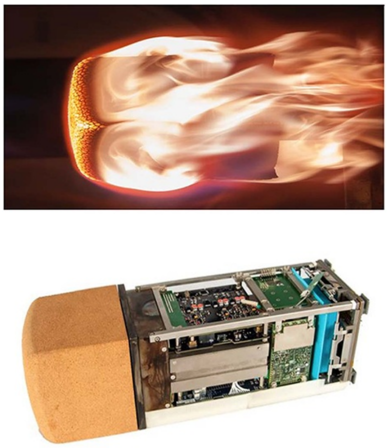

Figure 26. Top: ablative material testing in the plasmatron facility of the von Karman Institute For Fluid Dynamics (16 g s^{-1} air mass flow, 10 000 Pa pressure, 2.5 MW m^{-2} calorimeter heat flux) for the QARMAN ablative heatshield made of cork P50 from Amorim^{TM}. Bottom: QARMAN (34 × 10 × 10 cm^3) platform with INES payload including emission spectrometer and photodiode to measure simultaneously the shock layer radiation and ablative material recession.

Current and future challenges

Many challenges of plasma assisted combustion and hypersonics are related to reaction kinetics. The term aerothermochemistry was coined by von Kármán to denote the multidisciplinary field involving physical chemistry in addition to fluid mechanics and thermodynamics [192]. One of the challenges in the LTP assisted combustion kinetics is quantifying the boundary between (a) prevailing radical recombination/chain termination processes and (b) predominant chain propagation/chain branching reactions. In conventional combustion, this boundary is known to be controlled by temperature, pressure, and equivalence ratio. In the plasma, it is also affected by the concentrations of the primary radicals. Answering this question is critical for understanding the range of applicability and efficiency of plasma-assisted combustion technologies. This would require the time-resolved measurements of temperature and concentrations of low-temperature radicals, such as HO_2, at well characterized conditions, during and after the plasma excitation (see figure 27 [193]). Another challenge is the use of plasma excitation to obtain new insight into the kinetic mechanism of conventional ignition and fuel reforming. This may include targeting the highly reactive but elusive hydroperoxyalkyl radicals (QOOH), produced by the alkyl radical recombination with molecular oxygen ($R + O_2 \rightarrow$ QOOH) and isomerization of the alkylperoxy radical ($R + O_2 \rightarrow RO_2 \rightarrow$ QOOH), after the alkyl generation in the plasma (e.g. by H atom abstraction from the fuel, $RH + O \rightarrow R + OH$). The QOOH radical was detected by the photoionization mass spectrometry in the oxidation products of 1,3-cycloheptadiene (*c*-hpd) precursor [194], initiated by chlorine atoms, RH + Cl → R + HCl. The use of O atoms and R radicals generated in the plasma may well be an alternative approach to the study of QOOH kinetics, without the complications of chlorine chemistry.

High-fidelity databases of cross-sections and rate coefficients are being developed for hypersonic applications by means of theoretical chemistry calculations (see also section 20). In particular, rovibrational mechanisms for air chemistry dissociation and Zeldovich reactions need to be completed, by adding the associative ionization processes that

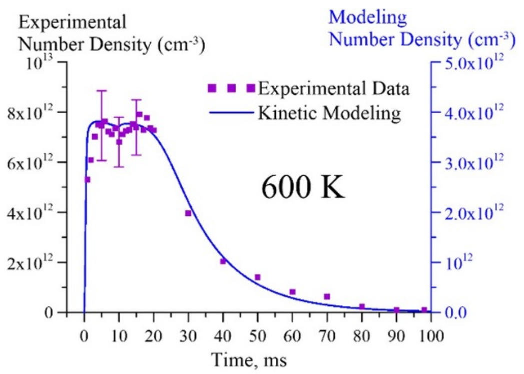

Figure 27. Measured HO_2 number density vs modeling predictions. The 2% H_2–2% O_2–Ar mixture at $T =$ 600 K, $P = 130$ Torr, excited by a ns pulse discharge burst. Sustained reactivity due to chain propagation reactions after the burst (at $t > 10$ ms) is apparent. Reproduced with permission from [193].

dominate the plasma generation behind hypersonic shocks [195] and may be strongly affected by reactions involving electronically excited metastable atoms. However, the rate coefficients of these reactions have never been measured over a wide temperature range. Detailed chemistry is also expected to play a role in the formation of the plasma sheath for disruptive technology applications, such as electron emission for transpiration cooling of hypersonic vehicles [196], for which suitable mechanisms need to be developed. Finally, aerothermochemistry challenges include the reduction of detailed mechanisms and their efficient coupling to flow solvers (see also section 18) for both the rarefied and continuum flow regimes to achieve predictive simulations [197].

Advances in science and technology to meet challenges

Spectroscopic detection of HO_2 and other peroxy radicals (RO_2), e.g. by near-IR absorption, is complicated by the spectral interference from H_2O_2 and hydrocarbon species [198]. This difficulty may be circumvented by making the measurements in a supersonic expansion flow at low temperature and pressure, downstream of the plasma flow reactor, which would simplify the isolation and identification of the absorption transitions. This approach has been used recently for cavity ring down spectroscopy (CRDS) measurements of metastable $N_2\left(A^3\Sigma_u^+\right)$ molecules in a Mach 5 flow of nitrogen [199]. An alternative diagnostic technique is Faraday Rotation Spectroscopy, which has been used for HO_2 measurements during dimethyl ether oxidation in a heated, atmospheric pressure, slow flow reactor [200]. Detection of QOOH radicals would require the efficient generation of large amounts of O atoms and alkyl radicals (R) in preheated high-pressure ns pulse discharge plasmas, due to the low yield of the QOOH formation reactions [194], as well as isolating the absorption transitions for the CRDS measurements at low pressure and temperature.

Experimental validation is also a crucial step in the development of hypersonic databases. For instance, measurements of the rate coefficients of associative ionization in collisions of metastable atoms necessitate meeting several technical challenges, (a) measurements of excited atoms, e.g. by tuneable diode laser absorption spectroscopy or atomic resonance absorption spectroscopy; and (b) measurements of the product molecular ions, N_2^+ (by cavity ring-down spectroscopy) and NO^+ (by quantum cascade laser absorption spectroscopy). Perhaps the biggest challenge of these measurements is isolating the associative ionization in atomic collisions from that in collisions of excited molecules, forming complex molecular ions such as N_4^+ and $(CO)_2^+$, and from the electron impact ionization. This would require generation of high concentrations of metastable atoms, e.g. by the rapid energy transfer from other long-lived metastables, such as $N_2\left(A^3\Sigma_u^+\right)$ or $Ar^*(3p^54s)$ in low-temperature, high-pressure ns pulse discharges [193], or by using thermal excitation in high-temperature, high-pressure inductively-coupled plasmas [201]. A difficulty encountered in the validation and calibration of models by means of experimental data is to consider jointly both experimental and model uncertainties. Bayesian inference is a powerful stochastic technique to extract model parameters, for instance allowing us to reduce the standard deviation on the catalytic efficiency of thermal protection materials [202]. Finally, efficient computational strategies can be used to compute detailed thermochemical effects coupled to flow solvers, such as using a Lagrangian diffusive reactor moving along the streamlines of a steady baseline flow simulation. This technique has been successfully used for the interpretation of meteor trails observations by accounting for aerothermal heating and ablation [203]. It could be applied to the infrared (IR) and radio-frequency signature of space debris, as well as dual applications.

Concluding remarks

Elucidating the kinetics of low-temperature radicals, over a range of temperatures, pressures, equivalence ratios, and primary radical concentrations (controlled by the discharge waveform and specific energy loading) would map the plasma induced chain propagation/branching region in the desired operation parameter space. Nonintrusive spectroscopic diagnostics of QOOH radicals would provide unique insight into the kinetics of plasma induced oxidation and ignition of complex hydrocarbon species. Both of these goals are critical for the development and wide engineering applications of plasma-assisted combustion and fuel reforming technologies. At this time, the use of plasma-assisted combustion technologies in mass-produced engines remains limited, in spite of recent progress in the development of MW discharge igniters [204].

Understanding and quantifying the role of aerothermochemistry, in particular excited atoms in the plasma generation in hypersonic flows, is essential for the reliable communication with atmospheric entry and cruise vehicles operating in the upper atmosphere, enabling their confident remote control and guidance. Simulating plasma–surface interactions is crucial to thermal management. Multiphysics solvers coupled to detailed chemistry mechanisms requires some validation using uncertainty quantification based on experimental data obtained in ground facilities and in flight.

16. Thermal plasma applications

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Status

Thermal plasma applications are part of our everyday life. Arc welding, plasma cutting, arcs in circuit breakers, light sources and thermal waste treatment are some of the more common applications. Some specialized applications include analytical instrumentation, metal AM [205], nano-particle production, specialized thermal chemistry, plasma spraying [206]. Arc welding, plasma cutting and plasma spraying were discussed in the 2017 Plasma Roadmap as three of the most important applications. Significant advances in the science relating to modeling of various aspects of these applications were made in the past 5 years, largely addressing the challenges identified [207]. In recent years, some thermal plasma applications play more and more important roles in the low-carbon and green growth development worldwide as was also mentioned in the 2017 Plasma Roadmap.

Seeking eco-friendly SF_6-alternative gases and studying their arc plasma properties and arc-extinguishing mechanism have been a hotspot [208]. Several gases like perfluoroketones $C_5F_{10}O$ and perfluoronitrile C_4F_7N have been introduced within the last several years. Based on these gases, the industry has developed gas insulated switchgears. In addition to the technical performances, their fundamental physicochemical properties have been studied [209–211]. Researchers have also tried to build relationships between these intrinsic properties of the gas and their arc-interruption capability [212].

Plasma gasification is a high temperature technology, specifically developed for efficient destruction of the organic content of waste, producing either a safe off gas (nitrogen, carbon dioxide and water) or syngas (nitrogen, carbon monoxide and hydrogen). Due to the high energy density and direct heat transfer of thermal plasma, lower power is needed to supply sufficient energy for the gasification, compared to conventional technologies. Plasma gasification technology is particularly well suited to be applied for destruction of dangerous, unsorted mixed waste streams such as nuclear-, medical-, chemical- and pharmaceutical waste [213].

The increased interest in metal AM (see also section 7) for complex designs places emphasis on spherical powder production. RF induction plasma spheroidization of metals, alloys and ceramics is receiving renewed attention in industry especially relating to *in situ* alloying.

Current and future challenges

Even for the up-to-date SF_6 substitutes, their arc-quenching properties are far from well understood. The large current interruption involves multiple decomposition and

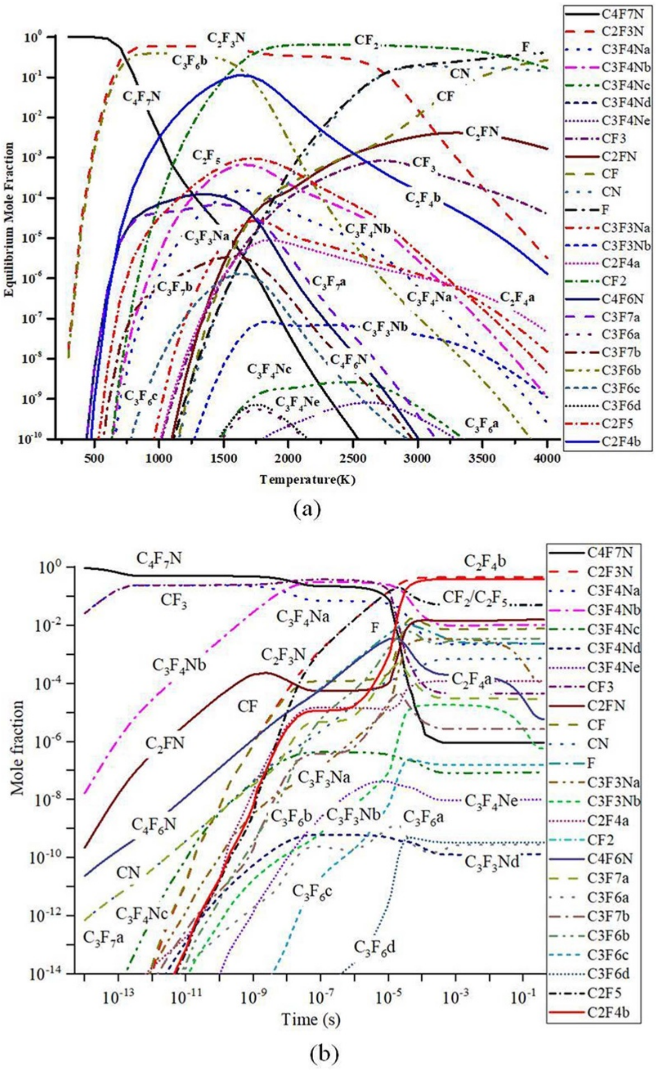

Figure 28. (a) LTE composition of pure C_4F_7N as a function of temperature at 0.1 MPa. (b) Chemical kinetic analysis of the time-dependence of the composition for a non-LCE state C_4F_7N arc plasma at 2000 K. (a) and (b) Reprinted from [209], with the permission of AIP Publishing.

recombination reactions under high pressure and high temperature, high efficiency energy dissipation under turbulences and controlled flows, as well as electron transport and dielectric strength recovery after current zero. Advanced arc quenching principles should be proposed to match the specific properties of these novel gases, which faces both numerical and experimental challenges.

Due to the irreversibility of the decomposition of the SF_6-alternative gases, MHD modeling linking chemical kinetics should be developed to better describe the arc behaviors, because most present arc models are based on the local thermodynamic equilibrium (LTE) and local chemical equilibrium (LCE) assumptions. Besides, the interaction between the arc and electrode or nozzle should be studied [214]. The above two challenges are also mentioned for other thermal plasma applications in the 2017 Roadmap and they remain to date. Moreover, the lack of electron-neutral

Figure 29. Containerized plasma waste to energy system.

scattering cross sections of these new gases and their decomposition species is another challenge. The calculation of the dielectric strength of residual hot gas after arc burning based on particle transport or Boltzmann analysis requires the complete and accurate sets of cross sections of all species present. The question of the accuracy, self-consistency and completeness of datasets for different LTP applications is detailed in section 20.

In the case of the plasma gasification, local supply of specialized parts, like the power supply, is preferable, but in many cases not possible. A high capital cost negatively influences the economical viability of plasma gasification waste treatment systems.

On the scientific side, computational fluid dynamics (CFD) modeling of the gasification reactor could aid the design, taking mass transfer, thermal and dynamic flow characteristic of the plasma tail flame into account.

CFD modeling of the RF induction plasma spheroidization system to predict the optimal particle size and density for a particular plasma power is the current challenge in the market. Especially for specialized metal alloys, and super alloys. Spherical Zr, ZrO_2, Al and U_xAl_y particle application in the nuclear industry is also riddled with its own challenges relating to part quality and alloy composition.

Advances in science and technology to meet challenges

Advanced arc modeling should pay more attention to chemical kinetics while calculating the plasma composition under non-LTE and non-LCE states [209]. A comparison of a C_4F_7N arc plasma composition under LTE and a non-LTE/LCE state is shown in figure 28. Besides, the dissociated species of SF_6-alternative gases should be precisely evaluated, to be able to determine an optimal formula of the gas mixture [215] and judge the interruption reliability. Advanced diagnostic tools continue to be of strong interest, including turbulent flow observation with laser probes, post-arc current measurement, and especially optical measurement techniques that do not rely on the LTE assumption. For example, Thomson scattering or wave-front sensors have been used to characterize the electron dynamics during arc decaying [216].

The search for new SF_6-alternatives continues. In analogy with the material genome approach [217], the discovery, screening, design and optimization of SF_6-alternatives could benefit from high-throughput computations. The multi-dimensional structure-activity relationships can be built by machine learning strategies. Meanwhile, high-throughput experiments such as pulsed Townsend experiments and self-consistent physical models based on the cross sections can provide the validations. Finally, unified methods with high test efficiency for both insulation and arc-extinguishing properties of SF_6-alternative gases should be established.

The establishment of small, medium and micro enterprises for plasma gasification application in developing countries is beneficial to the local economy. Therefore, starting a local supply chain for specialized plasma equipment, either through local development and manufacturing or a local agency, is a possible solution to the equipment supply limitation.

Optimization of RF induction reactor, the non-transfer arc plasma torch and gasification reactor equipment by CFD modeling, in collaboration with local and international Universities will be needed in order to meet the challenges. Government support in these programs is of utmost importance.

Some developing countries are also starting to implement the 'zero waste to landfill' protocol, forcing local industries to evaluate modern technologies. This opens the door for the market to accept a plasma waste destruction or waste to energy processes as a more efficient alternative to conventional processes. An example of such a system is presented in figure 29.

Concluding remarks

Tackling climate change is one of the greatest challenges of our generation. Some countries have solemnly promised to take direct and meaningful action to reduce carbon emissions and to develop SF_6-alternative gas-based power equipment is an important contribution to this task. An efficient way to search for new SF_6 substitutes and more accurate approaches to evaluate the insulation and arc-quenching properties need to be developed.

All the well-known and specialized plasma technologies (including plasma waste gasification and plasma waste to energy technologies) will address several key environmental requirements of the modern world. Although some challenges are experienced in the application of this technology in developing countries, the opportunities outweigh the challenges.

Spheroidization of ceramic, metal alloy and super alloy particles and determining their optimum operational parameters will have far reaching consequences in the nuclear, specialized materials and jewelry industries.

17. Plasma diagnostics

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Status

Plasma diagnostics remain one of the cornerstones of advances in LTP science. Over the last 20 years, major progress has been enabled by plasma technology in the development of devices for applications in materials synthesis and processing, environmental remediation, space propulsion, and human health. This progress has significantly broadened the range of plasma conditions and parameters to be tackled with diagnostics. While empirical approaches for the optimization of industrial plasma devices are commonplace, the inherently complex nature of plasma devices leads to a growing need for advanced diagnostics and modeling to enable the prediction of device behavior and ideal processing conditions. As illustrated in figure 30, further development and implementation of plasma diagnostics will continue to play a key role in advancing plasma science and its underpinning applications.

In the last few years, there are several areas in which diagnostics have contributed to device optimization and to an improved understanding of the fundamental physics of LTPs. Firstly, the increased availability and reduced costs associated with equipment such as femtosecond and picosecond lasers, high-efficiency detectors (permitting, for example, single photon detection), and narrow band filters [218], have provided opportunities to greatly enhance the capabilities of diagnostics, such as Thomson scattering and laser-induced fluorescence diagnostics. This has been achieved by increasing the detection sensitivity and expanding the implementation to a broader range of plasma conditions previously not readily accessible. A second area of progress (aided also by the availability of new radiation sources and detectors) has been the development of new diagnostics, such as THz-domain spectroscopy [219, 220] and E-FISH [221].

Researchers have also continued to implement established diagnostics to investigate previously unexplored plasma regimes. Examples include the use of coherent Rayleigh Brillouin scattering to probe nanoparticle formation in plasmas [222] and laser induced fluorescence to measure OH densities in discharges in bubbles in liquid [223]. In addition, the implementation of diagnostics well-established in other research areas provides new insights in plasma science, for example, using second harmonic generation (SHG) to probe the plasma–liquid interface and *in situ* Raman spectroscopy to measure plasma-produced liquid phase species during plasma–liquid interactions [224].

The improved coordination of numerical, theoretical and experimental efforts has accelerated advances in plasma science. A notable example can be found in the plasma propulsion community. The lack of understanding of anomalous electron

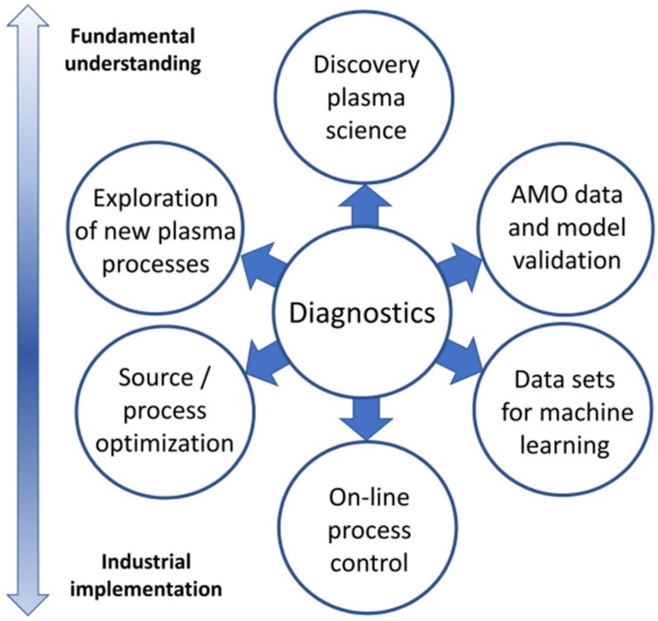

Figure 30. Schematic representation of the impact of diagnostics on the field of modern plasma science and engineering. The entire spectrum of current plasma studies, spanning fundamental laboratory investigations to industrial plasma-based processes, relies on diagnostics implementations (AMO = atomic, molecular and optical physics).

transport in magnetized plasmas such as Hall thrusters has motivated several research initiatives, including direct comparisons between numerical and experimental findings, and mutual code benchmarking by international teams [185]. Such an integrated approach has ensured that information from diagnostics has contributed to the revision of existing models and the emergence of new fundamental understanding around, for instance, plasma instabilities [225]. Such an integrated collaborative approach might also benefit other areas in LTPs.

Current and future challenges

Even with many avenues to progress now available, several challenges and research questions (some longstanding) remain to be fully addressed.

While advances in technology continue to expand the boundaries of current measurement capabilities, it is worth emphasizing the critical importance of building and maintaining core expertize in diagnostics in the research community. Plasma diagnostics are inherently *in situ* tools and often require a coordinated effort between reactor design and diagnostic implementation. The model of diagnostic facilities mainly enabling *ex situ* characterization, which has been proven to be highly successful in material science, is hence not readily transferable to the field of plasma science. Stability and reproducibility requirements on plasma sources for many diagnostics often exceed typical requirements for applications, with many additional source design challenges, as touched upon in section 1. In addition, most advanced diagnostics are not turnkey systems and require a high degree of training for their correct implementation and interpretation to maximize their intrinsic value. This requires investments, not only in equipment, but in the support and creation of dedicated research teams.

As mentioned earlier, significant value can be added to diagnostics when numerical, experimental and theoretical efforts are combined. One important challenge is the recognition and understanding of differences between the information accessed in experiments (often 3D systems) and that available from existing numerical and theoretical models (often 1D and 2D). In many instances where plasma diagnostics are used, parallel efforts in simulation are lacking; where they exist, assumptions and limitations of numerical models may at times be downplayed.

Practical challenges limit the applications of diagnostics, although significant progress has been achieved on some fronts. Measurements near the material boundaries in which plasmas are contained, while exceedingly important for many applications, remain challenging, as do investigations of sheaths (micron-scale in many magnetized LTPs and collisional high-pressure plasmas). This challenge has limited diagnostic insights on aspects such as plasma–wall interaction, which can dictate the operation of many devices. Obtaining diagnostics access within plasmas created in, or interfacing with, liquids remains challenging particularly when extending diagnostics into the liquid phase near the plasma–liquid interface. There is also a general need for highly temporally and spatially resolved diagnostics: this is particularly important given the presence of larger gradients in plasmas near boundaries, the fast dynamics of pulsed discharges, and the presence of non-uniformities and self-organization in many devices [226]. The sheer range of technological applications of LTPs makes diagnostic implementations which permit *in situ* measurement in industrial devices of high value and could narrow the gap between laboratory and practical source implementations. In particular, *in situ* surface diagnostics are largely unexplored and are of major importance for advancing our understanding of plasma–surface interactions as described elsewhere in this roadmap (section 19).

Advances in science and technology to meet challenges

Despite the complexity of the challenges associated with the exploitation of plasma diagnostics, several factors suggest that they will play a sustained, and even amplified, role in research in LTPs. Plasma diagnostics already play an indispensable role in all areas of modern plasma science: the investigation of new physics, the validation of existing and new models for plasma behavior, and the development and optimization of plasma-based applications throughout industry.

With the emergence of more diverse and advanced simulation techniques (such as sparse grid approaches [227] and 3D PIC codes), there is a renewed opportunity to challenge existing and new models with diagnostics measurements, to a degree previously impossible. New simulation approaches should offer the chance to model atmospheric and low-pressure plasma discharges, within shorter time frames and to a higher degree of fidelity. Coupled with diagnostics information, this would represent a leap forward in building predictive capabilities for plasma devices.

As mentioned earlier, advancements in detector and laser technologies also contribute to the diversity of available diagnostics. As an illustration, even in plasmas of very low densities (10^{16} m^{-3}), advancements such as the availability low-noise complementary metal-oxide-semiconductor (CMOS) detectors used for Thomson scattering place within reach the measurement of electron velocity distribution functions even in the most challenging cases where deviations from Maxwellian behavior have so far proven difficult to measure. Technological advancements, even when not necessarily leading to the creation of entirely new diagnostics, can revolutionize the implementation of existing tools for a broader range of plasma conditions.

The development of new approaches to data handling which have been exploited in other research domains provides new opportunities for progress in how diagnostics are used. Exciting new studies in laser plasma physics and fusion research [228] show how insights into the underlying physics of source operation can be gained using large data sets; LTPs could benefit from seeking inspiration from these areas of research. In LTPs, the array of available diagnostics, upgraded diagnostics approaches, and emergent diagnostics, may all now be used to constitute these data sets. In support of this idea, the standardization of sources for diagnostics observations would not only speed up ongoing investigations and simulation development, but would also promote collaboration between national and international teams. Such efforts, using devices such as the Gaseous Electronics Conference cell [229], applied to the study of plasma processing science, and the COST Reference Microplasma Jet [230], developed to study plasma–bio interactions, have proven to be valuable in developing a clearer understanding of underlying plasma processes in the past. The development of standardized devices for fundamental studies, is also under consideration in other communities [178]. While such devices are often designed to facilitate diagnostics and simulation investigations, their architectures are typically constructed to achieve operation conditions directly relevant to specific applications.

Concluding remarks

Plasma diagnostics remain at the forefront of efforts to understand the physics of LTP devices. The value of such diagnostics is enhanced by recent progress: in related technologies (detectors, laser sources for non-invasive measurement), in modeling approaches (multidimensional codes), and in data exploitation (machine learning). In the coming years, there will be a need for focused community efforts to take advantage of such progress. The development and maintenance of specific expertize around plasma diagnostics is an important priority; this will not only enable the emergence of new diagnostics ideas but will also ensure that outputs from diagnostics studies can contribute more effectively to advances in plasma science.

18. Theory, modeling and simulations

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Status

Theory, modeling and simulations complement experimental investigations of LTP sources, providing access to quantities that are difficult or impossible to determine experimentally and allowing their knowledge-based optimization. Computational techniques have been applied in LTP science from at least the early 1960s and their importance has been increasing ever since. The most recent decadal study [231] states 'computational modeling capabilities are critically important in advancing LTP science and technologies'. A large fraction of this work is carried out using standard tools, which existed in recognizable form by at least the early 1990s. These tools include solvers for the Boltzmann equation in various formulations, chemical kinetics models ('global models'), 'fluid' models based on moments of the Boltzmann equation (including hybrid models which combine fluid and kinetic elements), and fully kinetic models such as Monte Carlo methods and PIC (PIC/MCC) simulations. There has been considerable evolution in the way these techniques are applied, in response to both changes in the application focus and improvements in computational methods. For instance, increasing emphasis on atmospheric pressure discharges has motivated the introduction of local mesh refinement schemes in fluid and hybrid models, and the increasing availability of high-performance computing (HPC) resources has allowed kinetic simulations to greatly increase in ambition. A variety of other models are commonly linked to these plasma models, treating interactions with solids, liquids, and even biological systems, reflecting the broadening of the field of applications of LTPs in, e.g. material processing, agriculture, and medicine. So, in spite of the stability of the basic techniques used, there has been steady progress in the scope and power of computer simulation of LTPs, and this progress continues. These powerful and evolving techniques have allowed simulation work to play an important and sometimes central role in the remarkable scientific progress that LTP physics has achieved over the last several decades. Besides numerical studies, theory is still a major source of understanding physical effects in plasma sources. In particular, significant achievements were obtained during the past years in various fields, like transport phenomena [184, 232] physics of plasma sheaths [233–235] and of plasma–solid interface [236].

Current and future challenges

The field faces challenges of several kinds. Some problems appear not accessible with present techniques, e.g. transport in some magnetized plasmas requires 3D kinetic treatment. Such challenges seem likely to be met by expanding the capabilities of the tools mentioned above. Other challenges may require far reaching methodological changes. Reference [231] remarks 'predictive computational modeling capabilities are critically important' and 'models are required that are fully fundamentally physics based, but also have the robustness to be used for design and optimization of devices'. These goals call for a simulation approach with more rigor than is usually seen in studies of LTPs. Experience in other fields, such as CFD, suggest that quantitative prediction is difficult without the formal approach usually called 'verification and validation' or 'V&V' [237]. This approach, however, can greatly increase the cost and complexity of a computational study. Since the traditional approach has proved highly productive, careful navigation is needed between the rapid progress permitted by less formal approaches, and the predictive power promised via the machinery of V&V.

Increasing computer power can broaden the range of challenges that can be addressed, for example by increasing the number of spatial dimensions, extending of the parameter space (uncovering effects under extreme values of operation parameters [238], see figure 31), and/or executing computations based on models with increased complexity. In recent decades, increased computer power has become available mainly by adding various kinds of parallelism, such as vectorisation and multiple execution threads. This is broadly true for both conventional processors (CPUs) and graphical processing units (GPUs). Using these facilities effectively is not at all straightforward and requires a large commitment to specialized software design and implementation. Moreover, the target moves, as computer architecture changes on a timescale often shorter than the lifetime of a particular code (which is often decades). Consequently, developing a code that fully exploits the opportunities offered by modern HPC while satisfying the requirements imposed by formal V&V procedures is extremely difficult, and this difficulty is especially acute for a field like LTP physics which is characterized by rather small research groups with limited resources.

Advances in science and technology to meet challenges

So far, most codes developed in the LTP community are CPU based and the diversity of plasma conditions studied has limited collaborative code developments. The transition of these codes to GPU platforms will not be straightforward and could be aided by joint efforts of several research groups [239]. The development of open-source codes could allow the LTP community both to carry out multiscale and multiphysics simulations that are out of reach now and to become more visible among the leading scientific communities using HPC.

In recent years, PIC/MCC models, initially developed for low-pressure plasmas, have been used for a wider range of plasma conditions, e.g. for atmospheric pressure where previously only fluid models were used. This overlap of both

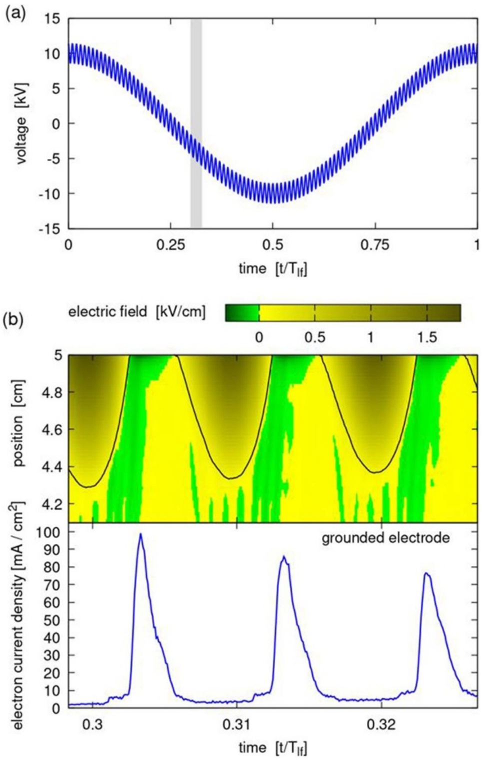

Figure 31. GPU-based PIC/MCC simulation results from [238] focusing on the charged particle dynamics in capacitively coupled plasmas operated at etching conditions: at a very low pressure and very high voltage. Identical electrode surface materials (SiO_2) are assumed at both sides of the plane-parallel discharge arrangement with a gap of $L = 5$ cm, the argon gas pressure is 1 Pa. (a) Excitation voltage waveform with 400 kHz low-frequency (lf) amplitude of 10 kV and 40 MHz high-frequency (hf) amplitude of 1400 V. The gray shaded time interval is shown magnified in the lower panels. (b) Current density of the electrons reaching the grounded electrode (situated at the position of 5 cm) as a function of time for three selected hf periods as a consequence of the spatio-temporal dynamics of the electric field (the black line indicates the position of the sheath edge). High peaks of the electron current appear at times of strong electric field reversals (shown by green color) created upon the extremely fast decay of the sheath. Such high flux of the electrons has a potential to compensate the positive charge deposited within the trenches during etching processes. Reproduced from [238].

approaches paves the way for the derivation from kinetic solutions of high-order fluid models and their closure terms for example for low-collisionality plasmas or for the modeling of non-local effects. A key point is also related to the use of dedicated numerical schemes for fluid equations. Recent efforts to derive new numerical schemes based on state-of-the-art numerical analysis have to be pursued [240].

Code verification and validation are two crucial issues. Recently, 2D benchmarks have been carried out on atmospheric pressure ionization fronts [241] and instabilities in $E \times B$ discharges [185]. This effort has to be pursued with the definition of benchmarks that allow to verify both different technical aspects of codes and provide confidence and a better understanding of the plasma physics simulated. Code validation by a rigorous comparison of simulation results with experimental results is a key challenge. Plasma simulation codes could be more systematically extended to include modules simulating different plasma diagnostics [242] to help better define the quantities used for code validation. To address these challenges, a regular workshop dedicated to V&V for simulations of LTPs could be very helpful for the community.

Finally, it is also important to underline the need for accurate input data (cross sections, rate coefficients, surface coefficients, etc), see section 20. Efforts to develop a database as LXCAT with standardized input data, accompanied with papers [243] and sessions in conferences have to be pursued.

Concluding remarks

Computational studies should be based on solid physical models and input data and it should be kept in mind that only the code verification can ensure that the numerical results follow exactly the underlying model. Code-to-code benchmarking can also enhance the credibility of results. At the same time, rigorous comparison of experimental results with simulation data paves the way towards the validation of discharge models. One should note, however, that some discharge characteristics can be determined experimentally with relatively large uncertainty and their computation is also based on models and input data with limited accuracy. This is indeed a difficulty in the experimental benchmarking of computational modeling. Sensitivity analysis could help quantifying the uncertainties of the computational results originating from the errors in the input data (cross sections, rate coefficients, surface coefficients, etc). Such an analysis is, however, a very demanding task especially over a wide domain of operation parameters. Finally, it is noted that robust plasma models may eventually help to determine missing fundamental data.

19. Diagnostics and modeling of plasma–surface interactions

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Status

Plasma is usually produced in bounded volumes, and in many cases is designed for interactions with surfaces, which can be dielectrics, metals, polymers, or even biological matter. The surface material interacts with the ions, radicals, excited neutral species and photons produced in the plasma, which can be utilized for growth, etching, or modification of surfaces or surface reactions in plasma catalysis. Many similarities exist between processes underpinning surface modification in material processing where the plasma is mostly at low pressures and those used for high-pressure plasmas in the context of plasma-catalysis and biomedical applications. Optimization of plasma materials processing relies heavily on trial-and-error experimentation. Often, the observed trends are reactor specific, rarely providing any insight into the microscopic mechanisms. Therefore, *in situ* plasma and surface diagnostics are required to establish mechanistic relations between fundamental plasma parameters and the processes that occur on surfaces. Ions, electrons, neutrals, and radiation from the plasma lead to modification in the surface composition, bonding, and structure due to chemical reactions, physical sputtering, ion-induced heating, secondary electron emission, and surface charging.

Multiple diagnostic tools exist for measuring fundamental plasma parameters (see section 17) including the electron density, and electron and ion energy distribution functions and absolute densities of neutral species. The determination of the surface composition and bonding in contact with a plasma poses challenges since most surface spectroscopic tools are not compatible with a plasma environment. While the plasma-exposed surfaces can be characterized *ex situ* using techniques such as photoelectron spectroscopy, the surface bonding and structure can change once removed from the plasma environment even with *in vacuo* transfer. In that respect, *in situ* attenuated total reflection Fourier transform IR (FTIR) spectroscopy, SFG and ellipsometry are more robust techniques for surface analysis in a plasma environment (see figure 32) [244]. In recent years, DRIFTS, diffuse reflectance infra-red Fourier transform spectroscopy has been applied to study changes in surface coverages of catalysts during plasma-catalysis *in situ*. In addition, some efforts on *in situ* detection in plasma-bio-interactions have been reported using electron-spin-resonance and matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy. Nonetheless, these *in situ* techniques remain the exception rather than the rule to date and most if not, all are not surface specific.

Even if all relevant internal plasma parameters along with the surface composition and structure could be measured and identified, the reaction pathways and reaction energetics of the radicals, excited neutral species and ions in the plasma with the surface must be visualized through either fluid, kinetic or hybrid models of the plasma discharge [30, 245, 246]. The coupling between plasma and surfaces in plasma models is often done through the introduction of phenomenological parameters such as sticking coefficients and secondary electron emission coefficients which are often poorly known (and mostly for species in their ground states) and sometimes even used as fitting parameters to match modeling results with experimental data [30]. While models of deposition and etching are relatively common, the introduction of surface reactions in plasma-catalysis only occurred recently. There has been an increasing amount of efforts on MD simulations to study fundamental interactions of plasma-produced reactive species on surfaces which has also been recently extended to biomolecules. Finally, whenever feasible, the energetics of reaction pathways of radicals with surfaces predicted by MD simulations should be validated with electronic structure calculations [247, 248].

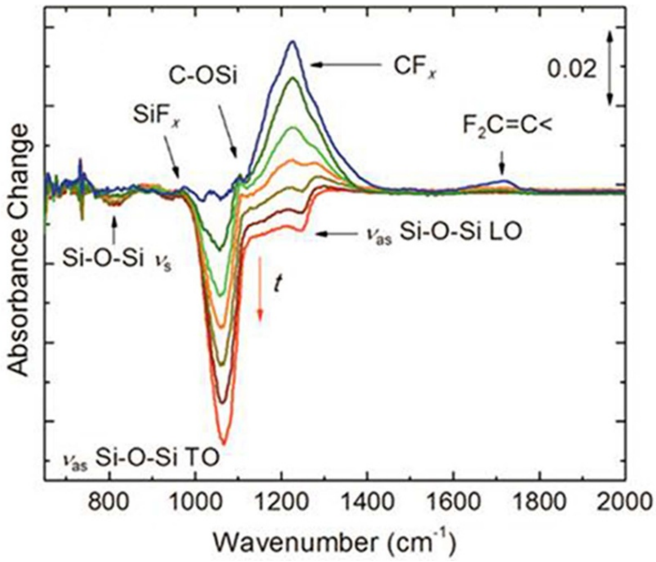

Figure 32. IR absorbance change obtained from *in situ* ATR–FTIR (attenuated total reflectance FTIR) spectroscopy during one complete plasma ALE cycle. Spectrum in blue corresponds to CF_x deposited onto SiO_2 from a C_4F_8/Ar plasma. The remaining 6 spectra correspond to 10 s increments (dark green to red) of Ar plasma exposure. The reference spectrum for all spectra was recorded prior to the CF_x deposition half-cycle. Reprinted with permission from [244]. Copyright (2017) American Chemical Society.

Current and future challenges

PALD and ALE processes are increasingly being adopted in semiconductor manufacturing (see also section 5) [249]. Development of *in situ* surface diagnostic tools to identify the sidewall surface composition versus the planar areas during deposition on and etching of high AR structures will be

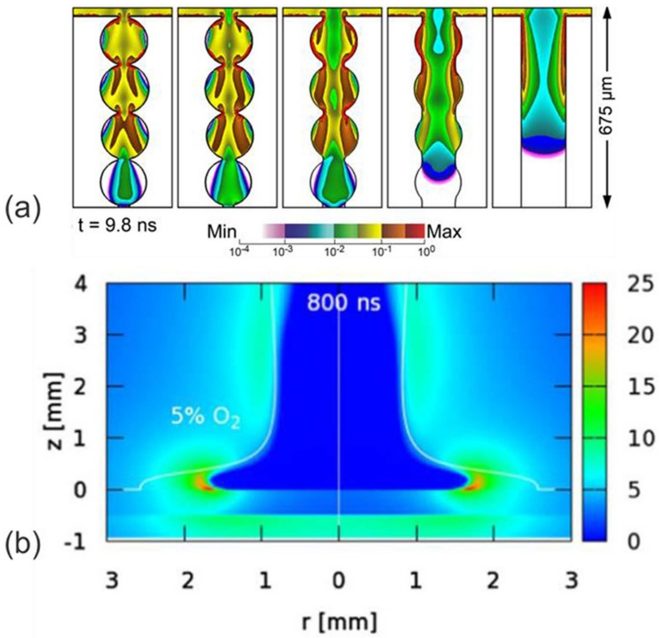

Figure 33. (a) Electron density in pore-chains with varying pore-opening sizes (left to right) of 37, 50, 75, 112, and 150 μm. Plasma formation becomes surface-discharge dominated as the openings become larger. Reprinted from [255], with the permission of AIP Publishing. (b) Electric field (kV cm^{-1}) produced by a plasma jet during its spreading on the target surface. Reproduced from [253].

invaluable. The diagnostics and modeling of plasma–surface interactions will have to also be extended to new materials in semiconductor processing, catalysis, and biomedicine. One such area is the introduction of extreme UV lithography in semiconductor device manufacturing to replace traditional 193 nm UV lithography for pattern transfer where new resist materials will be incorporated including transition metal element-based resists [250]. In plasma-assisted catalysis [251] and in plasma medicine [144], the interaction with the catalytic surfaces or the biological surfaces, respectively, of charged species, radicals and excited neutral species needs to be better understood [144, 251].

One challenge for modeling of plasma surface interactions is the treatment of topographically nonuniform surfaces. For example, in the treatment of biological surfaces by atmospheric pressure plasma, the surface may have convex, concave or sloping topography with deep cracks. Plasma can propagate in a conformal manner along such nonplanar and rough surfaces, penetrate into deep cracks and trenches with high AR (see figure 33(a)). Atmospheric pressure plasma can generate high electric fields (figure 33(b)). These fields also determine the distributions of ion energies arriving to surfaces and the dynamics of surface charging. In plasma medicine they are important for the evaluation of cell electroporation, electrostatic rupture of cell membranes, and many other processes. The fluid or hybrid plasma simulations at atmospheric pressure should go further and evaluate the electric fields at different elevations over the surface and either confirm or correct the experimental measurements [252, 253].

Yet another important challenge is related to the problem of coupling of bulk plasma parameters and their effect on the surface [30, 254]. Furthermore, the properties of the surfaces such as oxidation or coverage by an adsorbate can also have an impact on the plasma. More detailed descriptions might require coupled plasma–solid models and simulations as discussed in a recent review [30].

Advances in science and technology to meet challenges

The recent development of *in situ* plasma and surface diagnostic tools should play a key role in coming years to better understand plasma–surface interactions for applications ranging from material processing to plasma catalysis. However, most of these techniques remain difficult to implement in industrial plasma processing tools and the development and implementation of additional complementary techniques might be extremely valuable. To advance emerging applications of plasmas such as plasma medicine, *in situ* surface spectroscopic tools compatible with biological surfaces [144] should be combined with plasma diagnostics and modeling to obtain mechanistic understanding of the plasma–surface interactions. This fundamental experimental knowledge of plasma interactions with surfaces will then have to be incorporated into multiscale computational models to enable model development of industrial-scale processes.

Some promising steps towards the development of integrated models coupling the processes in the bulk plasma and at the plasma–surface interface have been taken recently ([30] and references therein). Four main approaches have been identified: kinetic Monte Carlo and MD (that are able to treat complex processes on large scales), quantum kinetic methods based on the quantum Boltzmann equation (which give access to a more accurate treatment of surface processes using simplifying models for the solid), *ab initio* simulations of surface process based on DFT and time-dependent DFT. The fourth method is using non-equilibrium Green functions which can treat correlation effects in the material and at the interface. Still, these four methods indicate only the main directions to follow in order to create a comprehensive picture of individual reactions of neutral species with well-defined surfaces. While efforts to address plasma-specific species in such models is emerging, it remains a challenge particular for excited species.

Concluding remarks

The improvement and development of the diagnostics capable of measuring surface properties during plasma exposure remains of significant importance. Development of integrated models and codes including the coupling of plasma simulations with surface modeling will help supplementing experiments especially when it is difficult to measure the relevant quantities at surfaces. The knowledge gained through these activities can be combined with development and optimization of new plasma sources and processes for a broad range of applications.

20. Atomic, molecular and transport data

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Status

LTPs are at the basis of key-enabling technologies (e.g. material synthesis and processing and energy and environment), they have been used in biological and medical applications, and they are essential to pave the way to Space exploration. Modeling studies and experimental analyses are extremely sensitive to the quality of data describing the complex physical-chemistry processes sustaining the plasma and enabling its reactivity [2]. Hence, assessing these data is essential from both fundamental and applied perspectives, to identify dynamic paths of operation and to provide effective control on the plasma properties. The roadmap to meet these challenges involves combined experimental and simulation efforts, where reliable data are key to interpret outcomes and define next steps.

The LTP community revealed a grown maturity in the process of curating (i.e. collecting, categorizing, archiving and distributing) dynamical data relevant to the kinetic modeling of LTPs (see section 18), moving from the cold gas approximation to the state-to-state approach, in the perspective of deepening the knowledge on elementary processes involving both electron and heavy species collisions. Examples of these efforts are demonstrated by the design and implementation of several web-access databases for the displaying, downloading and comparing of data, e.g. the LXCat open-access project [243] mainly collecting electron-scattering cross sections relevant for modeling LTPs, validated with swarm data analysis or obtained from quantum calculations; Quantemol-DB [256], mainly intended for the macroscopic collisional-radiative modeling of plasmas, recommending complete chemistries for specific systems of technological interest; Phys4EntryDB [257] including state-resolved dynamical information for elementary processes relevant to the kinetic modeling of planetary-atmosphere entry conditions. It is worth citing also e-science infrastructures developed for easy access to research data and information, e.g. the virtual atomic and molecular data center [258] and INPTDAT The Data Platform for Plasma Technology [259], endorsing the findability, accessibility, interoperability and re-use (FAIR) of data for the LTP community.

Current and future challenges

The need of datasets for complex molecular and radical species; the scarce information on data for interactions with surfaces; and the lack of reliable data for benchmarking of cross sections and rate constants remain some of the major challenges in the field [2]. In most cases experimental data were obtained decades ago and are not easily accessible on databases, where recent data essentially rely on theoretical results. Figure 34 outlines our view of the workflow from the collection of the data needed to their distribution in the community.

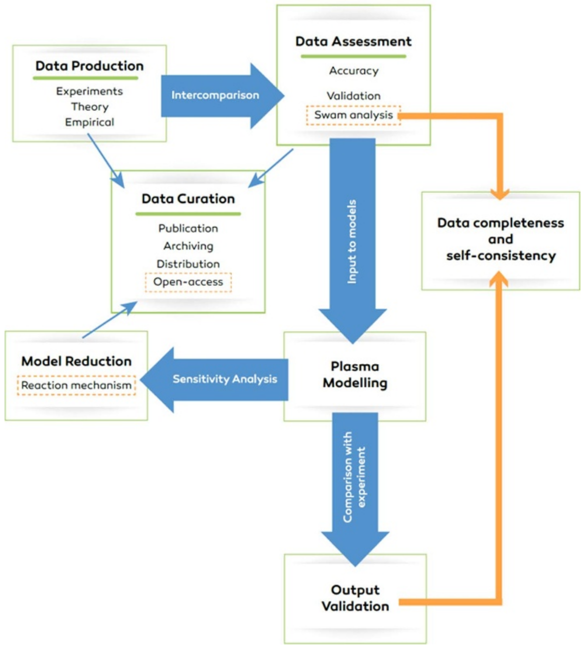

Figure 34. Data workflow: from collection to distribution in the community.

Assessing the accuracy of the data and the self-consistency and completeness of datasets, by comparing experimental results with theoretical calculations and simulations, are some of the most outstanding challenges to face. In the last decade, significant advancements have been done in AMO, with the calculation of accurate and state-specific electron-scattering cross sections [260], while polyatomic molecules and excited states are still the object of intense investigation. Modern quantum-chemistry approaches, assisted by HPC, allow obtaining high-quality electron-scattering data, where the complexity of the dynamics can be untangled by using information obtained with new experimental techniques able to follow transient species [261].

Dataset completeness is key to reliably accounting for the global transfer of momentum and energy in the plasma but should also intertwine with the detailed description of the plasma chemistry, including all relevant processes in a state-to-state approach that resolves the different internal degrees of freedom of the chemical species [259]. The correct inclusion of excited species brings additional complexity to the solution of kinetic schemes, requiring following the collisional dynamics on excited potential-energy surfaces, often non-adiabatically coupled to the ground state, to evaluate changes in the activation-energy barriers.

Future activities should focus on excited states as reactivity enhancers, e.g. the vibrational activation of CO_2 and NH_3 [155, 262], or the excited oxygen species in plasma-assisted combustion [263] (see section 15) and biomedical/agriculture applications [264] (see sections 9 and 11). Some of

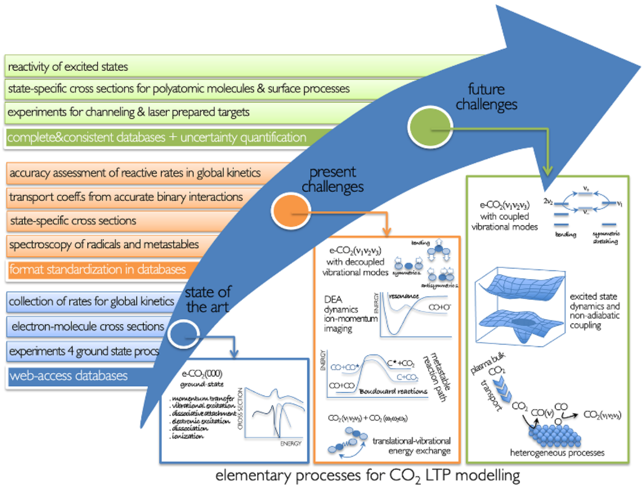

Figure 35. Conceptual scheme of expected progress in data for molecular plasmas, illustrated through the CO_2 LTP modeling.

these applications depend strongly on the transport of plasma species and their subsequent heterogeneous interaction with the boundaries. However, there is still a soft commitment in detailing and/or agreeing on the models and the data adopted in transport processes (especially in multicomponent scenarios and in the presence of negative ions), and in the plasma–surface interactions (especially when a reactive chemistry is activated).

Advances in science and technology to meet challenges

Improving the quality of data requires synergistic interactions between modelers and experimentalists. Dedicated experiments and/or advanced theoretical models can contribute to significantly improve the accuracy and the completeness of datasets: validating state-specific excitation cross sections; characterizing the vibrational excitation of polyatomic molecules; characterizing the channeling in dissociation dynamics; exploiting (surface-hopping) MD techniques to enlighten the role of non-adiabatic coupling; including multipotential approaches for collision integrals and estimating the role of anisotropy in accurate potential surfaces for binary interactions in transport models; consolidating the description of diffusion processes at various gas pressures and plasma electronegativities; obtaining particular data to describe surface mechanisms; assigning uncertainties to data. Figure 35 depicts the progress line envisaged in data for molecular plasmas.

There is increasing awareness about the importance of sensitivity analysis in the assessment of LTP-related data (see [265] and references within), but this analysis is not yet being systematically adopted in the efforts of model validation. Future challenges will probably include the use of machine learning algorithms to ease the computational burden related with sensitivity analysis and the reduction of kinetic schemes (also within real-geometry CFD codes), aiming for the definition of 'reaction mechanisms': sets of reactions and rate coefficients validated against benchmark experiments.

The open-access to data raises additional questions about the need and the choice of a format to standardize their archiving, search and distribution, facilitating the comparison and interchange, also between codes and particularly for complex species and models. So far, the LTP community has not decided the route to follow, and a more systematic discussion about the topic has started only recently [266]. The need for plasma-specific archival systems is not obvious, considering the very different requirements (both in the volume and the complexity of data) claimed by different users, and the existing platforms and codes already available that contributed to disseminate specific data formats. The challenges ahead are in finding the proper balance between methodological prescriptions and concrete steps to facilitate data distribution. The solution might require addressing not only the topic of data format, but also the development of associated tools for data processing.

Concluding remarks

The progress in obtaining, assessing, and curating AMO data is a key step for the reliable modeling of LTPs, and the time has come for a leapfrog towards the detailed description of the collisional dynamics, allowing to identify reaction mechanisms and, ultimately, to control the plasma. The outlined strategy, from the investigation of theoretical/experimental elementary processes to the recommendation of chemical models, will need the joint effort of the quantum chemistry and the plasma modeling communities.

Overcoming the challenges previously identified can be seriously undermined if a consequent level of funding is not targeted to the deployment of these community efforts. The current public policies worldwide that support the dissemination of data in open-access format often overlook the *a priori* need for obtaining the data, for example using quantum calculations and especially via complex expensive measurements. The calling for this awareness by the funding agencies is also part of our responsibility as a community.

21. Data-driven plasma science and technology

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Status

In the standard methodology of natural science, one understands nature first by observing it, second by forming a hypothesis to explain it, and then by testing the hypothesis to confirm that nothing is inconsistent with the observations. We typically use 'theory' to form a hypothesis and use 'experiments' to test the hypothesis. Modern technologies have allowed 'numerical simulation' to embody a theory in the form that can be easily compared with experimental observations (i.e. theory $\rightarrow$ experiments). Similarly what modern technologies allow to help one form a hypothesis based on the observations (i.e. experiments $\rightarrow$ theory) may be called 'data science' or 'data-driven science' [267].

Data science has been a subdiscipline of statistics and information science for many decades but recently attracted much attention in our society as a basis for paradigm-shifting technologies of handling a large amount of data. This is because the computational power has increased to the extent that those technologies significantly affect our daily lives, including commerce, politics, and culture. In 2011, then US President Barack Obama initiated a national project called the 'Materials Genome Initiative (MGI)', where material data were generated and strategically utilized to design new materials with a minimum number of experimental trials [268]. The success of this project has inspired new approaches in many other scientific disciplines, including plasma science. Existing but not fully exploited data or a large amount of data generated strategically may give us hints on the underlying physical mechanisms of extremely complex systems and allow us to study unchartered territories of science and technology systematically.

Compared with data science application to materials science (which is often called 'materials informatics (MI)') [269], where most data are static, data in plasma science are often dynamic (i.e. time-dependent). Because LTPs are used to process materials, we may want to predict how to make a material with given properties (which may be called 'process informatics'), rather than just to predict what properties a given material would have. In this sense, data science application to plasma science ('plasma informatics') may be far more complex than MI.

Current and future challenges

In plasma science, most studies using data-science-based techniques seem to fall into, at least, one of the following four categories; (a) real-time control of systems, (b) data analyses to extract desired information, (c) prediction of behaviors of complex systems, and (d) simplification of extensive numerical simulations. For example, as to the first category above, Mesbah *et al* [84, section 6] proposed a learning-based control of atmospheric-pressure plasmas. Park *et al* [270] explored techniques of virtual metrology (VM, i.e. inference of physical quantities based on available indirect information) for plasma processing systems. Techniques used in VM can offer complementary approaches to the development of new diagnostics discussed in section 17. For the second category, a study by Stokes *et al* [271] on the derivation of collision cross-section data may be a good example of raising productivity of data analyses. Automating the data analysis process can make the development of databases discussed in section 20 far more efficient. For the third category, a method to predict sputtering yields was discussed by Kino *et al* [272], using a regression model of existing experimental data [273]. The sputtering yields predicted by Gaussian process regression are now available on a website [274] and an example of a predicted sputtering yield is given in figure 36. These techniques may be applied to more complex systems of plasma–surface interactions discussed in sections 3, 5, 6 and 19. For the fourth category above, surrogate models, i.e. models that can reproduce the results of far more complex numerical calculations, for sputtering properties of various materials have been proposed

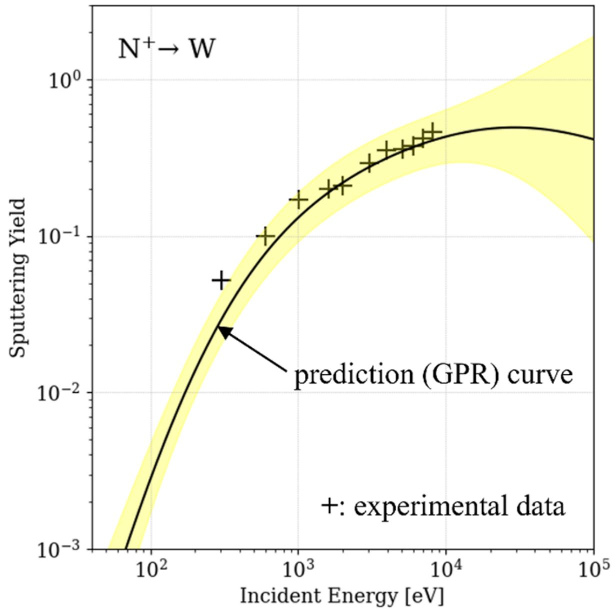

Figure 36. An example of the predicted sputtering yield (solid curve) of tungsten (W) irradiated by atomic nitrogen ions (N^+) as a function of incident ion energy. The angle of incidence is normal to the W surface. The experimental data given in [272] are also plotted. The shaded region represents the uncertainty of the prediction, which is based on GRP of all yield data given in [272]. The uncertainty is large for ion energies larger then 10^4 eV because there are not many experimental data in this energy range, whereas it is small even below 100 eV because yield data for other materials similar to W and/or incident ions similar to N^+ exist in this energy range. (Courtesy of Dr K Ikuse.)

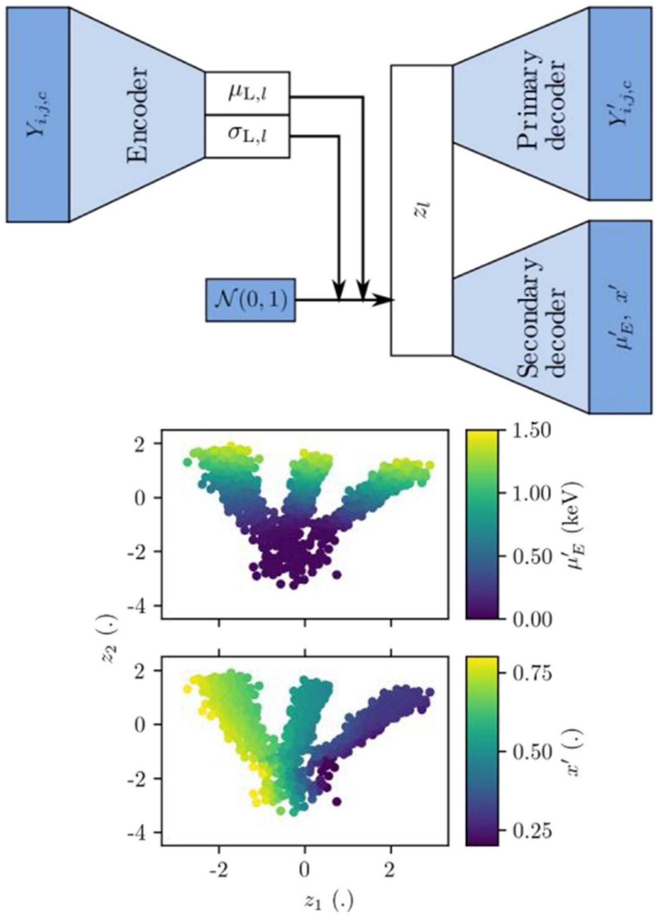

Figure 37. An example of a data-driven sputtering surrogate model. Above: variational autoencoder artificial neural network which reduces a high-dimensional physical parameter space (i.e. sputtered energy distributions) to a low-dimensional latent parameter space z. While the encoder and the primary decoder facilitate the dimensionality reduction, the secondary decoder ensures compliance of relevant physical conditions (i.e. projectile energy, material composition). Below: reduced parameter space for argon ions sputtering a titanium–aluminum compound of varying material composition x. Colors indicate the interpretation of the secondary decoder (i.e. mean projectile energy, material composition). Reproduced with the permission of the American Vacuum Society, from [276], accepted for publication in the *Journal of Vacuum Science and Technology* B.

by Krüger *et al* [275] and Gergs *et al* [276]. Figure 37 shows how such a model was formed with a variational autoencoder artificial neural network. Surrogate models of various plasmas have also been presented in, e.g. [277–279]. These examples are, of course, not meant to be exhaustive. Surrogate models of dynamical (i.e. time-dependent) simulations, as discussed in section 18, may be used to simulate and possibly control the system in real time.

The studies mentioned above typically processed a large amount of data, either existing ones or data the authors generated. However, in general, a shortage of data is a challenge in this field. We shall elaborate on this in the following subsection.

Advances in science and technology to meet challenges

A shortage of data, especially experimental data, may have resulted from a soft—if not the lack of—commitment to curate and use them systematically, as discussed in section 20. In MGI/MI, there have been concerted efforts to generate a large amount of data via high-throughput screening [280]. By searching or generating data systematically, one can generate not only a large amount of data but data that cover a large parameter space of the system. Bayesian optimization, one of the well-known techniques in data science, can be used for the design of experiments, which typically allows an efficient search of relevant data in a wide parameter space. The availability of large data sets with well-categorized metadata may be a challenge in plasma science. The diversity of plasma sources and applications may substantially limit the transferability of data. A community-wide effort to archive research data in plasma science and technology—possibly through interdisciplinary research data platforms such as INPTDAT [259, section 20]—should alleviate the problem of data shortage. Standardized metadata and availability of data following the findable, accessible, interoperable, reusable (FAIR) principles is an essential aspect that may facilitate comparable and collaborative scientific advances [281].

A shortage of experimental data may also be mitigated using complementary data obtained from numerical simulations. For example, the study of [271] used simulation data to supplement the available experimental data. The more fundamental advances that should occur in this field are to apply the constraints imposed by the laws of physics to data analyses. For example, physical constraints may be softly enforced during the regression of data by means of regularization or strictly enforced by structural embeddings. Such techniques are called physics-informed machine learning, e.g. as reviewed by Karniadakis *et al* [99, section 7]. Explanatory reasoning and inference of the underlying laws of physics from experimental or simulated data are the subjects of extensive study in the context of explainable artificial intelligence.

Concluding remarks

The application of data-science-based techniques to plasma science and technology offers novel pathways to a better understanding of the physical mechanisms of extremely complex plasma systems. For such approaches to be successful, the availability of data through various databases is a necessary condition, as discussed in section 20. Furthermore, the data quality and the systematic distribution of data in a given parameter space are important factors to be considered. So far various data-science-based techniques have been applied to characterize or understand complex systems related to plasmas and plasma-material interactions. It is generally believed that embedding physical constraints in data analysis and making the predictions by machine learning more explainable will further strengthen the data-driven analyses of plasma science and technology. How to achieve this is still a subject of ongoing studies.

Data availability statement

No new data were created or analyzed in this study.

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