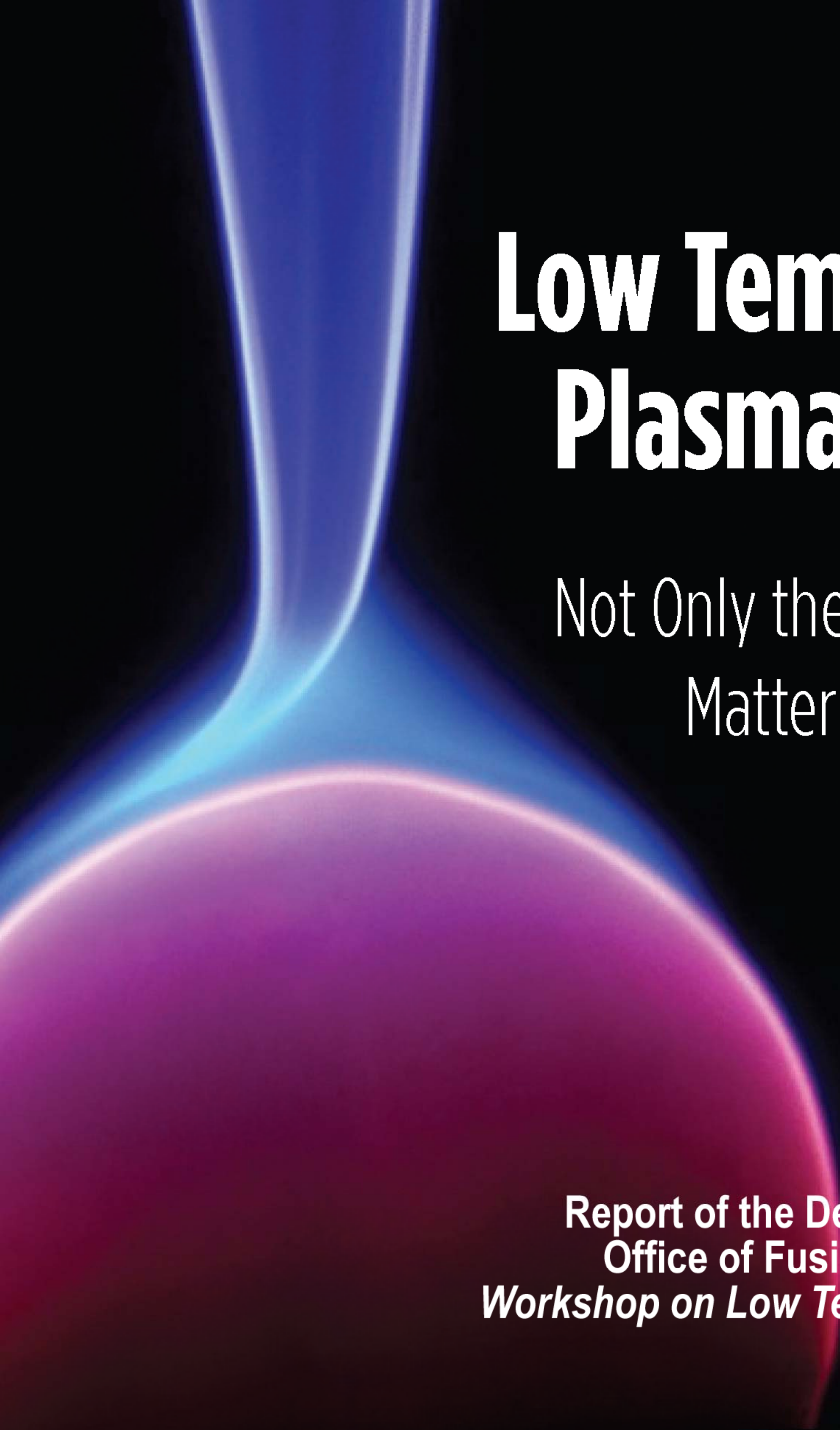

Low Temperature Plasma Science:

Not Only the Fourth State of Matter but All of Them

Report of the Department of Energy
Office of Fusion Energy Sciences
Workshop on Low Temperature Plasmas
March 25-27, 2008

Office of Science
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Excellent Science Attractive Energy

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Preamble and Acknowledgments

In 2007, the Decadal Study "*Plasma Science: Advancing Knowledge in the National Interest*" was issued by the National Research Council. This study, a broad survey of recent progress and future challenges and opportunities in plasma science, highlighted the role of low temperature plasmas (LTPs) as a vital subfield of plasma science. The report describes LTPs as a field rich in intellectually stimulating science challenges and a field where advances in the science quickly translate into technologies that provide societal benefits. LTPs already provide the enabling technologies for industries as diverse as microelectronics fabrication to lighting and displays. Addressing and fulfilling science challenges in LTPs has the potential of not only advancing the knowledge base but also of extending the technological reach of LTPs to even more diverse fields, such as biology and medicine.

A key recommendation of the *Decadal Study* is that the Department of Energy Office of Science assume responsibility for the health and vitality of the subfield of low temperature plasma science by coordinating an explicitly funded, interagency effort. In January 2008, Dr. Raymond Fonck, Director of the Office of Fusion Energy Science (OFES), requested that the *Low Temperature Plasma Science Workshop* be held with the goal of identifying the most pressing and important scientific challenges in LTP science for the next decade. In particular, Dr. Fonck charged that the *Workshop* should:

- Summarize the status of research in this subfield;
- Identify and communicate the outstanding major scientific questions in this subfield;
- Articulate the importance of these questions, both in terms of fundamental science and potential applications;
- Describe what basic research activities are needed to address these questions; and
- Develop a scientific roadmap for an initiative in low temperature plasma science.

The *Workshop* was also charged with producing a report to the broader scientific community that the Office of Fusion Energy Sciences can use in its programmatic planning. In response to this charge, the *Workshop* was held at the University of California at Los Angeles (UCLA) March 25-27, 2008. This report is the outcome of the deliberations of the attendees of the workshop.

The attendees of the workshop were:

Igor Adamovich	Ohio State University
Eray Aydil	University of Minnesota
Michael Barnes	Intevac, Inc.
Pascal Chabert	Ecole Polytechnique-CNRS
Jane Chang	University of California at Los Angeles
Steven Cowley	University of California at Los Angeles
Gregory Hebner	Sandia National Laboratory
Noah Hershkowitz	University of Wisconsin
Robert Hicks	University of California at Los Angeles
Igor Kaganovich	Princeton Plasma Physics Laboratory
Mark Koepke	West Virginia University
Vladimir Kolobov	CFD Research Corp.

Vincent Donnelly	University of Houston
Demetre Economou	University of Houston
Philip Efthimion	Princeton Plasma Physics Laboratory
Alan Garscadden,	Wright Aeronautical Labs
Walter Gekelman	University of California at Los Angeles
Matthew Geockner	University of Texas at Dallas
Steven Girshick	University of Minnesota
Valery Godyak	Consultant
William Graham	Queens University of Belfast
David B. Graves	University of California at Berkeley
Jochiam Heberlein	University of Minnesota

Uwe Kortshagen	University of Minnesota
Mark J. Kushner	University of Michigan
Paul Miller	Sandia National Lab
Gottlieb Oehrlien	University of Maryland
Alex Paterson	Lam Research, Inc.
David Schultz	Oak Ridge National Laboratory
Mark Sobolewski	National Institute for Standards and Technology
Tim Sommerer	General Electric, Inc.
Ken Stalder	Stalder Technologies and Research
Edward Thomas	Auburn University
Lev D. Tsendin	St. Petersburg State Polytechnic University

The workshop attendees worked tirelessly to produce an imaginative and wide-reaching document. We thank the attendees for their diligent efforts. We believe the report will serve its intended purposes, especially in helping to define and focus the roadmap for LTP science.

We particularly thank Dr. Raymond Fonck for his broad and inclusive view of plasma science and for acknowledging the importance of LTPs to the health of the discipline. We thank the OFES for its financial support of the *Workshop*. Drs. Michael Crisp and David Goodwin played pivotal roles as advisors to the *Workshop* organizers and as liaisons to OFES. Drs. Don Shapero and David Lang of the National Research Council were valuable resources for the *Workshop*. Ms. Jody Shumpert of the Oak Ridge Associated Universities and Oak Ridge Institute for Science and Education provided excellent organizational support and supervision of the production of the report; and Ms. Mary Jo Robertson provided expert local support at UCLA.

David B. Graves, University of California at Berkeley, *Workshop Co-Chair*
Mark J. Kushner, University of Michigan, *Workshop Co-Chair*
September 2008

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I. Low Temperature Plasmas: Science Challenges and Societal Benefit

Low temperature plasma science (LTPS) is a field on the verge of an intellectual revolution. Partially ionized plasmas (often referred to as gas discharges) are used for an enormous range of practical applications, from light sources and lasers to surgery and making computer chips, among many others. The commercial and technical value of low temperature plasmas (LTPs) is well established. Modern society would simply be less advanced in the absence of LTPs. Much of this benefit has resulted from empirical development. As the technology becomes more complex and addresses new fields, such as energy and biotechnology, empiricism rapidly becomes inadequate to advance the state of the art.

The focus of this report is that which is less well understood about LTPs—namely, that LTPS is a field rich in intellectually exciting scientific challenges and that addressing these challenges will result in even greater societal benefit by placing the development of plasma technologies on a solid science foundation.

LTPs are unique environments in many ways. Their nonequilibrium and chemically active behavior deviate strongly from fully ionized plasmas, such as those found in magnetically confined fusion or high energy density plasmas. LTPs are strongly affected by the presence of neutral species—*chemistry* adds enormous complexity to the plasma environment. A weakly to partially ionized gas is often characterized by strong nonequilibrium in the velocity and energy distributions of its neutral and charged constituents. In nonequilibrium LTP, electrons are generally hot (many to tens of electron volts), whereas ions and neutrals are cool to warm (room temperature to a few tenths of an electron volt). Ions and neutrals in thermal LTP can approach or exceed an electron volt in temperature. At the same time, ions may be accelerated across thin sheath boundary layers to impact surfaces, with impact energies ranging up to thousands of electron volts.

These moderately energetic electrons can efficiently create reactive radical fragments and vibrationally and electronically excited species from collisions with neutral molecules. These chemically active species can produce unique structures in the gas phase and on surfaces, structures that cannot be produced in other ways, at least not in an economically meaningful way. Photons generated by electron impact excited species in the plasma can interact more or less strongly with other species in the plasma or with the plasma boundaries, or they can escape from the plasma. The presence of boundaries around the plasma creates strong gradients where plasma properties change dramatically. It is in these boundary regions where externally generated electromagnetic radiation interacts most strongly with the plasma, often producing unique responses. And it is at bounding surfaces where complex plasma-surface interactions occur.

The intellectual challenges associated with LTPS center on several themes, and these are discussed in the chapters that follow this overview. These themes are plasma-surface interactions; kinetic, nonlinear properties of LTP; plasmas in multiphase media; scaling laws for LTP; and crosscutting themes: diagnostics, modeling, and fundamental data.

The following paragraphs provide a high-level overview of key challenges, both intellectual and scientific, and discuss how meeting these challenges can provide significant new scientific understanding that can be exploited to improve national competitiveness. These themes are followed by a prioritized discussion of research thrusts. Finally, each theme is discussed in detail in the following five chapters.

The surfaces that bound plasmas are subject to bombardment from the many species created in the plasma: electrons, ions, photons, and neutral species that may be chemically unstable (e.g., radicals) or in an excited state. Controlling these interactions to achieve desired surface functionality is now mostly a matter of trial and error. Some principles are understood, but the possible number of different combinations of plasma and surface conditions is so immense that truly systematic and exhaustive investigations are prohibitive. This then couches the basic scientific question: "How can fundamental plasma transport properties be optimized to produce a desired surface alteration?" This question has hardly begun to be answered. The most recent developments in the field suggest that plasma alterations of organic material—*soft matter*—including living tissue, will be the next major intellectual challenge for LTP-surface interactions. In addition, the effects of LTP on *surfaces* that include nano-structures or nano-textured porosity are known to be particularly difficult to control because plasma species will be transported into and react differently in the three-dimensional (3D) features. Under some conditions, unusually strong gradients in plasma properties near surfaces introduce synergistic effects that are not presently understood. And, finally, the plasma will itself be altered by the species leaving the surface, creating an intricately coupled dynamic that increases the complexity of this science challenge.

LTPs are strongly nonlinear environments. Plasmas *ignite* and *extinguish* based on processes that are very different from their steady-state operation. Waves traverse the medium as in other types of plasmas but have the unique attribute of being able to change the ionization state by orders of magnitude. The *mode* of the discharge determining its dominant form of power deposition can spontaneously switch with a small and sometimes imperceptible change in some parameter and display hysteresis behavior. In fact, the plasma properties may continuously oscillate with no steady state. In short, LTPs display many of the behaviors associated with other nonlinear systems but with a degree of internal complexity that is unusual to say the least.

As noted above, the internal energy states of many of the LTP constituents are not in local thermal equilibrium (LTE). That is, there is no thermodynamic *temperature* under these conditions, and kinetics dominate the behavior of the plasma. The challenges in measuring and computing the kinetic behavior of the coupled species in LTP are immense, particularly when these species are being driven by externally applied electric and magnetic fields that produce nonlinear responses in the plasma. In some cases, the electron dynamics are *nonlocal*, meaning that energy imparted to moving electrons from electromagnetic fields in one spatial location is transported with the electrons to another location, where that energy may be transferred via collisions or affect the electromagnetic fields in that remote location. Plasma nonlocality adds another level of complexity to the electromagnetic-plasma interaction. An especially rich source of unstable LTP behavior is associated with the presence of negative ions, due in part to alterations in the plasma dynamics when the mass of the dominant negative charge carrier changes by orders of magnitude. The nature and complexity of LTP instabilities are such that they may act as model nonlinear systems, mimicking the behavior of other systems with collective nonlinear dynamics, including biological systems, while being more amenable to diagnostics and modeling.

LTP can also be sustained in liquids, especially electrolytes, through the formation of vapor bubbles and the production of gaseous streamers through the condensed phase. LTP can also be sustained in the presence of suspended solid particles (or dust) or liquid aerosols. Plasmas in liquids and "dusty" plasmas are termed *multiphase plasmas*. The scientific challenges associated with multiphase plasmas are immense. The properties of multiphase plasmas are affected by phase interfaces and by coupled inter- and intra-phase dynamics. For example, the plasma-liquid boundary is virtually unexplored, but it is not difficult to predict that the electrochemical and fluid dynamical effects at plasma-liquid phase boundaries open new frontiers in electrochemistry, capillary, and free surface hydrodynamics, as well as plasma science. Improving the understanding of these complex processes will undoubtedly enable heretofore unpredictable technological advances.

Dusty plasmas have been a topic of study in astrophysics as well as laboratory plasmas. Even relatively low concentrations of dust in plasmas will introduce long-range particle-particle and plasma-dust cloud collective interactions. Dust particles can be very heavy negative charge carriers, and, as noted above, a plasma containing negative charge carriers with very different masses introduces novel dynamics. Typically, the number of negative charges far exceeds unity. In fact, a broad spectrum of charge states exists and evolves during physical processes, a unique dynamic dimension compared to ordinary plasmas. These unique conditions may enable new materials to be created and studied. For example, dense suspensions of nanoparticles in LTPs may behave as a "metamaterial" with quantum dominated properties. If particles such as quantum dots or magnetically active materials are suspended in the plasma and interact with each other and the plasma, novel collective processes may emerge, resulting in optical, magnetic, chemical, or dielectric effects.

Challenges of scale pervade LTPS. The principles involved with controlling plasma length scales are linked with the coupling between the externally applied electromagnetic fields and the transport and partitioning of this energy among and between the plasma particle constituents. One aspect of this problem was noted earlier—nonlocal electron dynamics. Even under relatively low pressure conditions, the effects of electromagnetic wave phenomena coupling to plasma in realistic geometries causes spatial nonuniformities due to standing wave and skin effects. At higher pressures, when electromagnetic fields transfer energy to charged species that lose that energy rapidly in collisions with neutrals, avoiding arc or streamer formation can be difficult when the goal is to produce a broad, uniform plasma. Due to the highly nonlinear and rapid response of high pressure plasmas to electromagnetic waves (ionization fractions can change by four to five orders of magnitude in only a few ns), novel techniques are required to avoid instabilities. One possible technique is to use rapidly ionizing but short pulses of energy. Electrons are energized and ionization avalanche occurs, but the electromagnetic fields are terminated before the heavy particle dynamics can act to generate thermal instabilities. An extension of this concept is to excite the plasma with properly chosen sets of frequencies so as to exploit the very different dynamics of electrons and ions. This scheme is sometimes termed *waveform manipulation* and has only begun to be explored. Finally, it is clear that the coupled electromagnetic power supply-plasma system is itself complex, nonlinear, poorly understood and in need of systematic analysis.

Progress in these focus areas demands major advances and breakthroughs in experimental diagnostics and theoretical and computational methods. Surfaces are notoriously difficult to probe under realistic conditions, and the presence of the plasma complicates matters. The nonequilibrium velocity distributions and the internal energy degrees of freedom of the plethora of plasma species need to be measured and computed in order for the plasma surface interactions to be understood. The range of conditions prevalent in LTP implies that a single theoretical or computational description may be too complicated to be useful. However, at the same time, the highly coupled and nonlinear nature of these phenomena begs a comprehensive modeling approach, and this dichotomy represents an exciting science challenge. The extraordinary sensitivity of the plasma to perturbations, a consequence of the nonlinearity of the medium, implies that effective experimental diagnostics must be minimally perturbing. The extreme dynamic ranges of timescales and length scales challenge both experimental and computational methods.

Neither diagnostics nor modeling can be performed in the absence of fundamental atomic and molecular data. A major challenge is to measure or calculate the fundamental kinetic, transport, and spectroscopic data needed to interpret measurements and populate reaction mechanisms in models. These data include, but are not limited to, collision cross sections or rate coefficients for charged and neutral species, surface reaction probabilities, and atomic and molecular physics data for spectroscopic interpretation. The sheer magnitude of different possible species and transitions in LTP is staggering (and is increasing as new molecules are brought to bear for technological applications). The number of species for which data are needed dwarf the analogous needs in other areas, such as fusion plasmas or even atmospheric chemistry, for which the range of possible species is bounded or smaller. The central importance of the need for these data should not be underestimated and cannot be overstated. The challenges of producing, collecting, assessing, storing, and disseminating the data require special considerations.

Priorities

The great diversity of LTPS compels one to prioritize the themes and thrusts of the field as opposed to specific research topics.

Priority 1: Predictive control of plasma kinetics

Plasma kinetics underlie the fundamental means of transport in and utilization of LTPs and the generation of chemically reactive species. These kinetic processes are ultimately expressed in the ability to craft and control the distributions of velocities and energies of electrons, ions, and, in some cases, neutral particles that originate as ions. The character of these distributions will determine the efficiency with which power is transferred from electromagnetic and electrostatic fields to atoms, molecules, and surfaces and the selectivity with which excited, chemically active species and surface structures are produced. Being able to predictably control velocity and energy distributions based on fundamental understanding of the coupling of electromagnetic energy into LTPs underlies the ability to advance the field, control plasma chemistry, and utilize LTPs for societal benefit. For example, the entire worldwide informational technology infrastructure is predicated on bringing to the surface a carefully crafted set of plasma produced, energy selected fluxes of ions and reactive neutral species.

Priority 2: Collective behavior and nonlinear transport

The nonequilibrium and partially ionized nature of LTPs produce unique collective behavior and nonlinear transport rarely found in other fields of science and plasma physics. For example, the ability to change the degree of ionization by many orders of magnitude in a few ns at temperatures of only a few electron volts is a highly nonlinear process that is only approached in extremely high energy density physics. The nonequilibrium nature of LTPs with their broad array of positive and negative ions of varying mass and transport coefficients, neutral particles, and electrons provides for a rich possibility of waves and instabilities not encountered in other plasma systems or otherwise in nature. Extending and improving the knowledge base of these nonlinear processes and collective effects will enable us to customize, for example, extremely large area quiescent plasmas for material processing, controlling plasma chemistry for production of selected species, or to optimize the efficiency of combustion for high utilization of fuel by creating radicals of critical densities in specified locations.

Priority 3: Interfaces and multiple phases in plasmas

A unique attribute of LTPs is their ability to interact with multiple phases: solid, liquid, and gas. At one extreme, plasmas in liquids are being developed as surgical instruments. At the other extreme, low pressure plasmas are being used to create nano-crystals of unique composition, morphology, and properties. Plasmas interacting with surfaces are now the basis of microelectronics fabrication. In some cases, such as micro-discharges, the electrons in the solid material confining the plasma may merge with the electrons in the plasmas. In all cases, there is a phase boundary with which plasma-activated species (ions, radicals, electrons) either pass through or interact with. The means of generating and optimizing plasmas in contact with multiple phases based on fundamental science principles, particularly those in liquids, is currently not possible. LTPs provide a unique opportunity in which nanoparticles of sufficient density and critical composition could create a new class of meta-materials.

Supporting Priorities: Crosscutting and facilitating science and technology— diagnostics, modeling, and fundamental data

Making science advances in each of the scientific priorities listed above requires that there be an available and evolving state-of-the-art foundation in diagnostics and modeling supported by a robust knowledge base of fundamental data (e.g., electron impact cross sections). The diagnostics and models must both be able to resolve multiple phenomena on extremely disparate time and spatial scales. The disciplines providing the fundamental data supporting these activities must have the ability to rapidly, accurately, and inexpensively produce, assess, catalogue, and make available to the community these data. Although diagnostics, modeling, and fundamental data are couched here as supporting priorities, they also hold extreme science and technology challenges in developing the experimental and computational techniques required to span these very large dynamic ranges.

In the chapters that follow, the themes discussed above are elaborated. A set of *priorities* is identified for each theme. Of course, it is recognized that neither the selection of topics nor the priorities themselves are exhaustive or exclusive. They should be considered examples of the many challenges and priorities of the field. Other choices are possible. However, the point that is beyond debate is that the scientific investigation of LTP is an intellectually vibrant and exciting field with exceptional opportunities to advance the understanding of the natural world and to set the stage for future technological advances.

II. Plasma-Surface Interactions: From Nano-structures to Living Tissue

The interaction of LTPs with surfaces is an inescapable consequence of these plasmas being nearly always bounded. Many of the most intriguing fundamental science challenges facing the field are linked directly or indirectly with the plasma altering or being altered by its bounding surfaces. The effects of nonequilibrium plasmas on surface nanostructures, including highly porous and extended surfaces, and, perhaps most excitingly, biological materials, are known to be profound. It is suspected that the *synergistic* effects of the multiple plasma-created species, with a variety of energies and momenta, chemical activity, and transport characteristics, are responsible for the unique surface modification that sometimes occurs. However, the operational parameter spaces are so large and the effects are sometimes so subtle and apparently complex that establishing even qualitative guidelines linking the plasma characteristics and their effects at surfaces has largely eluded researchers to date.

The scientific challenges associated with controlling plasma-surface interactions to achieve the subtle and delicate alterations necessary to create controlled inorganic nano-structures are immense. Perhaps there are more daunting challenges associated with interactions among plasmas and organic and biological materials. Novel experimental and modeling tools are needed to make significant progress in a field that is just emerging from its empirical beginnings. It is difficult to measure the relevant quantities at surfaces, including potentially mobile chemical species, surface bonding structure, and composition for both organic and inorganic surfaces. It is also true that interactions do not take place on strictly two-dimensional (2D) surfaces. There are subsurface phenomena invariably occurring, implying there may be strong depth gradients of properties and processes. Length scale and timescale disparities also abound.

Some of the most promising priorities for studies of plasma-surface interaction are outlined, while it is recognized that plasma-surface interactions are central to many of the other chapters.

Science Challenge 1: How does the multitude of plasma species coming to a complex surface synergistically interact to provide unique reaction pathways for materials processing?

The interface between LTPs and a material is a complex environment that involves interactions of multiple plasma species with the surface. Adsorption and reactions of neutral species on the surface depend not only on their chemical reactivity and energy but also on factors such as the surface temperature; presence and nature of ion, electron, and UV bombardment; and angle of incidence. The surface reaction rates depend on the local structure and composition of the plasma-modified surface.

A unique feature of the plasma-surface interface is the presence of *synergistic interactions* between multiple plasma species that enable unique surface reactions and processes. Such synergistic interactions often include a leading role for energetic ion bombardment, enabling reactions that would not otherwise occur under standard LTE conditions. These non-LTE synergistic interactions among multiple plasma species on surfaces has made possible the synthesis, patterning, and modification of materials, even when the bulk material is at relatively low temperatures. Examples of such materials include metals, insulators, semiconductors, polymers, textiles, liquids, biomaterials, and living tissues. These materials find applications in many scientifically and technologically important areas, such as microelectronics, optoelectronics, "spintronics," lighting and displays, sensors, catalysis, biological imaging, and medical sterilization, as well as in energy conversion, such as photovoltaics and fuel cells.

The interaction of plasma species with surfaces is intricately coupled to the *atomic and molecular physics* within the plasma because the energies, relative fluxes, and chemical identities of the ions, atoms, and molecular fragments uniquely define their reactivities on a surface. The rates of surface reactions are likely to depend on the electronic and vibrational states of species arriving at the surface. The interaction of the plasma flux with surfaces relates closely to *solid state physics and chemistry* and *surface science.*

Reactions of plasma species with surfaces depend on the electronic band structure of the surface interacting with the plasma flux, its surface and bulk composition and structure, as well as diffusivities and reactivities of species adsorbed to the surfaces and through complex reaction layers formed on the surface.

Science Challenge 2: How do LTPs interact with organics, living tissue analogues, and living tissue?

Interactions of plasmas with organic materials, living tissues, inorganic materials in the human body (e.g., tooth, bone), and living tissue analogs are scientifically complex. Even though synthetic, *conventional* organic material surfaces (such as polymers) are much simpler than living tissues, they can still have complex molecular and mesoscopic structures that can be modified by exposure to plasma. Plasma exposure of organic materials results in chemical and surface morphological changes of both their surfaces and bulk structure. The scientific study of this problem is challenging because of the large number of possible reactions between organic materials and the plasma species. For example, even small changes in surface temperature (~10–50 K) can dramatically alter surface reaction mechanisms. Synergistic interactions among UV radiation and other plasma species result in changes even deep inside the bulk of the material.

To date, the investigation of interactions of plasmas with living tissue has been primarily empirical. The unknowns range from the interaction mechanisms through which plasmas might modify bacteria, living cells, and tissue to detailed chemistry and physics of the specific plasma systems used for treating such biological materials. The field of *plasma medicine* is growing rapidly as new uses of LTPs are developed. It is likely that the nature of these plasmas—and the associated chemistry—will vary dramatically, depending on the use. This presents the field with a number of basic and new challenges. A comprehensive investigation of the effect of all particles on living tissue, organic materials and living tissue analogues arriving from the plasma, including photons, appears essential. In addition, comprehensive models of the multitude of chemistries and reactions with these materials need to be formulated.

Organic photoresists have been and will continue to be at the heart of integrated circuit manufacturing. Photoresists have enabled the continuing revolution in integrated circuit technology because they enable patterning of solid-state devices on surfaces with unprecedented nanometer resolution. The interactions of plasmas with photoresists have been studied, although mostly empirically. In contrast, scientific studies of plasma modification of polymer materials at high (atmospheric) pressure and in roll-to-roll processing have only begun.

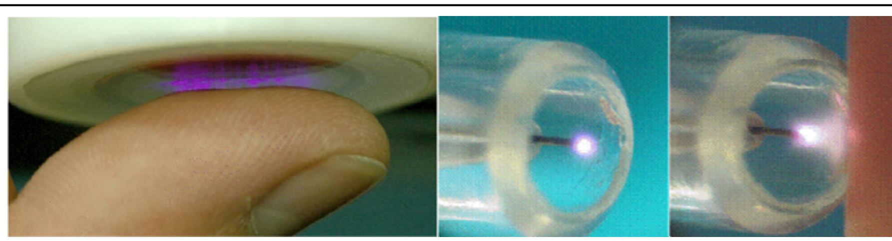

Figure II.1. Two examples of direct contact between plasma and tissue for therapy.

While there has been some progress on the interaction of plasmas with organics, the study of plasma/living tissue interaction is an almost unexplored field (see Fig. II.1). For simplicity plasma/living tissue interaction will be subdivided into two areas, destructive and nondestructive. Within the destructive category, plasma sterilization of medical devices based on H_2O_2 and capacitively coupled discharges is exemplary. Other examples of plasma-tissue interactions include those that occur in surgery with “plasma knives,” a small plasma torch used in surgery. Plasma knives cause simultaneous cauterization and sterilization during cutting and are therefore potentially superior to other methods. The cutting action may be due to intense localized heat transfer that explodes individual cells and may include complex plasma-liquid interactions. This technology competes with alternatives, such as hot-wire knives.

In comparison to destructive processes, there are fewer examples of plasma-tissue nondestructive processes, which are intended to be beneficial to the tissue. Many such beneficial plasma processes are of an indirect nature—the surface of choice is first modified or coated by plasma and then implanted into a living host. An area only now beginning to be explored is the use of plasmas to modify cell/tissue surfaces. Such modification might be used for direct or controlled-release drug delivery from an applied film to select tissue. Other modifications might include the creation of cell growth structures on which new cell growth might occur. These growth zones might allow the regrowth of, for example, bone, tooth enamel, islet cells (insulin), heart valves, and arteries. Plasma treatment has been proposed as a means to promote localized wound healing. The field of "plasma medicine" looks, from a maturity standpoint, very much like the plasma-semiconductor processing field in 1970.

The complexity of the processes at the plasma-biological surface interface is at a scale that rivals most areas of science. This field will by necessity link *medicine, biology, chemistry, physics, bioengineering, material science, electrical engineering, chemical engineering*, and others.

Science Challenge 3: How do collisions in nanostructures, porous materials, and textiles change the transport and reaction of plasma species?

Many surfaces have 3D complex structures (see Fig. II.2). These surfaces include planar surfaces roughened at the nanometer or micrometer scale, surfaces intentionally patterned with nanometer-sized structures (e.g., as in integrated circuit manufacturing), and porous surfaces (such as textiles, aerogels, or zeolites). A significant complication in the interaction of LTPs with such complex surfaces is the spatial inhomogeneity of the surface reactions and surface reaction mechanisms. Complex species transport and reactions within the 3D surface structures lead to inhomogeneities in fluxes and energies of the plasma species to different portions of the surface. Understanding plasma-surface interaction mechanisms for complex 3D objects in contact with plasma requires that many fundamental issues be addressed.

What are the fluxes of incident plasma species and the plasma-surface interaction mechanisms for surface elements that are *not in direct line of sight of the plasma*? How does transport within the complex 3D substrate change magnitude, composition, and energy content of the species flux? Since surface reaction mechanisms will vary locally due to the changed species fluxes and energy partitioning within the surface during transport, how reaction mechanisms change as a function of surface location and time within a complex 3D substrate must also be established. How do the interactive effects among different plasma species evolve as a function of surface location and time for a complex nano-structured surface? How are volatile species transported away from the interior surfaces and how do they influence the plasma?

To answer these questions, a much improved characterization of the fluxes of plasma species arriving at surfaces within the 3D structures in contact with plasma is needed. The characterization should include fluxes of ions, neutral free radicals, excited atoms and molecules, electrons, and photons. The distributions of kinetic energies and angles of incidence should be known for the composition-resolved fluxes of particles. Most commonly available measurement tools cannot be easily applied to address these issues when applied to 3D structures. Part of the scientific challenge is to develop proper experimental and theoretical tools for the study of plasma-surface reaction mechanisms for 3D complex surfaces.

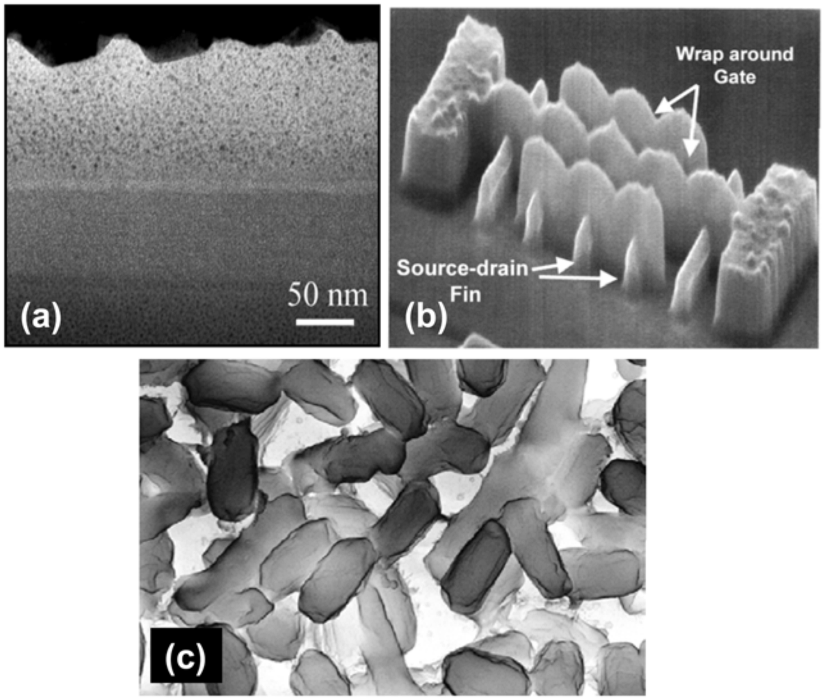

Figure II.2. Examples of complex surfaces in contact with LTPs: (a) nano-porous organosilicate, where open pores can lead to plasma-induced surface roughness, (b) a complex semiconductor gate structure, and (c) *Bacillus atrophaeus* spores wherein up to three layers interacted with plasma.

Progress has been made in the characterization of the plasma flux at planar surfaces, though even that is incomplete. Progress in characterizing fluxes within a complex 3D has not been systematically investigated. For example, measurements have been performed on the effect of wall collisions on ions in multi-capillary surfaces. Information on surfaces of nanostructures has been obtained but typically only consists of surface topographic characterization based on scanning electron microscopy or transmission electron microscopy (TEM) analysis. Surface analysis methods, including X-ray photoemission spectroscopy, have been demonstrated in conjunction with 3D model structures. This method exploits geometrical and materials properties of the structures themselves to enable spatial analysis. In selected cases, novel plasma-surface interaction insights have resulted.

Science Challenge 4: How do plasmas create and modify nanometer-sized materials and their surfaces to make novel functional nano-structures?

Interactions of plasma species with the surfaces of nanometer-sized materials may be fundamentally different than their interactions with bulk material surfaces. The scientific challenge is to understand these differences and to elucidate the role of fundamental plasma-surface interactions in modifying nanometer-sized materials, nano-structures, and their surfaces. A second challenge is to find ways to control these plasma-nano-sized material interactions and to use the unique plasma environment to create new materials that cannot be made in any other way. A third challenge is to understand how the presence of nanometer-sized materials, such as nanoparticles, affect the plasma properties.

The unique nonequilibrium environment and the combination of reactive and charged species created by the plasma provide the means to synthesize and modify nanometer-sized materials in ways that may not be achieved by any other means. However, a fundamental understanding of how reactive radicals, ions, electrons, and photons interact with nano-materials is necessary for extending the current state of the art to produce scientifically exciting and technologically important discoveries. Nanometer-scale materials occupy a size range between molecules and bulk macroscopic materials and may interact with plasmas in ways different from molecules and conventional bulk materials. For example, reactive species impinging on the surface of a nanoparticle may easily diffuse through the entire particle and so interact rapidly with the nanoparticle, whereas such interactions are limited to the near surface region in bulk materials. The interaction between plasmas and quantum-active nanoparticles is a heretofore uninvestigated boundary between plasma and solid-state physics.

Plasmas, of course, have already been used to synthesize nanoparticles and to modify nanoparticle surfaces for technologically important applications. Plasma-based synthesis methods are known to have key advantages. For example, while group II–VI semiconductor nanoparticles can be made by using solution synthesis methods, it has been difficult to use these methods to make group IV and group III–V semiconductor nanoparticles.

An example of how fundamental understanding of plasma-nanoparticle interactions can lead to new breakthroughs is the recent discovery of a plasma-assisted synthesis method that produces diamond and lonsdaleite (hexagonal diamond) at room temperature. This invention occurred from improved fundamental understanding and a synergistic coupling among experiments, plasma diagnostics, and modeling. The known fact that exposure of amorphous Si to H atoms in a plasma can induce a transition to a nano-crystalline Si motivated a coupled modeling (molecular dynamics) and experimental (in situ infrared spectroscopy) study to identify the mechanism. This study led to the hypothesis that a similar mechanism may be operative in carbon thin films and eventually to novel observations of multiwall carbon nanotubes transformed to cubic diamond and lonsdaleite at room temperature (see Fig. II.3). This was an unusually powerful demonstration of the value of fundamental scientific insight leading to synthetic creativity.

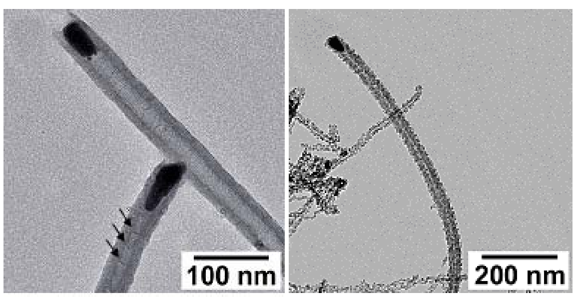

Figure II.3. Multiwall carbon nano-fibers before (left) and after (right) exposure to H atoms from a downstream dihydrogen plasma at room temperature. Graphene walls are transformed to diamond and lonsdaleite at room temperature.

Science Challenge 5: How do extreme changes (gradients) in plasma properties influence plasma-surface interactions, resulting in heat fluxes ranging from manageable MW/m^2 to destructive GW/m^2?

For certain types of (relatively) LTPs, large gradients in plasma properties can form near surfaces. Electrodes in high intensity discharge lamps constitute a plasma-surface interaction with particular challenges because of the possible destructive nature of this interaction. The extreme temperature gradients ($>10^8$ K/m) and heat fluxes (several GW/m^2) lead to surface melting and evaporation. Current and energy transport are largely determined by the electron density gradients. Changes in the surface conditions will affect both temperature and density gradients in front of the electrode and the exchange of charge carriers between the plasma and the solid (see Fig. II.4). Discontinuities in temperatures are likely to exist. Thermionic electron emission from anodes and ion emission from cathodes are both observed, requiring new approaches for characterizing these phenomena. A complicating factor is that these phenomena are tied to fluid dynamic instabilities in the bulk plasma. Compared with the other plasma-surface interactions discussed here, the multitude of species is lower; however, the fluxes are orders of magnitude higher.

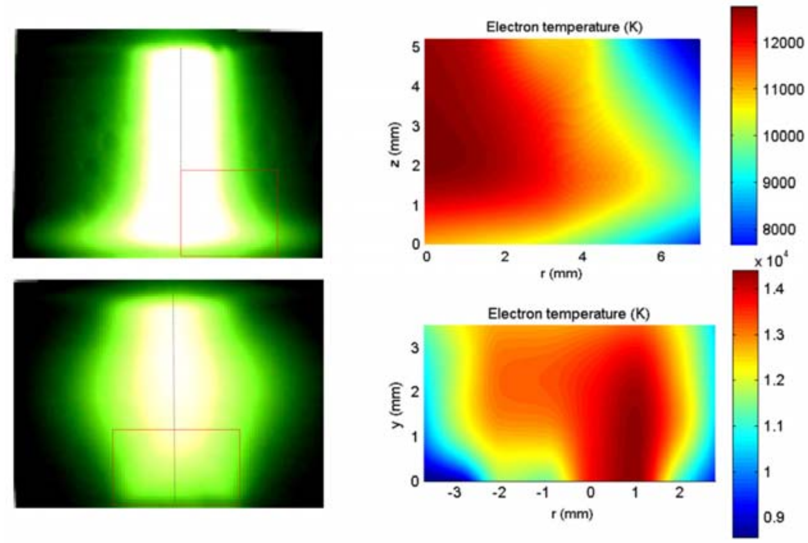

Figure II.4. Photograph and electron temperature distributions of arc anode attachment derived from laser Thomson scattering experiments. Top: manageable; bottom: destructive.

These conditions of ultrahigh heat fluxes and electrode erosion exist in a large number of LTP applications, including circuit breakers, discharge lamps, and plasma materials processing devices, most of which are considered undesirable. On the other hand, they are intended to be used in applications such as plasma cutting, melting, and welding. Improving the understanding of the energy and charge transfer between the plasma and the surface will lead to improved control of the plasma surface interactions, with potentially new electrode designs, increased life of the plasma devices and novel processing methods.

For example, electron density gradients can determine the current flow to an anode. Under these conditions, it appears that for conditions where electric potential gradients and electron density gradients are opposed, an electron heating instability occurs, leading to a discontinuous increase in heat flux and destruction of the surface. No model currently exists for this transition. Experiments are extremely difficult to perform because of the requirement for high time and spatial resolution and signal-to-noise ratios. With regard to cathodes, thermionic emission is well understood, while evaporative-explosive emission is poorly understood. The transition from one to the other, which occurs under extreme conditions, has not been investigated.

The most important milestones to advance the understanding of ultrahigh power loading of surfaces and their beneficial or destructive effects would be a theoretical description of the physical effects occurring under these extreme conditions. This fundamental theoretical understanding would be followed by multidimensional modeling, demonstrating the relative importance of, for example, current densities and temperature and electron density gradients. A first principles description of the transient energy and charge transfer to an electrode under ultrahigh power loadings requires development of new modeling approaches, combining atomistic and fluid dynamic descriptions and comprising the bulk plasma flow, boundary layer, sheath, and details of the surface. Properly addressed, this would enable quantifying the advancing melt front into the solid and the evaporation rates. The fluid dynamic interaction of the plasma flow with the liquid metal also needs to be described. Sheath and surface-solid state models need to be time dependent on different time scales and 2D or 3D as radial diffusion fluxes strongly influence the energy and charge transfer to the surface. The magnetic fields produced by these extremely high current densities likely produce instabilities that have not previously been quantified.

Experimental validation of any such model will encounter the difficulty of vastly different timescales and length scales for the different effects. Gas phase measurements will require approaches that will find an optimal balance between time resolution and accuracy. New approaches for studying the surface conditions will be required. A challenge will be to find a diagnostic method for determining neutral species densities and temperatures in an asymmetrical plasma with high background radiation. Previous approaches of separately studying current transfer, electron and ion emission, and heat flux have neglected the strong synergistic or feedback effects that are encountered in practical devices. This would include, for example, where evaporation of electrode material changes the current density distribution and therefore also the fluid dynamics. Experiments are required that would allow the gradual approach to destructive conditions with a combination of global, detailed, and post-experiment diagnostics.

Science Challenge 6: How do plasma-surface interactions affect the composition, stability, and dynamics of the plasma?

All solids and liquids have a vapor pressure, the pressure at which the evaporation rate from the surface is balanced by the condensation rate. Such processes are well known, with the vapor pressure being modeled by the Clausius-Clapeyron equation. When plasmas contact surfaces, the standard model of a vapor pressure often no longer holds. For example the process of sputtering via high-energy ion impact allows the release of "gas" from low temperature surfaces. This sputtering phenomenon occurs in plasmas as diverse as fusion plasmas (diverter plate) to fluorescent lighting, arc welding, and metal coating systems. In other plasmas, a multitude of chemical reactions, often driven by ion bombardment, can produce chemical species of high vapor pressure from species of low vapor pressure.

Indeed, through a feedback link, vapor production from surfaces in plasma often plays a fundamental role in the system dynamics. Production of some chemical species from surfaces can alter neutral or electron temperatures. Other species will modify the mixture of ionic species. Such changes will in turn cause changes in ion transport, affecting the charge and current balances in the discharge and to the surface. The end result is that surfaces will influence the plasma state as much as the plasma state influences the surface.

While the basic processes outlined above are well known, there is a lack of a firm understanding of the complex interplay among surfaces and plasmas that ultimately defines the state of the plasma. In fusion plasmas, sputtering of the face of the diverter plate is well known. This is also true with sputtering systems (magnetrons) used for metal deposition. In more complex systems, the processes are largely unknown. For example, C_4F_8 plasmas are known to produce significant amounts of CF_4 in the gas through surface reactions. n-Hexane (C_6H_{14}) plasmas produce methane (CH_4) and acetylene (C_2H_4). Such daughter species are produced with other organic feed gases. Because little is known about the surface during plasma contact, little is known about what drives the production of these species.

Science Challenge 7: How can plasma sources be optimized for producing desired plasma-surface interactions?

The development of new diagnostic and modeling techniques will have significant impact on advancing the science of plasma-surface interactions. The multitude of plasma species reacting with a complex surface and evolving from that surface will require both in situ gas-phase and surface diagnostics to quantify and optimize the species types, fluxes, and energies arriving at and leaving a complex surface and to determine the chemical nature of an evolving surface or the reactor inner walls. Conventional line-of-sight diagnostics need to be extended to configurations with limited optical access. These diagnostics will provide the data and insights required to design plasma systems that will deliver the desired species and fluxes to the surface and remove the undesired fluxes that evolve from the surface.

An extreme challenge in optimizing plasma-surface interactions is the design of the plasma source. Ultimately, the delivery of fluxes to (and removal of fluxes from) a surface depends on a gradient between the source of the fluxes to the surface. These gradients can be affected by changes of the thermal boundary layer, changes of the plasma thermal conductivity or specific heat (e.g., by changing the plasma gas composition), or controlled cooling of the surface. Characterizing these interactions in order to optimize the plasma source requires diagnostics with sufficient signal-to-noise ratios to resolve the temperature and density distributions of neutral species in extreme proximity to the surface and in an extremely hostile environment and models for description of the plasma-surface region on different length scales and timescales. Combined atomistic and fluid dynamics models appear to be central to any advancement of the understanding of the plasma-surface interactions required to design the plasma sources.

Priorities

The prioritization of the research in plasma-surface interactions is as follows:

1. Develop novel experimental and modeling tools to understand and control the production of desired functionality on surfaces, including the synergistic role of multiple species. The materials priorities are (a) organic materials and living tissues and (b) nano-structures, nano-materials, nanoparticles, and porous materials.

2. Investigate in order to understand and predict plasma-surface interactions in the presence of large plasma gradients.

3. Understand and predict the effects of plasma-surface interactions on plasma composition, stability, and dynamics.

4. Design and model validation of plasma systems aimed at elucidating the governing principles of high-priority plasma-surface interactions.

III. Exploring and Utilizing Kinetic Nonlinear Properties of LTPs

In addition to the fundamentals of plasma transport, low-temperature plasma physics represents a synthesis of physical kinetics, nonlinear electrodynamics, chemistry, and surface science. Breakthroughs in fundamental science usually happen in such interdisciplinary fields, and, indeed, many such breakthroughs in the understanding of basic concepts in plasmas occurred in the study of low-temperature plasmas (e.g., Landau damping, beam-plasma instability, Bohm anomalous diffusion in magnetic field). A distinctive property of partially ionized plasmas in gas discharges is that they are nearly always in a nonequilibrium state. The electron temperature is typically much larger than the temperature of the ions, and the temperature of ions is usually greater than the neutrals. The electrons are not in thermodynamic equilibrium within their own ensemble, which results in a departure of the electron energy distribution (EED) from a Maxwellian. These nonequilibrium conditions provide the possibility of crafting the velocity distributions of electrons and ions and thus make gas discharge plasmas a remarkable tool for a variety of plasma applications, including plasma materials processing, gas lasers, discharge lighting, plasma propulsion, sources for particle beams, and nanotechnology.

Notwithstanding the significant improvements of LTP sources for various technology applications during the last several decades, the majority of commercial plasma devices have far from optimal performance due to the lack of a detailed understanding of the underlining plasma kinetics and its relation to plasma chemistry. The creation of LTPs with controllable parameters (in particular the plasma density, electron temperature, and electron and ion energy spectra) is one of the major grand challenges of modern plasma physics. These phenomena rely on *kinetic and nonlinear transport processes* that are at best poorly understood.

It is clear that the study of nonlinear plasma kinetics in LTP physics is ripe for breakthroughs due to recent and likely near-future progress in plasma diagnostics, numerical modeling, and analytical theory. Developing the knowledge base of how such complex structures originate in LTPs is the key for further progress in the field. In this chapter, three key science challenges are identified, all associated with nonlocal kinetics.

Furthermore, advances in the understanding of kinetic and nonlinear properties of LTPs can be extended in a number of important ways. For example, formalisms developed to describe kinetic, nonlocal, and non-Maxwellian electron transport in LTPs can be applied to plasma heating and transport in magnetized plasmas. Phenomena such as radio frequency (rf) heating, ponderomotive forces, electron kinetics, nonlocal collisionless heating, and electron runaway (with perhaps its electron multiplication in LTPs) are closely related to the corresponding problems of fusion plasmas (e.g., wave heating, current drive, kinetic effects in field-reversed-configuration reactors, secondary electron emission in the diverter region). All these phenomena are more easily measured and characterized in LTPs.

One of the features of LTPs is that experimental research can be performed in clean, well-diagnosed, tabletop systems that can be easily modified and often operate over many orders of magnitude in pressure or power. These plasmas may be diagnosed with many different types of probes to directly measure the electron density and temperature, plasma potential, flow velocities, and EEDs. Probes can be made quite small to provide spatial resolution of a fraction of a millimeter, capable of measuring the fluctuation of these parameters. Laser diagnostics, such as laser-induced fluorescence (LIF) techniques, can make measurements of the density of specific ion and neutral species and their velocity distributions and of the electric field. Advances in diagnostics are reaching the point of being able to directly measure particle transport by means of optical tagging, something of a molecular analogue of particle-based laser-Doppler velocimetry. With this large array of diagnostics, low temperature, low-pressure plasmas can be the best characterized of all plasmas; and thus, form the basis of improved understanding of kinetic plasma transport that is extendable to other plasma regimes.

Science Challenge 1: What are the fundamental principles governing generation of nonlinear structures appearing in LTPs?

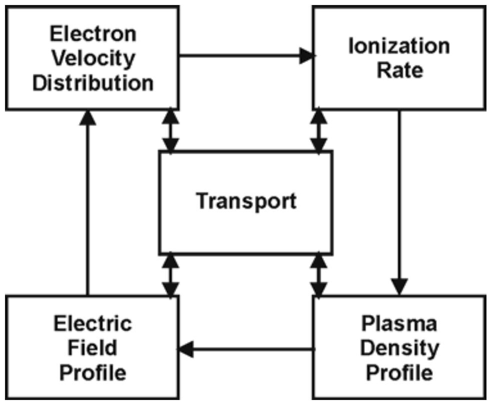

Figure III.1. Schematic of nonlinear couplings in electric discharge self-organization, where the profile of the electric field is coupled to that of the plasma density through transport and ionization rate.

Most interesting processes in LTPs result from nonlinear coupling of plasma production, transport, and heating through electrostatic and electromagnetic fields (see Fig. III.1). The richness of LTP phenomena stems from the great variety of these nonlinear mechanisms, often further complicated by a *nonlocal* behavior, where streams of energetic particles originating in one location affect the plasma properties far away. *Typically, the end result of the interplay of these processes is the appearance of highly nonlinear regimes, where plasma self-organization yields a complex form in space, time, or energy content.* LTPs are partially ionized, and the evolution of *ionization in the absence of instabilities* is a critical barrier to overcome in order to achieve spatially and temporally uniform plasmas at high pressures. In such plasmas, the electron temperature is much smaller than the ionization potential, and thus the ionization rate is a very strong nonlinear function of the electron temperature. Any positive feedback between the plasma density and ionization frequency (as often happens when excited state densities become significant) leads to instabilities. Such instabilities manifest themselves in the formation of novel spatial or temporal self-organized structures, such as the formation of a constricted discharge in inert gases (see Fig. III.2).

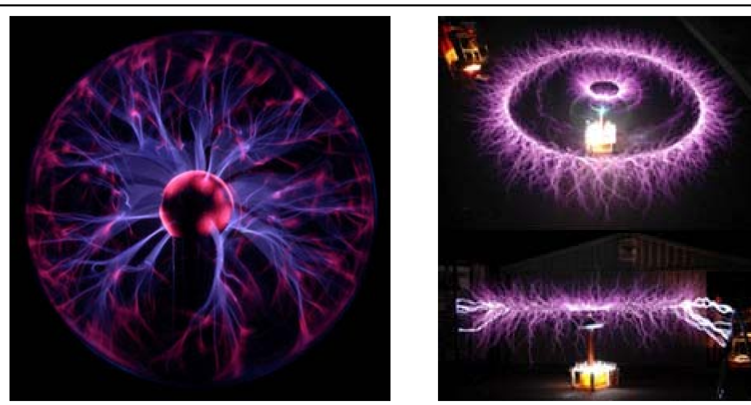

Figure III.2. Constricted discharges, while producing dramatic displays, are the result of nonlinear kinetic processes that confine regions of ionization to streamers as small as a hundred microns.

Ionization waves in the form of striations are another impressive example of self-organization in gas discharge plasmas (see Fig. III.3). This instability phenomenon was first observed by Michael Faraday in the 1830s. The nature of striations in direct current (dc) discharges of rare gases is only now beginning to become understood. It is only through recent advances in diagnostics and modeling that the formation of striations has been predicted through the collective interplay between electron kinetics and electric fields. Models of several varieties of the striations have only recently been developed and combine three necessary processes: energy resolved diffusion, ionization, and nonlocal electron kinetics. Recently, considerable progress has been made in physical understanding of these phenomena.

In spite of recent progress, the nature of ionization waves and striations in molecular and electronegative gases remains poorly understood. The importance of understanding these kinetic, nonlinear phenomena is emphasized by the observation of striations in virtually all LTP application devices. The exceedingly large dynamic range in pressure and timescale of these devices emphasizes that fundamental, application-independent phenomena are responsible for the nonlinear processes. Furthermore, the high sensitivity of striations to the state of electron gas and ionization kinetics makes them an ideal tool for testing advanced simulations and diagnostics.

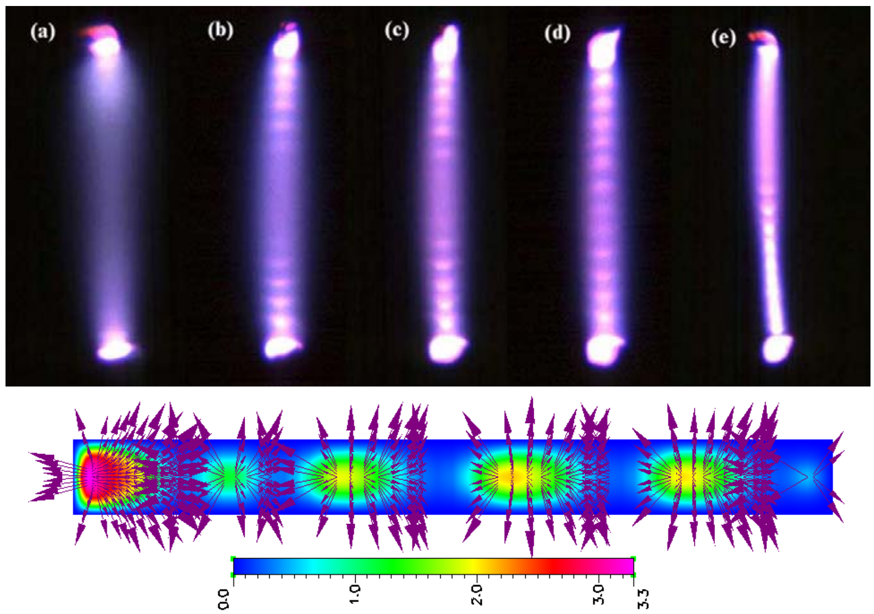

Figure III.3. Images of a plasma column in an atmospheric pressure glow discharge. Top: (a) homogenous mode, (b)–(e) various striation modes; bottom: simulation of a snapshot of a plasma with striations (contours of electron density with units of 10^{12} cm^{-3} and vectors of electric field).

Fast ionization phenomena dominate the behavior of a variety of plasmas both in technological devices, such as streamers in plasma sterilizers, and in nature, such as "sprites" in the upper atmosphere. Many novel approaches, both experimental and theoretical, have improved the understanding of isolated cases of fast ionization processes. However, the crosscutting understanding of the nonlinear behavior of streamers and ionization waves that transcend man-made and natural scale lengths (e.g., from tens of microns to tens of kilometers) has not yet been achieved. A common feature of these phenomena is the self-organized concentration of energy into small relative scale lengths.

Electronegative plasmas contain, in addition to electrons and positive ions, significant fractions of negative ions. Electronegative plasmas are, in fact, the most common of terrestrial plasmas, since they occur in any discharge (man-made to natural) occurring in air or in many molecular gases. Electronegative plasmas have additional temporal instabilities and spatial structures that are not understood and that, to date, have not been computationally predicted. Understanding the complex nonlinear dynamics of electronegative plasmas represents one of the most exciting intellectual frontiers in LTPS.

The difference in kinetic timescales between negative ions and electrons can lead to relaxation oscillations in low pressure discharges that can, in fact, disrupt the stability of the plasma. At the same time, they may also be useful for creating special plasmas with very few electrons. Current-free double layers of imbedded space charge, both stationary and propagating, have been observed in expanding plasmas and are attributed to kinetic collective effects (see Fig. III.4). Large self-established and stable differences in the plasma composition and electron temperature between downstream and upstream are observed when, by analogy with related phenomena (e.g., Rayleigh-Taylor instabilities), they should not be stable. Multicomponent plasmas tend to stratify into regions having different compositions and form bright localized "plasmoids" that have not yet been predicted.

Ionization waves, striations, and collective phenomena in the presence of magnetic fields are other examples of nonlinear processes and nonlocal kinetics that are poorly understood. These phenomena differ from those investigated in the context of fusion due to the nonlinear feedback of ionization, presence of negative ions, and nonequilibrium nature of the particle distributions. Ionization in an applied magnetic field can amplify nonlinear structures due to non-Maxwellian particle velocity distributions or other persistent correlations in the plasma. Understanding these correlations requires modeling, simulations, and experiments of ionization and transport phenomena capable of resolving these collective effects. Many other communities, including plasma propulsion, space plasmas, and astrophysics, can greatly benefit from such fundamental studies.

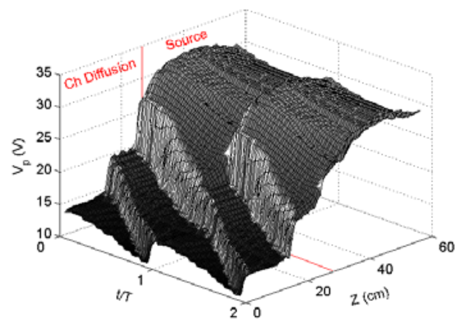

Figure III.4. Periodic formation and propagation of double layers in expanding electronegative plasma.

Another poorly understood collective phenomenon in LTPs is the dynamics of cathode spot in arcs. Many questions remain unanswered: Why do spots move in the opposite direction to the E × B drift? What governs spot motion on the surface? Understanding cathode spot dynamics can help to understand the similar problem of unipolar arcs in diverters of fusion reactors.

The dynamics of strongly nonlinear structures can be further complicated by the stochastic nature of the temporal evolution of these structures. Unlike fusion plasmas or other fully ionized plasmas, the extreme nonlinearity of electron avalanches in LTPs, which can change plasma densities by ten orders of magnitude in tens of ns, intimately depends on stochastic phenomena that seed the initial conditions. Examples include branching of streamers and leaders in lightning. At the other extreme, the stochastic nature of fluxes from LTPs entering small features during the etching of nano-structures can lead to unpredictable and generally undesirable deformations.

The state of the art of modeling in LTPs lacks a predictive capability for many of these nonlinear phenomena. Due to these complexities, assumptions must often be made that compromise the self-consistency required to provide the fundamental understanding that transcends the many orders of magnitude of time, space, and physical conditions observed in LTPs. This is, in fact, the major challenge for modeling and simulation in LTPs compared with other fields. To make the necessary advances in modeling and simulation in LTPs, the field requires comprehensive, multidimensional, parallel kinetic codes capable of advancing understanding of forming such complex structures but also capable of addressing many orders of magnitude of dynamic ranges.

Science Challenge 2: Developing theoretical and numerical tools for active plasma control via plasma boundaries and external electromagnetic fields.

In low temperature partially ionized plasmas, experimental, theoretical and numerical studies reveal that electrons almost never achieve a Maxwell-Boltzmann velocity distribution. In some ways, they carry a unique signature according to their origin and their individual lifetime experiences. Due to the small frequency of electron-electron collisions, the distribution function is not in equilibrium and can be far from Maxwellian (see Fig. III.5).

In spite of progress in describing the kinetics of LTPs, establishing the connection between the interaction of electromagnetic fields with a realistic, bounded LTP created with this field has been and continues to be a high priority research area. Nonlocal electron kinetics, nonlocal electrodynamics with collisionless electron heating, and nonlinear processes in the sheaths and in the boundary of plasmas are phenomena that remain challenging. For example, as the frequency of excitation of low pressure, capacitively coupled plasmas increases, mixed short wavelength, capacitive, and inductive effects begin to dominate in a realm where electron transport is nonlocal. The anisotropic nature of electron velocity distributions has recently been demonstrated, where the electron temperature in one direction can be much larger than in another direction (see Fig. III.6).

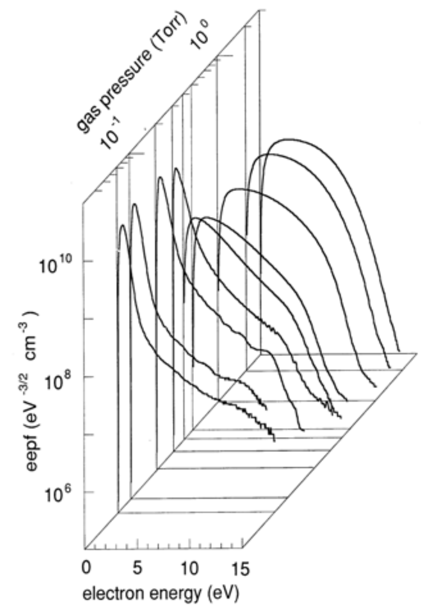

Figure III.5. The EEDs in capacitively coupled discharges can dramatically change as the pressure is changed over modest dynamic ranges.

In many systems the typical distance for electron energy relaxation is much larger than the plasma size. Electrons gain energy within boundary layers (sheaths or skin depths) and release their energy far away from these layers. As a result of this nonlocal power deposition, the plasma density and temperature profiles do not correspond to the electromagnetic field amplitude distribution. Moreover, the plasma conductivity is also nonlocal. Since the transit time of thermal electrons across regions of the electric field with large gradients can be short compared to the rf period, the high-frequency current may not be a local function of the high-frequency electric field. As a result, the spatial distribution of these quantities can be very different from that given by simple drift-diffusion descriptions, leading to anomalous field penetration, collisionless power absorption, and even negative power absorption.

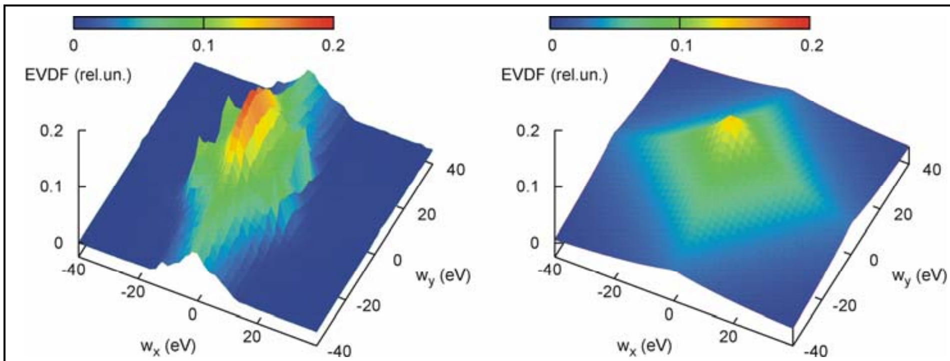

Figure III.6. Complex structure of a (left) strongly anisotropic electron velocity distribution function in the channel of a Hall thruster discharge versus (right) an isotropic Maxwellian electron velocity distribution function (EVDF).

These nonlocal and kinetic effects have recently been experimentally observed, theoretically studied, and modeled in inductively coupled, capacitively coupled, and magnetically enhanced rf plasmas (see Fig. III.7). The future challenge is to generalize these concepts to complex geometries and over larger parameter spaces of pressure, frequency, and gas composition. With this improved understanding, plasmas may be scaled to achieve unprecedented uniformity and stability over large areas and times.

A fully kinetic, 3D computational description of LTPs capable of resolving this nonlinear transport may ultimately require highly coupled solutions of Boltzmann's equation. These techniques have historically relied on algorithms, such as particle-in-cell, propagator, or hybrid methods, all of which are highly challenged to resolve timescales as short (or shorter) than the plasma frequency while simultaneously including the much longer ion or gas dynamic timescales. To overcome such disparities in temporal and spatial scales, advanced computational techniques need to be developed. These issues are discussed in section VI.

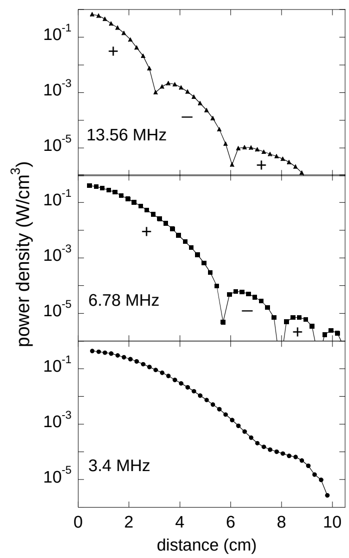

Figure III.7. Time-averaged power absorption measured in an inductive discharge at different frequencies. Regions of negative power absorption are net energy flux from electrons to the electromagnetic field.

Science Challenge 3: Application of concepts in nonlinear dynamics from LTP physics to chemical and biological systems

Biological systems exhibit a great variety of spatiotemporal behavior and self-organized phenomena. Their behavior can sometimes be described by a set of complex nonlinear equations, where their components are far from equilibrium, but their perturbations may be correlated spatiotemporally. Often the obstacle to understanding biological systems is related to a lack of identification of all dynamical variables that are responsible for system behavior. The theory of complex and nonlinear dynamical systems has developed a number of tools that can be applied to such incompletely defined systems. In LTPs, there are a variety of complex structures like striations that are traveling periodic structures associated with ionization instabilities. These phenomena are examples of pattern formation; some of them are well understood. For example, collective phenomena due to close-range interactions among neighboring species produce large-range order as in dusty plasmas. By the investigation of complex dynamical behavior of well-parameterized plasmas in which fluctuations and kinetic variables are measured precisely and reproducibly, the underlying principles of pattern formation may be elucidated and used for achieving the next level of understanding of complex, extended, interacting responses in biological systems, from collective motion of bird flocks to bee swarms.

Priorities

The prioritization of the research in kinetic nonlinear properties of LTPs is as follows:

1. Establish an understanding of the kinetic phenomena associated with nonlinear structures in LTPs, especially focusing on electronegative plasmas.

2. Translate this understanding into the creation of comprehensive, multidimensional, parallel kinetic codes.

3. Develop novel experimental diagnostics that allow the measurement of electron and ion velocity distributions in the presence of complexity of real discharges, including magnetic and rf electric fields.

4. Develop and exploit methods to control plasma parameters and their nonlinear behavior through manipulation of external electromagnetic fields and plasma sheaths.

5. Relate LTP nonlinear dynamics and structures to analogous phenomena in biological and other collective, nonlinear systems.

IV. Plasmas in Multiphase Media

The study of LTPs in multiphase environments is a new area of research. Examples include discharges in liquids, where the LTP first forms through a breakdown in a gas bubble, and plasmas in the presence of suspended nanoparticles in which the particle growth leads to the nucleation of a solid phase within the gaseous plasma environment.

Research on discharges in liquids has been motivated by developments in biomedical engineering and specifically in the area of plasma-based surgical devices. In spite of this near-term application of the technology, the understanding of the formation of LTPs in liquids is in its infancy, leaving fascinating science issues unexplored, such as the breakdown in gas bubbles suspended in conducting liquids, the plasma interaction with moving liquid boundaries, and the coupling between plasma and liquid dynamics. Some fascinating phenomena have emerged from the investigations of plasma interactions with liquids that have shown that the volatile and controllable dielectric nature of liquids opens up new avenues for plasma research (see Fig. IV.1). Discharges in liquids are believed to form close to electrodes in bubbles and vapor layers. When electric potentials are applied to conducting liquids, large electric fields appear in these bubbles and vapor layers that lead to the production of micro-plasmas. Since many of the processes are very fast and transient, plasmas in liquids tend to be in nonstationary states, often bordering on chaos.

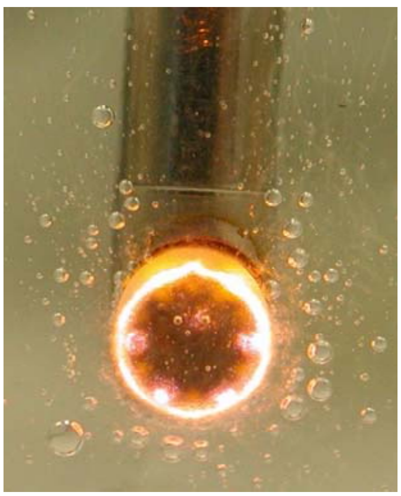

Figure IV.1. An rf plasma maintained in a saline solution.

LTPs are also being investigated for the production of nanoparticles and quantum dots of materials that are hard to produce in other media. Among the first demonstrations of the benefits of LTP-produced nano-crystals was deliberate inclusion of 2–5 nm sized silicon nano-crystals into amorphous silicon; the nano-crystals were found to have an increased stability with respect to light-induced defect creation. Mixed-phase films that incorporate plasma-synthesized ceramic nanoparticles in a matrix deposited by plasma-aided chemical vapor deposition also show promise for superhard, wear-resistant coatings. LTP-produced nanoparticles and nanoparticle plasma processing are also being investigated for nano-electronic devices (e.g., nanoparticle-based transistors, nano-crystal memory, electron emitters), renewable energy applications (e.g., rechargeable batteries, ultra low-cost solar cells), and biomedical applications.

Since plasma processes can produce, capture, and manipulate such nanoparticles and quantum dots, a new field of plasma science has opened, with the study of the novel properties that such multiphase plasmas may have compared with pristine plasmas.

Science Challenge 1: Nucleation and growth—how do entities of a new phase nucleate and grow in a plasma?

The processes leading to nucleation of a new phase in multiphase plasmas are crucial for the understanding of these LTPs. Nucleation of solid particulates in plasmas has significant impact on the plasma properties and is at the heart of the multiphase behavior. The nucleation and growth of vapor bubbles are an important step in the formation of discharges in liquids.

Homogeneous nucleation and growth of particulates occur in many types of LTPs. However, the ability to predict particle nucleation and growth in plasmas is limited, because these phenomena in turn involve a number of other, strongly coupled mechanisms, each of which is itself poorly understood. Plasma chemistry decomposes a reactant gas to generate small chemical species such as radicals and ions. These species undergo a series of chemical reactions to grow clusters of increasing size. In subsequent reactions, particles can grow by heterogeneous reactions on their surfaces and can coagulate with each other. Being in a plasma, they can become charged, which strongly affects coagulation. The nucleation, growth, and charging of particles in turn affects the chemical composition and charge balances in the plasma, causing a strong two-way coupling. When of sufficient size and densities, the particles become sources of collective behavior spanning the reactor. Understanding the fundamental nucleation of particles in plasmas is ultimately required to understand naturally occurring meter-sized collective phenomena (or kilometer-sized interplanetary regions). The spatiotemporal evolution of the plasma during these transient processes cannot be correctly understood unless nucleation and growth, as well as particle transport, can be correctly diagnosed and modeled.

Particle nucleation and growth in low-pressure processing plasmas can be divided into three temporal phases: a short nucleation burst producing a high concentration of very small (~2 nm) particles; a rapid growth phase, believed to be caused by coagulation of these particles; and a slower growth phase, attributed to heterogeneous reactions at particle surfaces (see Fig. IV.2). The accuracy of nucleation kinetic models is constrained by a lack of rate data for anion-molecule reactions and the large number of chemical reactions involved. Particle coagulation, which strongly depends on particle charging, remains a puzzle. Once particles grow beyond a certain size, they are expected to charge negatively in the plasma, but observed coagulation rates can only be explained by coagulation of negatively charged particles with either positively charged or neutral particles.

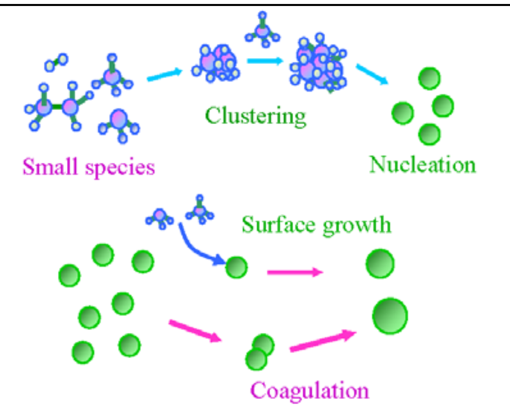

Figure IV.2. Schematic illustrating the particle nucleation and growth process in LTPs.

Nucleation of new phases in LTPs exhibits a rich spatiotemporal structure and a chemical complexity that pose a challenge to both experiments and modeling. The main needs are as follows:

- *Experimental studies of particulate nucleation.* Experimental studies that measure densities of key reacting neutral and ionic species and of clusters are important. Diagnostic methods are also needed that can measure particulate concentration, size, size distribution, and charge distribution for particles as small as 1 nm in diameter, with mm spatial resolution and ms temporal resolution. Fundamental studies are needed of coagulation among charged and neutral particles.

- *Particulate nucleation modeling.* Models are needed that self-consistently predict particle nucleation, growth, and transport together with the resulting spatiotemporal evolution of the plasma. These models require fundamental data on the properties and kinetics of molecular and ionic clusters. Comparisons of experiments with model predictions are limited.

- *Particle nucleation in thermal plasmas.* Nanoparticle synthesis in high pressure thermal plasmas is an important problem with many unsolved scientific questions. Studies are needed that address issues such as the chemical composition and crystalline phase of multicomponent particles that nucleate and grow in an environment with steep temperature gradients that characterize such systems.

This is an interdisciplinary area, with linkages to aerosol science, computational chemistry, and materials science among others. In the case of plasma in liquids, there are linkages to research in cavitation, hydrodynamics, and, often, organic chemistry.

Science Challenge 2: Plasma-nanoparticle interactions—what processes govern the coupling of the plasma to suspended nanoparticles?

LTPs with suspended particulates show complex coupled and collective interactions. The physical and chemical properties of the nanometer-scale particulates are modified by the plasma, but also the plasma *itself* is predictably, and in some cases stochastically, altered by the presence of the particles. The unique feature of these systems that distinguishes them from other coupled systems (e.g., colloidal suspensions) is the presence of the plasma charge carriers (e.g., ions and electrons) of highly disparate masses and temperatures and chemically reacting species that can change the properties of the particles. In particular, the morphology, size, and charge state of particulates or vapor regions are quantities that can have significant temporal and spatial fluctuations.

Investigating phenomena at very small scale lengths is an ongoing challenge to plasma science. The stochastic nature of particle charging has been theoretically examined in simple systems; however, experimental studies of this effect are lacking. Since the size of the suspended nanoparticles (microns or less) is significantly smaller than the relevant Debye lengths (tens to hundreds of μm), an understanding of the sheath structure and screening mechanisms has yet to be achieved. Expressions for charging and ion/electron fluxes are among the key outstanding issues in understanding the interaction of the plasma with nanoparticles.

In order to advance the fundamental understanding of the role of nanoparticles in plasmas, there are several areas in which significant advancements are necessary.

Understanding the influence of the plasma on immersed particles. In addition to a reactive plasma being the source material from which the nanoparticles are formed, many of the physical and chemical processes influencing these particles are determined by the properties of the plasma. Among these are the following:

- *Surface and volume interactions with plasma species.* Even in low-gas-temperature environments, often perfect single crystals of very high melting point materials are obtained. The temperature history of immersed nanoparticles is different from that of the reactor walls and even the surrounding gas. As exothermic surface reactions occur stochastically, the temperature evolution is expected to be nonsteady. Experimental studies of these phenomena are nearly totally lacking.

- *Charging mechanisms of particulates.* Because the nanoparticles are in a plasma environment, they charge through a variety of mechanisms. The often stochastic charging of nm-sized particles is poorly understood.

- *Particulate transport and trapping.* Nanoparticles are under the influence of thermophoretic, electrostatic, and a variety of drag forces. While electrostatic forces are often well defined (provided the particle size and charge are known), they are complicated by plasma-particle interactions such as ion focusing. Quantitative expressions for drag forces are lacking.

Understanding the influence of the immersed particles on the plasma. Growing nanometer-sized particles affect the plasmas, for instance, by giving rise to large-scale, low-frequency oscillations in the surrounding plasma. There is a need for research on how collective plasma-nanoparticles interact:

- *Understanding fundamental plasma physics at sub-Debye scales.* Many of the physical processes that influence the plasma interaction with nanoparticles occur at sub-Debye length scales. Not only are the nanoparticles much smaller than a typical electron or ion Debye length, the plasma environment itself is often highly collisional with typical mean free path lengths that are also smaller than the Debye length. Thus, fully kinetic models of the plasma are required.

- *Diagnostics.* Experimental studies of the above effects entail significant diagnostics challenges. Studying temperature fluctuations of nanoparticles suspended in plasmas is a significant challenge. Observing the dynamics of nanoparticles <10 nm is currently only possible at large particle concentrations. Diagnostics of particle charges and their fluctuations are nonexistent.

This field has strong linkages to astrophysics, ionospheric physics, and fusion plasma physics. In *astrophysical systems*, the coagulation and growth of dust grains parallel the formation processes of nanoparticles in LTPs. In the *ionosphere*, nanometer-sized ice and dust particles are known to agglomerate in the lower ionosphere at 80–90 km heights above the Earth's surface. In the relatively cool ($T \leq 20$ eV) edge (or "scrape-off layer") of *fusion plasmas*, nanoparticles are generated due to physical and chemical sputtering of materials from the plasma-facing first wall.

Science Challenge 3: Plasmas in liquids—how do plasmas interact with liquid-gas multiphase media?

Plasmas immersed in or contacting a liquid are coupled to it through self-consistent electric fields. The liquid boundaries move in response to the fields, and these then alter the boundary conditions seen by the plasma. The processes by which individual electrons in liquids get absorbed by liquids, thermalize, and eventually become solvated are at best poorly understood. There are knowledge bases of the highly disparate aspects of fluids and plasmas, but few studies have attempted to unify the two. For example, much is known about surface tension, capillary and other types of waves in fluids, and electro-hydrodynamic fluid flow in traditional liquids. In plasmas, much is known about the formation of sheaths at the boundary of plasmas as well as the chemical kinetics occurring in the plasmas. Little is known about the coupling of plasma sheaths to liquid boundaries.

Compared with other areas of LTPS, discharges in liquids are a nascent field. The few existing studies to date have yielded an initial understanding of discharges in liquids. It is likely that discharges in liquids initiate in randomly nucleating gas bubbles or in gas films around electrodes. The forming plasma then heats the gas contained in the bubbles, leading to their expansion, which propagates discharge formation. The mechanisms for conduction of current through the gaseous plasma contained in the encapsulated vapor phase through the liquid are not clear. The presence of mobile ions in the some liquids may to some degree support conduction current, but representing these processes remains a particular modeling challenge, since it requires the solution of the Poisson equation in both the plasma and the liquid phases. However, since timescales for screening in the liquid may be much longer than typical plasma timescales, approximations such as immobile liquid ions may be applicable at least during the fast discharge initiation phase.

Understanding the formation and growth of vapor bubbles during discharge breakdown is of fundamental importance for understanding discharges in liquids. The uniqueness of this system lies in the fact that the vapor phase is produced using electrical energy to heat the liquid locally, which subsequently forms a thin (tens of microns thick) layer of gas with a very large reduced electric field. Electrical discharges develop in this high field environment and produce a plasma in the vapor; the plasma contains reactive radicals under conditions that induce reactions on nearby surfaces. The details of the coupling between plasma and liquid dynamics, as well as the processes important in plasmas in vapors, represent an exciting new direction in plasma science.

Recent modeling and experimental investigations suggest a strong coupling between plasma and fluid dynamics during bubble formation in plasmas. High-field regions in conducting liquids locally produce large Ohmic heating rates. If the heating rate exceeds the rate at which thermal energy is dissipated, then local vaporization may occur. As the vapor has significantly lower electrical conductivity than the conducting electrolyte, the electric field increases to the point where the gas breaks down and plasma discharges develop. Subsequent molecular fragmentation and collisional energy transfer between the plasma charged species, and the vapor molecules lead to increases in vapor species density and the growth of a gas bubble. The compelling research issues include the following:

- *Plasma mechanisms.* Discharges in liquids are driven at radio frequencies or by dc fields. Understanding how these fields are modified by the formation of vapor layers, as well as understanding the interaction of these fields with the liquid boundaries and any nearby solid surfaces (for example, biological tissue), is critically important. Models and experiments of the plasma chemical kinetics (both in the vapor phase as well as plasma-surface interactions) and plasma formation mechanisms are necessary to understand and optimize these important mechanisms. How hydrated ions emerge from the liquid and become dehydrated, neutralized, and excited as they incorporate into the gas and plasma phase is unknown yet necessary to understand the optical emissions observed from discharges in liquids. Fundamental studies of plasma initiation, especially in the case of very small pressure-diameter products are needed. The processes for maintaining ionization in the plasma, such as Auger, field, photoelectric, and secondary emission in the presence of liquid boundaries, need to be studied in greater detail.

- *Plasma-material interactions.* The LTPs in liquids interact with nearby surfaces. Little knowledge exists of which chemical species produced in liquid discharges interact with inorganic and organic surfaces. Fundamental measurements of the interaction of radicals with surfaces (e.g., OH or H-atoms) are vitally important.

- *Liquid-plasma dynamics.* The unconstrained and nonrigid boundaries of the liquid respond to the plasma and vice versa. Imaging with good temporal, spatial, and spectral resolution is required to reveal many of the processes involved. The role of surface tension in micron-scale liquid discharges is largely unexplored. Large-scale hydrodynamic effects are important for understanding how bubbles grow and detach. Conductive liquids are also affected by the effects of liquid motion and vice versa, so improved coupled physics modeling as well as experimental visualizations is required to improve understanding. Research is needed to elucidate the nature of instabilities.

- *Nucleation of vapor bubbles and layers during plasma formation in liquids.* The physics of nucleation of vapor layers on surfaces in contact with liquids in the presence of plasma is virtually unstudied. Understanding what triggers the plasma and how it evolves chemically and physically in space and time is needed. Studies characterizing the interactions of the plasma species with surfaces are scarce and with phase boundaries are even scarcer. Modeling studies incorporating hierarchical levels of spatial and temporal detail are essential for an understanding of the physics and chemistry of plasmas in liquids.

Science Challenge 4: Plasma metamaterials—what unusual properties can be found in plasma metamaterials containing dispersed nanoscale and quantum-confined objects?

Studies in the field of plasma-nanoparticle interactions have historically focused on questions such as how plasmas lead to the formation of nanoparticles and how these particulates change basic plasma properties such as the charged species densities and temperatures. However, the viewpoint of looking at a plasma containing immersed nanoparticles as a novel kind of metamaterial with new, unusual properties that are different from those of the individual components in isolation has been little pursued. (Note, the term metamaterial is used here in a broader sense than in its traditional use to describe a medium with new electromagnetic properties.) An impressive precedent for novel properties found in multiphase plasmas is the strong coupling of dusty plasmas, which manifests new types of plasma waves, and a novel thermal conductivity. Yet little attention has been paid to modifying the properties of a plasma metamaterial by exploiting the materials properties and possibly quantum-confinement effects of the immersed particles.

This new field of plasma metamaterials is now enabled by the increased capability of creating nanoparticles with controlled properties. While a large community studies the properties of nano-materials in colloidal solutions or in the aerosol state, similar work in the area of plasmas is virtually nonexistent. Processes unique to the plasma environment, such as transient charging and heating of suspended nanoparticles, may lead to entirely new properties of plasma metamaterials. While there has been no identifiable work to date studying the properties of plasma metamaterials, there has been significant progress in synthesis methods for nanoparticles with controlled properties and the modification of their surfaces.

There is a wide range of properties of plasma metamaterials that needs to be studied in order to assess the full potential of this new field of LTPS. These are summarized below.

- *Optical properties.* LTPs with dispersed luminescent quantum dots may exhibit optical properties that are entirely different from the pristine plasma or that of the quantum dots contained in any other nonionized medium. First, the optical properties of the individual quantum dots may be changed due to nanoparticle charging. Because it is known that the sources of nonradiative processes, such as dangling bonds, are located at the surfaces of quantum dots, these might become terminated when the particles become charged and the quantum yield for photoluminescence may increase. Furthermore, the charging and presence of charged species is likely to distort the excitonic potential of quantum dots, changing the spectral distribution of emission. Bombardment of quantum dots with plasma electrons and ions may lead to exciton formation and thus electrical pumping of quantum dots, a process that has been notoriously difficult to achieve in any other medium.

- *Interacting quantum dot liquids.* Suspended nanoparticles are likely to form a colloid in the liquid state when suspended in the plasma. As the wave functions of excitons may reach many tens of nanometers out of the quantum dots for some materials, stochastic quantum interactions such as energy or charge carrier transfer among the suspended dots may become possible. While such interactions have been observed in other colloids as well, the presence of the plasma that adds stochastic charging, a charged environment, and stochastic heating to the mix introduces a new level of appealing physics.

- *Magnetic properties.* Pristine plasmas are intrinsically diamagnetic and tend to expel magnetic fields. Dispersing para- or ferromagnetic particles into plasmas may change the overall magnetic properties of the plasmas. These properties may be transient and change on applications of magnetic fields, potentially leading to a drift of the magnetic particles that promotes their segregation from the plasma. Since other properties of the plasma, such as charge carrier density and temperature, will depend on the properties of particles, applying magnetic fields to extract or inject magnetic particles may open up new applications in switching plasma properties.

- *Dielectric properties.* Dispersing particles with high dielectric constants in plasmas, such as ferroelectric materials, may be a novel way of tuning the plasma dielectric properties. This may enable plasmas with dielectric constants larger than one or enable wave propagation at sub-cutoff frequencies compared to pristine plasmas.

- *Chemical properties.* It has long been known that the presence of dispersed particles in plasmas changes the charge carrier temperatures and densities in the plasma, thus modifying its chemical reactivity. However, deliberately dispersing nanoparticles in the plasma to modify their chemical properties by introducing chemically active surfaces or exploiting photoactivated or electrically activated catalytic activity of nanoparticles has been little utilized to date.

The preparation of functional nanoparticles and nano-structured materials crosses the boundaries with *materials science and chemistry* and with *solid state physics.* For instance, the propensity of nanoparticle surfaces to emit secondary electrons may depend on the band structure of the nanoparticle material, which becomes a strong function of the nanoparticle size for particles smaller than the exciton Bohr radius.

Priorities

The prioritization of the research in multiphase plasmas is as follows:

1. Develop a fundamental knowledge base for the production and sustaining of plasmas in liquids and plasmas in contact in liquid boundaries.

2. Leverage the unique abilities and properties of particles in plasmas for the possible creation of new classes of multiphase metamaterials.

3. Develop techniques for nucleation and growth of solid phases in plasmas producing unique and otherwise unattainable functionality.

4. Quantify plasma and nanoparticle interactions.

V. Plasma Scaling Laws: Micro-plasmas to Large Area/Volume

Insight into the scaling of low-temperature plasmas requires understanding processes that initiate and sustain these plasmas across a wide range of spatial dimensions, from a few microns to ~1 meter, and pressures, from a few milli-torr to hundreds of torr to many atmospheres. Characteristic velocities for these processes range from the speed of sound (characteristic velocity of gas dynamics perturbations in the neutral species flow) to near speed of light (velocity of fast ionization wave propagation in short-pulse generated plasma).

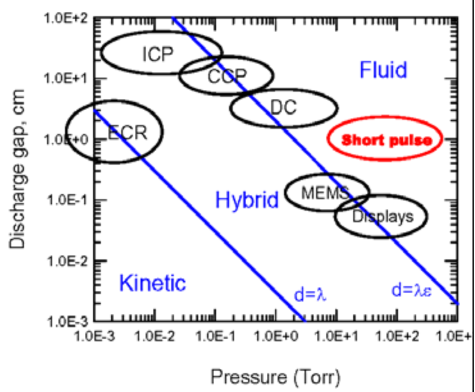

Figure V.1. Comparison of different types of nonequilibrium plasmas, including inductive coupled plasma (ICP), capacitively coupled plasma (CCP), DC glow, electron cyclotron resonance (ECR), and their applications, including micro-electromechanical systems (MEMS).

The different types of nonequilibrium plasmas can be characterized by the "discharge gap," characteristic distance over which the electric field is applied, and the pressure (see Fig. V.1). Note that in some systems, two different scale lengths can be identified, the discharge gap, ***d***, and "spatial extent of the plasma" in a different spatial dimension, ***L***. Different modeling approaches are typically used to address plasmas in different regions of this parameter space. Kinetic approaches (essentially solving Boltzmann's equation) are typically used to describe nearly collisionless plasmas. Fluid approaches (hydro-dynamic conservation equations) are used to describe most collision-dominated plasmas. Hybrid techniques (e.g., a fluid model for heavy species and a kinetic model for electrons) are often used in intermediate regimes. Note that the latter approach may also apply to highly collision dominated plasmas such as those generated by short duration, high amplitude ionization pulses. These may produce runaway electrons and nonlocal ionization, which cannot be described by a purely hydrodynamic model.

In most large-volume, collision dominated plasmas, as the gas pressure is increased, the discharge gap size (***d***) has to be reduced because the breakdown voltage, at a fixed gap, increases with pressure. Due to this constraint, the discharge gap is limited by peak voltage that can be generated by a plasma excitation source. Therefore, scaling the plasma to large areas/volumes requires increasing the aspect ratio, ***L/d***, while maintaining plasma uniformity, stability, and values of key plasma parameters.

Micro-plasmas have perhaps a unique role in LTPs and so may provide a laboratory for investigating many of the phenomena discussed here. These plasmas typically have lateral dimensions of less than 1 mm (to as small as a few microns) and volumes less than 1 mm^3 (to as small as 10^{-9} cm^3); and, although individually small, can cover areas of tens of centimeters (or larger) as arrays of devices. They typically operate stably at high pressure, quasi (or truly) dc with extreme power densities yet, by virtue of their small sizes, are surface dominated.

Science Challenge 1: Electromagnetic-plasma coupling for high-aspect-ratio, low-pressure plasmas with extreme uniformity constraints.

In low-pressure, high-aspect ratio rf and microwave plasmas, there are many interactions that affect plasma uniformity, such as power coupling from the periphery, edge effects, wave propagation, frequency conversion and harmonics generation, and power deposition. In this case, electrical power is usually applied at the edges of electrodes and then propagates to other parts of the plasma. For cases in which the physical extent of the plasma is comparable to or larger than the electromagnetic wavelength in the plasma, many complex phenomena occur. For example, the wavelength of TEM modes in plasma sheaths can be a small fraction of the free-space wavelength. Spatial nonuniformity can arise from edge effects where the power is applied and from gradients in electromagnetic wave propagation to other parts of the plasma. Wave convergence can focus power at the center of circular electrodes in competition with wave attenuation due to absorption by the plasma. The waves can propagate either confined to sheath regions or distributed throughout the plasma, depending on skin depth at the rf frequency.

The electrical nonlinearity of the sheaths can result in frequency conversion as the wave propagates. This conversion is manifested by generation of harmonics in the case of single-frequency excitation and by generation of intermodulation products for multifrequency excitation. The waves at these other frequencies will themselves propagate with their own nonlinear interactions. These new frequencies can interact with the rf excitation circuitry to change plasma modes. Electromagnetic power in low-pressure, high-aspect-ratio plasmas can also be coupled inductively through insulating surfaces into the bulk of the plasma. This case can give rise to all the foregoing phenomena as well as excite a variety of other modes in the plasma.

For any particular plasma geometry, a magnetic field can be applied to change electron transport. This will necessarily cause asymmetry and modify power coupling and wave propagation. Time-dependent variations of the magnetic field may be used to adjust the time-averaged spatial distribution of plasma.

Power absorption by the plasma electrons, as well as heating mechanisms, can be collisional or collisionless with long-range kinetic effects. There have been many studies of different aspects of energy transport and absorption by low-density plasmas. In most cases, analysis pertained to particular isolated phenomena and elaborated key features of power transfer. Often, idealized plasma systems and excitation have been assumed for clarity in the analysis. In order to develop predictive capabilities for plasma design at the kinetic level, previous work must be extended to comprehensive models incorporating all accessible phenomena for actual experimental geometries. Comparing model predictions with experimental measurements by using extensive diagnostics will lead to development of validated design tools with predictive capability.

Science Challenge 2: Generating uniform high-pressure plasmas generated by short ionizing pulses.

In high-pressure plasmas (~0.01–1.0 atm), scaling to large areas or volumes requires plasma generation at shorter timescales or use of external ionization to preclude rapid development of ionization instabilities. One promising approach is to use short duration (e.g., short on the electron timescale, meaning nanosecond and sub-nanosecond), high electric field ionization pulses (tens of kilovolts, both single-pulse and bursts of pulses). Ionization during such pulses occurs on a timescale much shorter than the time over which ionization instabilities develop. As a result, these short pulses are more controllable means to excite high-pressure plasmas. During high-voltage, short rise time pulse excitation, electric breakdown develops as a fast ionization wave driven by electron impact ionization in the wave front. This results in the change of the state of matter (from nonionized gas to plasma), propagating at speeds comparable to the speed of light. This is much faster than velocities of ionizing electrons in the wave (see Fig. V.2). A propagating wave of ionization produces electron-ion pairs over large distances and increasing the spatial extent of the plasma, $\boldsymbol{L}$, up to tens of centimeters at atmospheric pressure. Generating ionizing pulses at a high pulse repetition rate (up to hundreds of kilohertz) before the plasma fully decays has the potential of producing a quasi-steady-state, stable, large-volume plasma. The mechanisms and means to optimize these ionization waves is at best poorly understood. It is known that their propagation is dramatically different in, for example, rare gases compared to molecular attaching gases. It is empirically known that instabilities forming at the cathode layer in high pressure discharges can stochastically and spontaneously launch ionization waves in the form of streamers, but the mechanism whereby this instability is initiated is unknown. Resolving these mechanisms is absolutely required to create collision-dominated plasmas at the meter scale.

Another approach is using pre-ionization of the gas before the breakdown voltage waveform is applied to ensure uniform plasma generation rather than highly localized filaments or arcs. Different pre-ionization approaches include injection of high-energy electron, UV light, and X-rays into the gas from external sources and the use of gases with high-lying metastable states to maintain ionization, through Penning ionization, between the applied voltage waveform maxima.

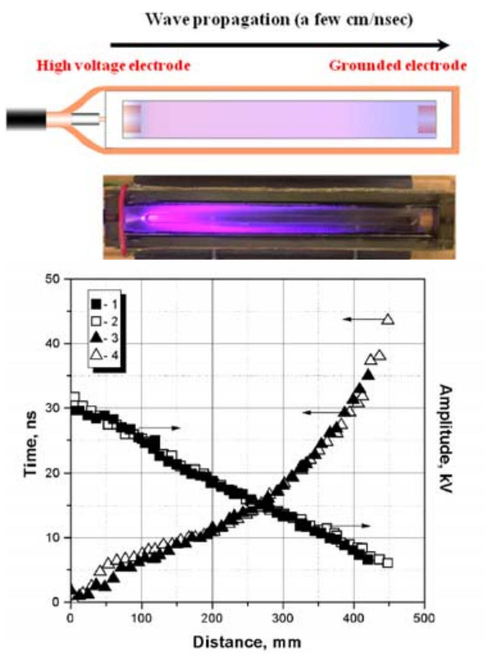

Figure V.2. A repetitively pulsed (10 kHz), fast ionization wave plasma in air. Top: optical emission; bottom: wave amplitude and arrival time versus distance. Ionization wave propagates left to right. Measured wave speed is up to 3 cm/ns (10% of speed of light).

At a fixed gas pressure, ***P***, as the discharge gap, ***d***, decreases, the dc breakdown voltage reaches a minimum before increasing again. This is known as *Paschen's law*. Experimental measurements show that for different combinations of ***Pd*** and plasma excitation frequency (ionizing pulse duration) there is considerable deviation from this behavior on the left-hand (i.e., low values of ***Pd***) branch of this curve. For example, the breakdown voltage may remain constant at the minimum value or it may become multi-valued. This deviation from the basic understanding of electrical breakdown requires further study. Many micro-discharges, micron-sized sheaths in high electron and gas density plasmas, and even relatively large-scale inductively coupled plasma (ICP) systems at low pressures operate in this regime. In particular, this issue strongly affects electric field penetration into repetitively pulsed high-pressure plasmas produced by very high voltage, nanosecond duration pulses. In this case, the sheath voltage fall can be abnormally high (up to several kilovolts) due to ineffective ionization in the sheath operating on the left branch of breakdown curve. Therefore studies of breakdown development on sub-Debye length scales would provide insight into both microscale plasmas and large-volume, high-pressure plasmas produced by short duration pulses.

Insight into the kinetics of short pulse ionization and preventing the development of ionization instabilities requires studies of temporal and spatial plasma evolution on short timescales, nanoseconds or less. These processes include breakdown development, sheath formation, ionization wave propagation, nonlocal electron kinetics, and generation of runaway electrons. Coupling of these effects with the neutral species flow and temperature fields produces high-speed hydrodynamics phenomena, such as shock waves and strong acoustic perturbations, which under some conditions may generate positive feedback amplifying ionization instabilities. This effect provides an opportunity of deliberate introduction of controlled ionization instabilities into quiescent plasma and studying resultant instability growth. This would provide insight into plasma stability limits and will lead to strategies suppressing instability development.

Science Challenge 3: Design at kinetic level; development of new approaches to affect and control plasma parameters by using waveform manipulation.

Using pulsed plasma sources offers the possibility of decoupling electron heating and ionization from plasma decay or loss processes. In a steady-state discharge, the EED and the effective electron temperature are both determined by the effective heating by the electric field, by electron energy loss through elastic and inelastic collisions, and by electron transport into and out of regions of varying electric fields. At steady state, these processes are constrained globally by heavy particle balances as well. With pulsed repetitive excitation, there are at least two distinct periods: the electron-impact induced ionization and excitation phase when the voltage is applied and the decay phase between the pulses due to heavy particle volume recombination and diffusion. Since the pulse-on stage can be much shorter than the pulse-off stage, the time-averaged electron temperature in a periodically pulsed discharge can be lower than in a steady-state discharge. In spite of this low time averaged temperature, the EED during the pulse can have a high-energy tail, producing instantaneous ionization rates orders of magnitude higher than in a steady-state discharge. Under select conditions, runaway electrons generated by high voltage nanosecond pulses can greatly reduce the cost of ionization by electron impact, which results in a lower plasma power budget compared with conventional, steady conditions.

Varying the plasma excitation source waveform in this manner may provide the means to uniquely manipulate EEDs and the ion energy distribution (IED) function to tailor the plasma properties in a manner not otherwise possible. In particular, this approach may enable formation of ion-ion plasmas that could not be generated in the steady state. Excitation parameters such as peak voltage, pulse duration, pulse rise time, repetition rate, and duty cycle can be used to tailor the EED and therefore plasma chemistry. Additional control of the EED is also possible when conditions are nonlocal—that is, when the electron heating and energy loss in inelastic collisions can be separated in space. Additional control of the electron energy spectrum in the decaying plasma generated by a short-duration pulse is possible by applying additional dc or rf electric fields between the pulses.

Previous results using these approaches have demonstrated the ability to target excitation of specific vibrational and electronic levels of molecules and control of negative ion formation in weakly ionized high-pressure plasmas. However, there is a lack of understanding of the fundamental physics involved and many questions need to be answered; for instance:

- How does the pulse rise time affect transient electron kinetics, including generation of runaway electrons?
- Can the EED in weakly ionized plasmas be measured with sub-microsecond to nanosecond time resolution to determine its evolution during the pulse?
- How does the excitation source type affect pulsed operation (i.e., capacitive versus inductive coupling)?
- How does the excitation waveform and duty cycle affect the plasma decay time between the pulses?
- At what stage do negative ions become the dominant charged species in the plasma?
- Can the negative ion density be controlled and can negative ions be extracted from the plasma?
- What are the processes governing the behavior of ion-ion plasmas?

Another novel excitation mechanism that has come to prominence over the last few years is multiple frequency sine wave excitation or non-sinusoidal excitation in low-pressure capacitive plasmas. In multifrequency schemes, applied voltages are manipulated to independently control electron heating and ion energy at surfaces. Non-sinusoidal excitation is used to induce a desired IED at a surface. The kinetics of multiple frequency excitation are not well understood; for instance:

- How do the excitation frequencies combine given the nonlinear coupling of sheaths?
- How does the charged species spatial distribution change with multiple frequency excitation?
- What is the effect of intermodulation on the plasma?
- How is the IED manipulated by multiple frequency excitation?
- How does multimode excitation affect plasma chemistry and plasma processing?

Science Challenge 4: Nonlinear interactions between rf power supplies and plasmas; constraints to short-pulse generation for high-power, high-E/N plasmas

The waveform manipulation discussed above requires the use of high-voltage excitation sources with flexible waveform characteristics (i.e., pulse polarity, amplitude and duration, pulse rise/fall time, and pulse repetition rate). At the present time, such flexible sources, with demonstrated capability of varying pulse characteristics over a wide range, are not readily available. Therefore, plasma generation hardware development is one of the most critical technical, albeit not scientific, issues. Two other key issues arise in providing electrical power for generation of large volume and high pressure plasmas, one associated with plasma nonlinearity and the other with power transmission.

Nonlinearity. The impedance presented by the plasma to the electrical excitation circuit is highly nonlinear and time dependent. At low pressures, the nonlinearity is primarily due to the properties of sheaths near electrodes. With rf excitation, this nonlinear coupling of the plasma and the rf circuit can lead to instability development, multiple modes of operation, and phenomena related to chaos, such as period doubling. These conditions limit reproducibility and constrain kinetic design of plasma processes. Experiments and analysis for a few isolated cases have been made, but no comprehensive studies of nonlinear coupling have been conducted. The state of the plasma is dependent on the impedance characteristics of the excitation circuit, including impedance-matching networks, over a wide range of frequencies. This phenomenon is also not well understood and empirical techniques are usually used to suppress these instabilities. For short duration pulses, the efficient coupling of the pulse energy to a plasma with an impedance varying by orders of magnitude over nanoseconds remains a critical issue. Investigations using detailed plasma models coupled to comprehensive circuit models are required.

Power transmission. Although this report is intended to address fundamental science challenges, these challenges cannot be addressed in isolation from the technology required to perform the experiments. For example, it is technically extremely challenging to generate and apply short duration, high peak voltage pulses to electrodes that are used to generate uniform, large-volume ionization at high pressures. Scaling up discharge volumes and pressures requires higher peak voltages and currents. The available electrical switches have limits on their current capacity and rise times that in turn place upper limits on the size of the plasma. New and innovative means to switch large voltages at high currents with a minimum of pulse-to-pulse variation are required. One possible approach to resolving this issue is by magnetic compression techniques.

Science Challenge 5: Understanding micro-plasmas and leveraging their unique properties.

Micro-plasmas refer to those devices that leverage pd (pressure × dimension) scaling to operate at small dimensions at high pressures. Micro-plasmas at pressures of hundreds of torr to atmospheric pressure (or higher) have dimensions of less than 1 mm to a few microns, with volumes of less than 1 mm^3 to small fractions of a picoliter. Although each micro-plasma is itself small, modern microelectronics fabrication techniques have been used to produce large arrays of micro-plasmas approaching meters in size. Industrial examples include arrays of micro-plasmas in plasma-display-panel (PDP) televisions; however, the plasmas in the individual pixels of PDPs are considered large by today's state of the art. Current research in micro-plasmas is overwhelmingly applications-led. Device geometries and operating regimes are empirically optimized to produce the best result for specific applications. Improving the fundamental understanding of these unique plasma sources would impact a large range of potential applications, including fast and patterned materials processing, large surface area sources, and biophysics.

The large surface-to-volume ratio of micro-plasmas enables them to operate stably in a quasi-dc (or true dc) manner not presently otherwise achievable. For example, power densities of tens to hundreds of kW/cm^3 and approaching a MW/cm^3 can be sustained, producing electron densities commensurate with those in the solid materials confining the plasma. With electric fields of tens to hundreds of kV/cm at the surface, the merging of the gas phase and solid-state plasmas may occur. This is a heretofore unexplored regime of plasma operation.

Arrays of $>10^5$ micro-plasmas with pixel dimensions of only a few tens of microns have been achieved. To date unexplained wave-like coupling and interaction among pixels during ignition have been observed. Explaining these phenomena may provide insights on plasma breakdown of macro-sized plasmas. In fact, the ignition of single micro-plasma pixels may not obey conventional breakdown scaling laws, such as Paschen's curve. Study of these micro-plasma phenomena could be applied to the avalanche fronts of macro-plasmas.

When combined with forced gas flow (or natural convection) through micro-plasma orifices, single apertures and arrays of plumes of plasma can be produced, which have the potential for unique interactions and coupling. For example, rf excited atmospheric pressure micro-plasmas have been observed to launch "plasma bullets" to distances of many cm, a phenomenon also presently unexplained (see Fig. V.3).

Micro-plasmas operate in fundamentally different parameter spaces than macro-plasma and display presently unexplained behavior. Understanding their operation and scaling has intrinsic value and challenges (e.g., How small can a micro-plasma be made?) but may also provide insights that are applicable to the scaling of macro-plasmas.

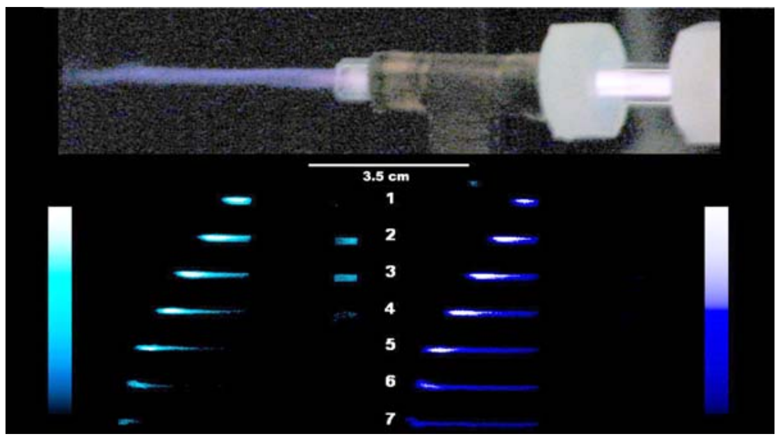

Figure V.3. Plasma bullets emanating from an atmospheric pressure micro-plasma. Left: optical emission from N_2^+ at 389 and 391 nm with a 5 ns gate separated by 10 ns; right: optical emission from neutral N_2 at 337 nm.

Science Challenge 6: Diagnostics and computations.

Development of time and spatially resolved diagnostics is key for addressing other science challenges. Specifically, tailoring the plasma parameters by waveform manipulation, such as short-pulse and multifrequency excitation, needs time-resolved and spatially resolved data on charged particle densities and the EED and IED function in the bulk plasma and the sheath. Development of nonintrusive diagnostics methods, such as filtered Thomson scattering, with high sensitivity making it applicable for weakly ionized plasmas (10^{10}–10^{11} cm^3) is critical for this purpose. These diagnostics need to be sufficiently robust to operate in the presence of significant, broadband noise that is typically produced by short-pulse generated plasmas. Indeed, without these diagnostics, EED and IED tailoring using custom pulse waveforms cannot be experimentally confirmed.

As noted above, plasma scaling is controlled by a set of highly coupled, nonlinear processes evolving over a vast range of timescales and length scales. The development of effective simulations will enable systematic analysis and design of uniform, large area/volume plasmas. These simulations are difficult due to there being strong interactions among gas dynamics, heat transfer, nonequilibrium chemistry, and coupled plasma-electromagnetic phenomena. Transport of different plasma species can be described by a variety of methods ranging from atomistic (kinetic) to hydrodynamic (fluid) models. Kinetic methods, such as particle-in-cell, direct simulation Monte Carlo, or direct numerical solution of the kinetic equations (e.g., Boltzmann, Vlasov, Fokker-Planck) are computationally expensive compared with the continuum models based on the solution of hydrodynamic equations. Models using hydrodynamic equations have benefited from developments in other fields. Methods of solving continuum equations developed for computational fluid dynamics have been recently coupled with electromagnetic solvers to produce practical engineering simulations of plasma systems. For example, 3D simulations of ICPs for deposition for semiconductor fabrication have been useful for development of new processes (see Fig. V.4).

Further development of simulation tools for LTPs should emphasize incorporating kinetic effects and improving accuracy and the efficiency of the numerical algorithms. Kinetic treatment is most critical for electrons because the electron-induced chemical reactions are very sensitive to the shape of the EED. Since kinetic methods are expensive they should be used only when and where necessary. In this regard, hybrid codes using kinetic and continuum methods for different parts of the system with matching kinetic and continuum solutions at interfaces have great potential. Successful multiscale simulations have been demonstrated for neutral gas flows (using adaptive domain decomposition into kinetic and continuum parts) and for weakly ionized plasmas using kinetic and continuum models for different species (ions, electrons, neutrals). Additional challenges are associated with vastly different timescales typical to LTPs from speed of light (fast ionization waves) to speed of sound (gas dynamics). This difference of the timescales poses numerous scientific and numerical challenges for proper domain decomposition and seamless coupling of the models describing different scales. Smart software with self-aware physics and adaptive numerics (e.g., adaptive mesh refinement) would greatly aid the development of the field.

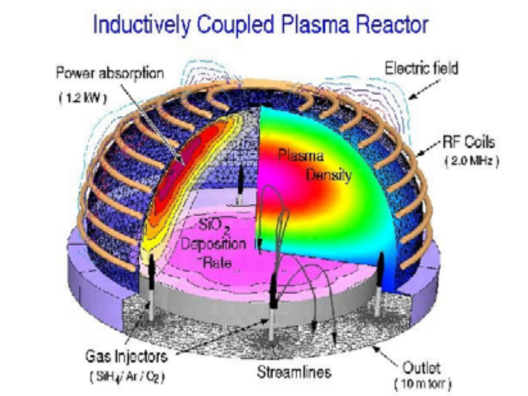

Figure V.4. 3D simulation of an ICP reactor.

Priorities

The prioritization of the research in plasma scaling, micro-plasmas to large area/volume, is as follows:

1. Quantify and explain nonlinear dynamics of the coupling of electromagnetic fields to plasmas in realistic geometries and molecular and electronegative gas mixtures and under transient conditions.

2. Understand the unique phenomena of micro-plasmas and their relationship to scaling of macro-plasmas.

3. Develop techniques that allow electric field penetration by using short ionizing pulses, including breakdown development on sub-Debye length scales.

4. Leverage multiscale dynamics by manipulation of the excitation waveforms and their optimization for desired performance.

5. Understand nonlinear interactions among power supplies and plasmas.

VI. Crosscutting Themes in LTP Physics: Diagnostics, Modeling, and Fundamental Data

Scientific understanding of complex systems can be thought of as the ability to measure and predict all of the important phenomena of the system. Experimental diagnostics are the means by which these phenomena can be observed and quantified. Modeling, theory, and simulation are the means by which the understanding is captured by calculating and predicting these phenomena. Validation of these predictions lends credence to that understanding. Both diagnostics and models require basic data in order to translate these measurements and calculations into meaningful and absolute values. Diagnostics and modeling—measuring and calculating or theorizing—are the basic activities of physically oriented science. This chapter highlights some of the most important challenges and opportunities in advancing LTP diagnostics, modeling, and basic data.

The scientific questions discussed in previous chapters create a new set of challenges for modeling, simulation, and theory and experimental diagnostic methods that are beyond the current state of the art. Despite advances in these fields, adequate methods are not available for measuring or predicting spatially and temporally resolved number densities and energies of species in the plasma to address these science challenges. The added challenges of measuring and simulating the dynamic chemical and physical nature of surfaces immersed in the plasma will only continue to rise in importance as LTPs find new applications in fields as diverse as medicine, biotechnology, and nanoparticle synthesis. Models are only as accurate as the kinetic data required to predict reaction and transport rates. The interpretation of many diagnostics also requires fundamental data. *The scope of available fundamental data is woefully lacking, particularly for gaseous radical neutrals and ions. The databases for reactions of neutral and charged particles with surfaces are nearly empty*.

The field is at the threshold of important advances in the theoretical (especially based on advanced computation), experimental, and fundamental data generation methods needed to accurately describe the structure and interactions of plasma constituents with each other and with surfaces. Advances in these three areas support the entire field of plasma science, as well as basic atomic and molecular physics, materials, combustion, and a host of surface science applications. While these three areas have their own scientific questions and challenges, as addressed below, they are also interdependent in that each relies on advances in the other areas.

A pervasive feature of plasmas is the range of scales that should be treated. Timescales range from that of surface reactions (picoseconds) to the plasma frequency (nanoseconds), gas diffusion (milliseconds), and surface evolution (minutes). Length scales range from that of a solar cell deposition chamber (meters) to biological cells (micrometers), nucleating particles (nanometers), and surface reactions (angstroms). This diversity creates a tremendous challenge for experimental measurement techniques. A similar set of challenges confronts modeling, simulation, and theory (collectively, “plasma modeling”) efforts within LTPS to translate physics into the mathematical form used to understand and quantitatively predict plasma behavior. It is not presently feasible to simultaneously integrate the coupled electromagnetic and kinetic-level transport equations for each plasma and neutral species and surface molecular dynamics with the required resolution over the desired timescales. As a result, hierarchical, multiscale approaches are used. In this approach, different physical processes are treated at an appropriate level of detail, and the individual sub-models are then linked together to describe the entire system. These approaches have been effective for describing aspects of complex plasmas, but their limits are also evident. For example, emerging needs in LTPS, such as treating the onset of plasma instabilities, require a very tight coupling of the important processes that may require an unprecedented degree of computational power. Models are nearly always lacking input data on elementary collision and reaction processes as well as experimental measurements of plasma properties for validation. Plasma modeling should be an integral part of a feedback loop that takes input data, makes predictions, compares with experiments, identifies gaps, and guides further research.

LTPS is highly multidisciplinary, incorporating aspects of fields as diverse as atomic and molecular physics, material science, spectroscopy, surface science, fluid dynamics, electromagnetism, and computer science. The crosscutting nature of this field is seen in the strong interplay among measurement and diagnostics, modeling and simulation, and fundamental data. Understanding, controlling, and applying LTPS requires not only deep understanding in each one of these three topic areas but also an interaction of these areas.

The advances in the applications of LTPS that have transformed society have stimulated exciting and useful advances in diagnostics and modeling efforts, which in turn have stimulated new needs and advances in obtaining fundamental data. Strong cases can also be made for the reverse—fundamental studies of LTPs have also led to discoveries and new applications and accelerated improvements in existing applications. This synergism extends to the present with ever-expanding needs for new diagnostics, simulations, and fundamental data for new gases, new materials, such as biomaterials and nano-crystalline particles, micro-discharges, plasmas in liquids, and the diversity of conditions discussed in other chapters.

The societal benefits of LTPS hinge on knowledge of the processes underlying the plasma phenomena, which require diagnostics, modeling, and data. In addition, advances in answering these fundamental science questions will have impacts on broader areas of science, such as astrophysics and fusion energy. Opportunities for advancement in LTPS and the opportunity to take advantage of these synergies are particularly promising because of advances in computational atomic, molecular, and plasma science, allied with similar breakthroughs in diagnostic methods. The scope and quality of data that could emerge will drive innovations in LTPS and its applications, as well as in other fields.

Each subsection below provides an overview of the history, important science challenges, potential benefits, and the path forward. Five science challenges in these areas for the next decade are identified and discussed. The three areas of measurement, modeling, and fundamental data are equally important and interdependent.

Plasma Diagnostic Methods and Measurements

The difficulty of measuring the fundamental properties of plasmas cannot be overstated. To completely characterize LTPs, measurements of the plasma potential, density and velocity distributions of electrons and the many ion and neutrals species, and state of surfaces in contact with the plasma are required, as well as their spatial and time variation. A large suite of diagnostics is needed to provide this detail, sometimes matching a particular phenomenon to be measured with the appropriate diagnostic technique.

At one extreme are electrical probes. These diagnostics provide fundamental measurements of plasma potential (not otherwise available), plasma densities, and distributions of energies. They are relatively inexpensive and have an impressive record of providing insights into the basic properties of low pressure plasmas. While the introduction of a wire into a plasma to measure currents and voltages is straightforward, the interpretations of these measurements rely on theory that is still being debated and improved more than 80 years after the first serious attempt to interpret the measurements was made by Irving Langmuir. This is due in part to the highly responsive nature of the plasma, making it difficult to avoid perturbing the plasma while measuring its properties.

At the other extreme are efforts to develop minimally perturbative diagnostics and measurement techniques. Over the past quarter century, many new diagnostic techniques have provided critical understanding of fundamental plasma mechanisms, as well as validation data for model development. A few examples of minimally perturbative diagnostics include spectroscopic measurements of the electric field in sheaths; optical methods for determining the electron densities, energy distributions, and drift velocities; and laser scattering for studying the dynamics of particle formation and transport in plasmas (see Fig. VI.1). Although there has been recent progress on surface diagnostic measurements during plasma exposure, such as infrared (IR) total internal reflection Fourier transform spectroscopy, most plasma-surface interaction studies to date have actually been done under molecular beam conditions that simulate but simplify the complex plasma environment. Although simplified plasma systems have their advantages to isolate a single phenomenon and validate new diagnostic techniques, diagnostics are required that are capable of interrogating complex evolving surfaces.

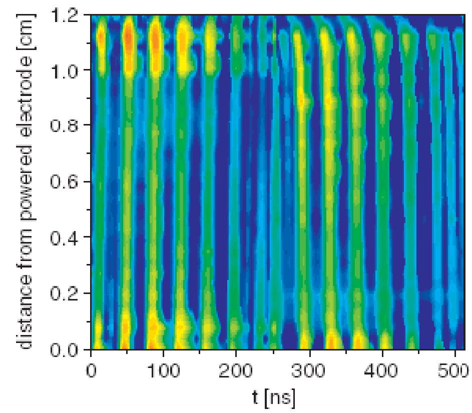

Fig. VI.1. Plasma optical emission spectroscopy, 2007. Phase and space resolved contour plot of the electron drift velocity in the discharge.

Science Challenge 1: Discover breakthrough methods to quantitatively characterize the complex chemical and physical nature of dynamic surfaces immersed in low-temperature, nonequilibrium plasmas.

In material processing, LTPs alter the properties of surfaces to achieve a desired result, such as etching or functionalization. Conversely, contact of the plasma with surfaces profoundly affects the plasma properties. Even a simple chamber wall intended to be nothing more than an inactive part of the vacuum system can alter a plasma process by collecting or releasing material or by becoming electrically charged. The surface is an integral part of the process and can be very complex, including living tissue. A collection of processes evolves over nanosecond to second timescales driven by the species and energy delivered to the surface. The scientific challenge is to discover breakthrough methods to quantitatively characterize the complex chemical and physical nature of this highly dynamic surface *while* it is immersed in a low-temperature, nonequilibrium plasma. This is particularly problematic at atmospheric pressure and in implementing diagnostics in confined spaces, such as micro-discharges, in high-aspect ratio features, and inside voids. Given that the state of the surface can influence the plasma, which in turn affects the fluxes to the surface, the transfer of fundamentally measured surface reaction coefficients between systems itself becomes problematic.

The surface diagnostics challenge can be broken down into several smaller sub-issues, all of which are necessary to characterize the plasma-surface interaction and all of which need breakthroughs:

- What particles strike the surface and what are their energies and fluxes? This includes neutral species, positive ions, electrons, and photons.
- What chemical constituents are on the surface?
- What is the physical nature of the surface?
- What products desorb from the surface?

Progress has been made to date but severe scientific challenges remain for plasma-surface characterization. For pressures greater than the milli-torr range and in the presence of electric and magnetic fields in an actual plasma, it is virtually impossible to use surface analysis methods developed for ultrahigh vacuum, such as X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), or electron energy loss spectroscopy. Surface IR absorption, enhanced by the total internal reflection technique, has the sensitivity to detect many surface-resident species. The technique is limited to IR-transparent substrates and cannot readily yield atomic concentrations, especially of metal residues. A popular approach is to expose the surface to the plasma and then transfer it under vacuum to a high vacuum diagnostics chamber equipped with XPS or AES.

Since the transient physical nature of the plasma-formed surface layer is also of prime concern, innovative techniques are required to preserve the state of the surface. For example, these ex situ transfer methods can be taken to the extreme with a spinning substrate method in which plasma exposure and analysis by AES are separated by as little as 0.3 ms, making it possible to study transient surface kinetics. Spectroscopic ellipsometry and atomic probe methods can determine grain size, porosity, and surface roughness in situ, subject to the availability of an effective medium model for interpretation of the measurement. Identifying which products desorb from the surface is perhaps the most difficult measurement to make, especially in high pressure plasmas. Desorption mass spectroscopy cannot easily be carried out because it is very difficult to sample the product flux without interaction with the plasma.

The benefits to science will be enormous if major breakthroughs are made in plasma-surface diagnostics. First, they transform the ability to answer a key question of LTPS: how does the plasma affect the surfaces and vice versa? With such knowledge will come improved abilities to verify simulations of atomic-scale processes at surfaces and ultimately enable confident predictions of optimum conditions for plasma operation in current and as-of-yet unforeseen applications. The benefits to other areas of science, such as catalysis, combustion, heterogeneous chemistry on dust particles and ice crystals, and chemical vapor deposition cannot be overstated.

Breakthroughs are needed in laser spectroscopy, embedded nano-sensors, surface plasmon resonance methods, surface acoustic methods, or hybrid techniques. In addition, innovative methods for carrying out electron spectroscopy at high pressure would be a major achievement. If it were possible to bring near-field scanning optical microscopy to this harsh environment, it may be possible to obtain both structural and chemical information. This latter method could revolutionize investigations of plasma interactions with living tissue.

Science Challenge 2: Invent new tools with unprecedented time and space resolution to measure the neutral and charged particle velocity and energy distributions in the bulk plasma and sheath.

The kinetic and potential energy in plasmas is partitioned into many particle degrees of freedom as well as in electromagnetic fields. The transport and transformation of this energy largely determine the physical-chemical transformation of the plasma species. LTP systems are weakly ionized with ionization fractions of 10^{-2} to 10^{-10}. In such systems, the charged particles interact strongly with the neutral background gas to produce a myriad of nonequilibrium radical and excited neutral species that drive the gas and surface chemistry. Measuring these species, including their velocity and energy distributions, provides information on the chemical and energy transfer pathways as well as data to compare with first principle models. Complicating these measurements is the fact that charged particles (electrons and ions) can be strongly affected in thin regions in space (e.g., sheaths and double layers) or during short periods of time, where relatively strong electromagnetic fields either penetrate the plasma or are created through plasma instabilities.

While charged particles are a minority species in most LTPs, they are usually the most energetic. The velocity distribution, spatial distribution, and excited state distribution of charged species are key properties to understand and control. Tools to measure these quantities are critical to address general questions, such as (1) What is the role of neutrals in plasma chemistry? (2) How is energy transported and stored in atomic and molecular plasma systems? (3) What are the origins of plasma instabilities? (4) How are dust particles charged, heated, and formed? (5) What are the neutral and charged species velocity distributions? (6) How do sheaths evolve and are there collective effects in the sheaths?

Although invasive electric probes can inexpensively and rapidly provide bulk plasma properties and sheath properties can be measured in scaled systems, the challenges for developing the next generation of diagnostic tools include the need to investigate length scales on the order of several microns and time resolution of ~1 ns with low particle densities. The measurement of plasma potentials and electric fields often poses a particular challenge under common conditions of interest. Charged nanoparticles can affect sheath structures. Could nanoparticles, therefore, be used as sheath diagnostics? To date, most progress has been made with non-perturbing optical methods, such as optical emission spectroscopy (OES) (see Fig VI.2). This method yields the most abundant and inexpensive data and, in rare instances, when combined with rare-gas actinometry, has provided a quantitative measure of number density. Extracting 2D profiles from OES measurements in cylindrical geometries requires an Abel inversion that can introduce noise and uncertainty and presumes symmetries that may not occur. Obtaining true 3D data requires tomographic methods. OES time resolution is limited to tens of nanoseconds due to the finite radiative lifetime of most species. LIF has been used to obtain quantitative 3D species maps but is only applicable for a few select species. Sheath dimensions can be estimated from OES or LIF measurements, but there are not direct measurements of sheath thickness (see Fig. VI.3). Sheath electric fields can be measured with laser techniques with resolution of 10 V/cm with 35 μm spatial resolution. Ion motion close to the surface is determined by surface charging and associated electric fields that vary substantially over submicron lengths. Measurements are difficult on these length scales.

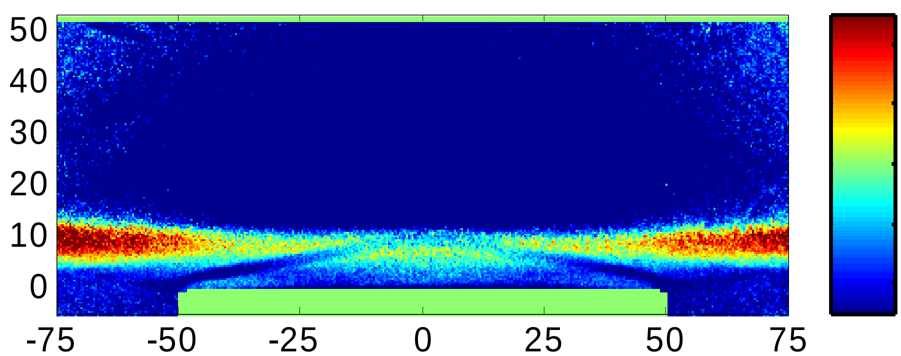

Figure VI.2. Spatially resolved optical emission of the Hβ/Hα line ratio in an rf-driven hydrogen plasma immersed in an 80 gauss magnetic field. The units are millimeters.

Dramatic improvements in the abilities of diagnostics to unobtrusively provide fundamental data on properties of plasmas are coming close to fruition. For example, advances in microelectronics fabrication are providing the ability to construct sensors of having dimensions approaching (or smaller than) Debye lengths. These sensors, for example a miniature ion-energy analyzer, could be equipped with wireless communication abilities to interrogate their positions in the plasma and send back their data. Hundreds or thousands of these probes dispersed in the plasma might provide 3D, time-dependent maps of plasma properties with minimum perturbations.

These challenges are fundamentally important to meet. With breakthroughs in time and space resolved measurements of species energies and number densities, some of the most persistent questions in the field will finally be answered, such as the role of neutrals in altering sheath dynamics, the importance of energy stored in metastable and vibrational levels to the state of the plasma, and the identification of what plasma chemistry takes place in sheaths and pre-sheaths in highly collisional plasmas.

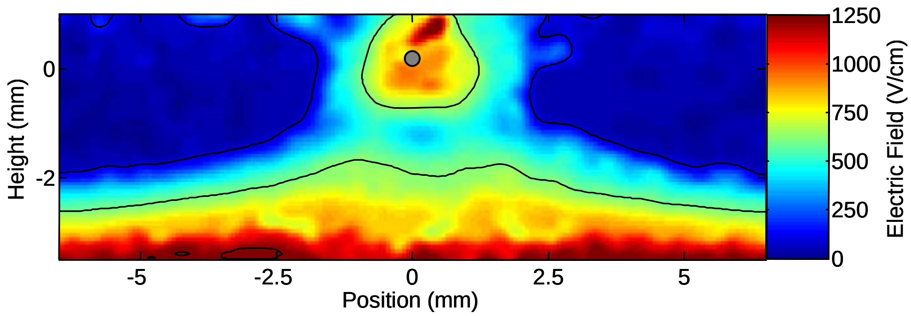

Figure VI.3. LIF measurements of the electric fields around a Langmuir probe above a radio-frequency driven electrode. The probe is biased at −60 V, located at (0, 0), and viewed end on. Spatial resolution is 0.1 mm.

Science Challenge 3: Develop techniques to understand the complex and nonlinear interaction between a plasma and external power sources.

In LTPS, the great complexity of plasma phenomena and plasma/surface interactions are further complicated by poorly understood interactions with the entire system of circuitry and equipment that surrounds and powers the plasma. The sheaths are inherently nonlinear, an effect that must be accounted for in equivalent circuit modeling. Sheaths driven at one frequency (or multiple frequencies) will generate voltages and currents at harmonic frequencies (or sum and difference frequencies). Harmonic generation is sensitive to even minor changes occurring anywhere in the electrical system. At microwave or radio frequencies, changing the position of a power lead by a few millimeters can produce a significant change in harmonic amplitudes, which in turn can affect the amplitudes at the driving frequency, power absorption, and ion bombardment energies. The sensitivity of this type of nonlinear interaction to small changes in system dimension is a significant source of irreproducibility in a single system over time or among multiple systems in different laboratories. This irreproducibility is not only of interest in applications, where the yield of plasma-processed materials may be degraded, but also of fundamental scientific importance. Progress in any experimental field, at minimum, requires that the relevant experimental conditions be capable of being accurately specified and reproduced.

Despite these disadvantageous effects on reproducibility, the interaction of plasma-generated harmonics with external circuitry also presents several potential benefits. The higher harmonic voltages and currents are closely related to sheath dynamics, power absorption mechanisms, and energy distributions of ions in sheaths and at surfaces. Consequently, harmonics represent an opportunity to monitor, optimize, and control these important aspects of LTPs. What is needed to enable such a novel diagnostic is a better scientific understanding of the fundamental nature of the nonlinear interactions that produce the harmonics.

Priorities

1. Innovate new methods for probing the chemical composition of surfaces while they are immersed in plasmas.

2. Develop diagnostics capable of interrogating 3D structures (e.g., the equivalent of TEM for use) inside the plasma.

3. Develop diagnostic techniques for 5 µm spatial and 5 ns temporal resolution that are capable of being used in the bulk plasma as well as the plasma sheath at conditions ranging from large, low pressure plasmas to atmospheric pressure micro-plasmas.

4. Develop techniques to understand the complex and nonlinear interaction between a plasma and its external power sources, including model, scalable systems.

Plasma Modeling and Simulation

Plasma modeling has made impressive progress over the past two decades. Fluid and kinetic models in one, two, and three dimensions addressing dc, rf, and microwave discharges in rare gases and molecular gas mixtures have been developed and applied to the investigation of fundamental science and applied technology. Theoretical developments such as nonlocal effects and collisionless power deposition have been incorporated in the models as have the consequences of surface chemistry and radiation transport. A relatively large (by LTPS standards) effort emerged to model low-pressure plasmas for semiconductor electronics manufacturing in parallel with more efforts to improve models of plasma torches, lasers, and lamps. Microscopic feature evolution simulations (mainly 2D) predict the shape of etched or deposited features on the wafer surface. Molecular dynamics simulations have been shown to be extremely valuable in understanding the interaction of plasma species with surfaces. Currently, 2D and 3D fluid and hybrid reactor scale simulations with electromagnetic power coupling and complicated chemistries are linked with 3D profile evolution tools (see Fig. VI.4). The output of such simulations is fed to molecular dynamics and profile simulators to predict phenomena over multiple length scales and timescales. Most recently there has been a trend to bring together models of high-pressure equilibrium plasmas with low-pressure, nonequilibrium plasmas to describe emerging high-pressure, nonequilibrium plasmas.

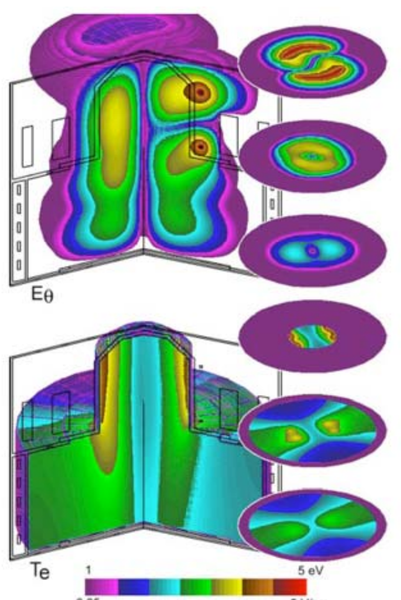

Figure VI.4. Top: 3D simulation of a helicon plasma source showing the azimuthal electric field; bottom: the electron temperature.

Plasma modeling encompasses *theory* that identifies the key physical and chemical processes and their mathematical representation as well as *simulations* that provide numerical predictions for specific conditions. Although advances in LTP modeling have been impressive over the last several decades, the field has underutilized the explosion in computational power and algorithms that have helped transform other areas of science. If freed from need to focus on relatively short term questions of technical and commercial importance, the LTPS modeling community would blossom, exploiting modeling techniques and computational resources that would transform the field.

The fundamental challenges of modeling LTP are due to the complex roles played by coupled, nonlinear phenomena interacting over a vast range of timescales and length scales. These challenges are daunting, but similar challenges and problems in other fields are being attacked and solved. These allied fields range from fusion science, atmospheric science, and astrophysics to catalysis, polymer science, and biophysics, among others. The creative and novel schemes being developed and applied in these fields are clearly relevant to LTPS, but little effort has been made to date in exploiting these analogies.

Science Challenge 4: Revolutionize modeling and simulation tools to predict plasma physics and chemistry spanning length scales from angstroms to meters and timescales from picoseconds to minutes.

Modeling is of fundamental importance to resolve long-standing issues, particularly when it shows that seemingly disparate phenomena are manifestations of the same underlying principles. For example, integrated models are of fundamental importance in the interaction between complex, ill-defined surfaces and the full plasma environment. Quantitative understanding of such a complex interaction requires a multilevel effort, from ultrahigh-vacuum experiments on pristine surfaces to long timescale molecular dynamics modeling and quantum mechanical description of adsorption, binding, reaction, and transport. Modeling uniquely integrates this disparate knowledge into a complete description that should be applicable to a variety of surfaces, independent of whether that surface is a particle floating in the plasma, nanostructure on a wafer, or biological cell immersed in saline solution. Any shortcomings of the model lead to the identification of knowledge gaps and directions for future research.

Integrated models and simulation tools are needed to capture phenomena that are coupled over large dynamic scales in time (picoseconds to minutes) and space (nanometers to meters). This is necessary to improve the predictive capability of models, uncover new physics, and answer outstanding scientific questions. For example, instabilities are pervasive in LTPS, due to coupled, nonlinear processes arising from kinetics and transport of neutral and charged species interacting with electromagnetic fields. Hypotheses purporting to explain these observations cannot be tested without the development of tightly coupled models and a critical assessment of their predictions against the wide range of observed phenomena.

Integrated treatment of the variety of coupled processes in LTPS is an extremely challenging task in some cases, requiring 3D unstructured meshes that must adapt to moving boundaries and interfaces. New methodologies such as using parallel computational algorithms must be developed that take advantage of high performance computing. Judicious coupling of simulation with theory must be a cornerstone. For example, theory might be used to provide (by integration over fast timescales) electron transport properties at the grid points of the computational mesh. At the same time, efficient combinations of molecular dynamics (to accurately resolve atomic-scale motion) with Monte Carlo simulations (to resolve longer timescale and length scale processes) must be developed for proper comparisons to experiment.

Integrated multiscale models and simulations (combined with theory) are needed to make predictions, uncover new physics, and answer outstanding scientific questions. For example: What is the mechanism of the glow-to-arc transition that limits the current density in micro-plasmas? What are the stability limits for these high pressure cold gas discharges? How do electronegative gases affect stability? What limits the size of micro-plasmas? How do local and nonlocal phenomena in the presence of nonlinearities affect the development of spatial and temporal "structures" in the plasma (streamers, sparks, arcs, striations, constrictions, etc.)? (see Fig. VI.5) How do collisional and collisionless heating operate in magnetized plasmas? How can EED and IED in the plasma be controlled, tantamount to "designing at the kinetic level"? How does plasma initiate and propagate in saline solutions in the presence of multiphase (gas-liquid) moving boundaries?

The fundamental goal of plasma modeling is for computationalists and theorists to work collaboratively with the developers of diagnostics and production of data to link models, diagnostics, and data into a feedback loop that leads to an improved scientific foundation that supports all the science challenges described above.

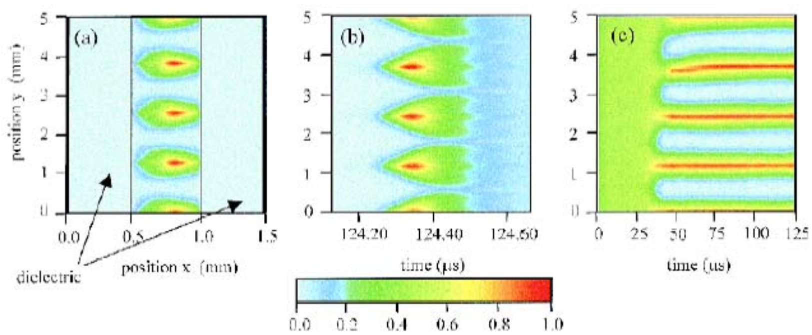

Figure VI.5. Plasma density distribution in a high pressure (1000 torr) dielectric barrier discharge showing the development of self-organized filaments.

Priorities

The specific priorities that will need to be addressed to achieve this goal include the following:

1. Expand plasma modeling capabilities to combine theory (e.g., nonlocal descriptions of the EED function), simulation (e.g., Monte Carlo and molecular dynamics), and reacting flow equations in order to model closely coupled, stochastic processes, such as breakdown, instabilities, and turbulence.

2. Improve the plasma modeling computational infrastructure to exploit state-of-the-art high-performance computing, parallel algorithms, and other advanced methodologies.

3. Identify the key mechanisms governing plasma-liquid interfaces. Important examples include plasmas interacting with aqueous solutions, nucleating aerosols, including metal melts, and living tissue.

4. Develop multiscale modeling methodologies that can describe interactions of plasma with nanoscale features such as nanoparticles and nano-textured surfaces.

5. Implement “diagnostics” into models, so that they predict directly measurable quantities (e.g., Langmuir probe current-voltage characteristics and optical emission spectra) and enhance the interpretation of diagnostics.

As noted previously, plasma modeling inherently has strong links to many other scientific disciplines. Plasma models rely on fundamental data, and their accuracy is proven only in comparison with experimental diagnostic measurements. These three areas must work in the closest possible manner. Furthermore, as noted in the following section, there are modeling, theory, and simulation needs and opportunities in creating and testing fundamental collision and reaction data.

Fundamental Data

LTPs are composed of constituent particles, fields, and surfaces. Knowledge of these constituents’ properties and interactions is fundamentally important to understanding and exploiting their interactions. This is said at a time when computational and experimental determination of fundamental data, such as particle-surface interactions, is at the forefront of advances in chemical, solid-state, and atomic physics. Since such elementary processes in LTPs are common to other fields of science and technology, advances in the production of fundamental data motivated by LTPS benefit other disciplines, such as fusion energy research and astrophysics. The basic knowledge obtained from the study of new species in more detail than has previously been possible will have clear linkage with atomic, molecular, and optical physics, computation chemistry, environmental science, plasma fusion, astrophysics, combustion, solar energy, and nanotechnology.

Despite decades of work in LTP, fusion energy, astrophysics, atomic physics, chemistry, and semiconductor manufacturing disciplines, among others, the production of fundamental kinetic and transport data has lagged far behind demand. Computational methods have advanced to the point where it is possible to compute electron-neutral collision cross sections for many species with accuracies of much better than 50%. Similarly, experimental methods have advanced so that excited states can be prepared and isolated for precise measurements. Despite these achievements, lack of long-term support has led not only to a lag in further breakthroughs in experimental and computational methods for obtaining cross sections of new species of interest but has even suppressed the evaluation, organization, and dissemination of data.

Science Challenge 5: Develop new methods to rapidly measure and calculate the fundamental atomic-scale interactions that support the entire field of plasma physics.

Since a large variety of atoms, molecules, ion particles, surfaces, and energies coexist in LTPs, accurate and timely understanding of the elementary atom-scale interactions is a considerable challenge. Atomic and molecular theory and computational methods are needed to provide the fundamental data (e.g., cross sections, reaction probabilities) that characterize interactions between electrons, atoms, molecules, atomic and molecular ions, and surfaces. Complete data sets for electron impact cross sections (in large part responsible for generating and sustaining the plasma) and ion-molecule reactions (responsible for determining the fundamental structures of collisional sheaths and pre-sheaths) in complex gas mixtures are required. For all but the simplest systems and limited parameter regimes, this is not possible today. Significant improvements in the techniques and methods to generate this data are necessary, particularly utilizing massively parallel computing as applied to quantum chemistry, molecular dynamics simulation, and many-body scattering and reaction methods. In addition to the energy dependence of gas phase total cross sections, the dependences on target excitation level, scattering angle of the particles, reaction channel, and energy dispersion are important to accurately describe most LTPs. This higher level of detail is not available for most atoms and molecules. Detailed simulation of collisions with surfaces spanning wide ranges of timescales and length scales and complex multispecies surfaces would also greatly expand the understanding of plasma-surface interactions. Key experimental measurements of these surface reactions are also crucial for complex systems beyond the capabilities of computations. In simpler cases, such experiments can also serve as benchmarks for validating calculations.

A number of databases are now available, assembled largely for other applications. For the most part, however, these data are not well tested nor widely available. In the United States, the most critical issue is human resources. The generation of scientists that produced the first measurements of fundamental data that are so heavily used in LTPS is retiring and passing on, with few young scientists to take their place and continue to advance the field. As described in the roadmap below, the goal is to remediate this situation taking advantage of the state-of-the-art of computation and measurement that can be developed in the coming decade.

Priorities

The prioritized list of recommendations for fundamental data is as follows:

1. Establish a clearinghouse for fundamental data for LTPS. A hierarchical evaluation, ranging from rough approximations to accurate and complete datasets, should be created. The data should be brought together, evaluated by experts, and made widely available by using up-to-date Web-based technologies.

2. Create and support a standing body to identify needs, set priorities, and validate fundamental data in LTPS.

3. Develop new approximate methods, scaling laws, and empirical formulas that can be used to quickly estimate unknown data.

4. Via computation, provide fundamental data for large molecules, clusters, nanoparticles, and interactions with surfaces. This effort would link closely with developments in other fields, such as quantum chemistry, atomic, molecular, and optical physics, and surface physics, and utilize such powerful techniques as molecular dynamics simulation, quantum chemical codes, atomic structure techniques, and emerging high accuracy atomic and molecular scattering codes.

5. A program of experimental measurements needs to be revitalized. New and existing laboratories and techniques should be used to measure key systems, providing key tests of theoretical and approximation method results, and to probe unique or complex situations not approachable with even the most powerful computational methods.