White Paper for *Frontiers of Plasma Science Panel*

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Indicate the primary area this white paper addresses by placing "P" in right column.
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	"P", "S"
• Plasma Atomic physics and the interface with chemistry and biology	P
• Turbulence and transport	
• Interactions of plasmas and waves	S
• Plasma self-organization	S
• Statistical mechanics of plasmas	

Indicate type of presentation desired at Town Hall Meeting.

	"X"
Oral	X
Poster	
Either Oral or Poster	
Will not attend	

Title:	Fundamental Science Challenges in Nonequilibrium Transient Plasmas Sustained in Liquids and at the Liquid-Vapor Interface
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- ***Describe the research frontier and importance of the scientific challenge.***

The kinetics of highly transient non-equilibrium plasmas sustained at a liquid-vapor interface present a number of formidable fundamental challenges [1]. This environment, generated by pulsed electric discharges in the vicinity of the liquid surface, inside macroscopic bubbles in the bulk of the liquid, in aerosols in the gas phase, or possibly in the liquid phase is complicated considerably by strong coupling of several classes of kinetic processes which remain poorly understood. These include (i) propagation of surface ionization waves, plasma self-organization, and plasma instability development over a liquid-vapor interface; (ii) transient surface charge accumulation, solvation, and decay, and its effect on plasma-liquid interface; (iii) coupled radical species kinetics / transport in the vapor phase, (iv) ionization and charge transport in dense media, (v) ion-molecule chemical reactions and multi-body collision induced processes in the liquid phase, (vi) their possible effect on liquid-vapor phase equilibrium, and (vii) extremely high spatial gradients and short relaxation / quenching times, generating shock waves. Although considerable effort has been made in this field over the last few years [1-3], these fundamental issues remain unresolved. Recently, a "critical mass" of crucially important capabilities, combining (i) non-intrusive plasma diagnostics with high spatial and time resolution, (ii) advanced theoretical insight, and (iii) highly efficient kinetic modeling tools has been gained by the research community. This suggests that a focused, collaborative effort in this field may result in a significant breakthrough and considerable societal benefit.

- ***Describe the approach to advancing the frontier and indicate if new research tools or capabilities are required.***

One of the difficulties encountered in quantitative studies of physical and chemical processes in liquid and vapor phase containing plasmas is sustaining the plasma at controlled and reproducible conditions in simple geometries with ample optical access. These conditions are required for *in situ* optical diagnostics, straightforward theoretical analyses, and kinetic modeling calculations allowing direct comparison with the experimental data. In many previous liquid / vapor plasma studies, the plasma has been generated in a two-phase vapor / droplet aerosol mixture, sustained as a manifold of stochastic streamers propagating over the liquid surface, or in macroscopic bubbles in the bulk of the liquid. Quantifying plasma parameters, in particular, time- and spatially-resolved measurements of electric field, electron density and electron energy, and transient species concentrations at these conditions is extremely challenging.

The second difficulty is the need for *in situ* diagnostics with high spatial and temporal resolution, and a high sampling rate, since many surface and vapor-phase kinetic processes, such as ionization wave propagation and generation / decay of radical species occur on very short time scales. At these conditions, capability for measurements with sub-ns time resolution and at a high sampling rate (~1-10 kHz), compared to conventional ~10 ns laser pulse duration, ~10 Hz repetition rate optical diagnostics systems, is critical. In particular, characterization of energy partition in liquid-vapor interface plasmas sustained by electron impact would be significantly advanced by measurements of transient electric field distribution near the liquid surface. This could be achieved by ps 4-wave mixing used for recent electric field vector measurements in a ns pulse discharge over a solid dielectric [4,5] (see Fig. 1). Also, second harmonic generation (SHG), sum frequency generation (SFG), and stimulated Raman scattering (SRS) of intense ps and fs laser light is augmented by the strong electric field produced by electrons accumulated at the liquid-plasma interface that alters the non-linear susceptibility of molecules in the surface layer [6,7]. This opens the door to solvated electron density measurements, with very high spatial and time resolution. In addition, ps CARS [8] and recently-developed fs CARS [9] can be used for highly transient temperature distributions in close proximity to the liquid-vapor interface, which are critical for determining the rates of chemical reactions among evaporating reactants and radicals generated in the plasma. Finally, at near-atmospheric pressure, when collisional quenching of excited species becomes the limiting factor for the accuracy of ns laser-induced fluorescence species concentration measurements [10] (see Fig. 2), the use of ultra-short (ps and fs) duration laser pulses would be essential. Ultra-short pulse two-photon absorption laser-induced fluorescence (TALIF) would also help mitigate laser-induced photochemistry, while simultaneously measuring accurate one- and two-dimensional distributions of atomic species (H, O, and N) with spatial resolution of ~50 μm [11] (see Fig. 3) and *in situ* fluorescence quenching rates.

The third challenge is the lack of experimental data providing a firm basis for development and validation of advanced kinetic models [12], and assessment of their applicability and predictive capability. This is especially critical since strong spatial anisotropy of highly transient interface plasmas (such as surface ionization waves) may well require fully kinetic (i.e. non-fluid) modeling, solving multi-dimensional Boltzmann equation for plasma electrons [13], using adaptive mesh refinement in presence of evolving interfaces, and incorporating an extremely wide range of time scales to encompass kinetic processes from electron energy relaxation time (~ ps to ns) to liquid phase chemistry (~ ms to s). For this, obtaining accurate time-resolved and spatially-resolved (in one or two dimensions [14,15]) data sets at controlled and reproducible conditions, in simple "canonical" geometry is critical. Models validated at these conditions can be applied with confidence for predictive analysis of liquid-vapor plasmas in far more complex environments, such as surface streamers, bubblers, and aerosols.

Based on the current state of the art, we have identified the following key science challenges in studies of liquid-vapor interface plasmas:

- What are the dominant processes controlling formation and propagation of fast surface ionization waves over a liquid-vapor interface (free surface, micro- and macroscopic bubbles, and liquid droplets)? What is the role of electrons and photons in these highly transient processes? How do electric field, electron density, and electron energy in the wave scale with applied voltage amplitude and rise time, and dielectric constant of the liquid?
- How is the vapor phase chemistry affected by high electric field and high-energy electrons in ionization waves over the liquid-vapor interface, amplified by ns rise time voltage pulses and high dielectric constant?
- How does the presence of high electric field and high energy electrons in surface plasmas affect kinetics of surface reactions and evaporation, and possibly phase equilibrium?
- What happens with plasma electrons at the plasma-liquid interface, over a wide range of time scales (~ns to ~s)?
- How do charge accumulation on the liquid surface during the discharge, and current through the bulk of the liquid in the afterglow, affect ion-molecule reactions in the liquid phase?
- What are the conditions when the plasma may be generated directly in the liquid phase?

Meeting these challenges would require a concerted effort involving (i) generation of highly transient plasmas (on ns and sub-ns time scale) at controlled and reproducible conditions, (ii) high time-resolution, spatial resolution, and sampling rate *in situ* diagnostics, and (iii) advanced theoretical analyses and first principles / high fidelity kinetic modeling. In particular, the following time-resolved and spatially resolved measurements of liquid-vapor interface plasma parameters would be essential:

- Electric field vector (ps 4-wave mixing [4,5])
- Electron density and electron energy (Thomson scattering [15], second harmonic / sum frequency generation (SFG/SHG) [6,7]
- Temperature (ps and fs rotationally resolved vibrational and pure rotational CARS [8,9])
- Atomic species number densities (H, O, and N, ps and fs two-photon absorption LIF [11])
- Radical species number densities (NO, OH – planar LIF, *in situ* UV absorption [16]; HO_2, H_2O_2 – cavity ring-down spectroscopy [17])
- Stable product number densities (O_3, NO_x, HNO_3 – *in situ* UV and FT absorption spectroscopy [18])

These measurements will need to be combined with adaptive and hybrid kinetic / fluid modeling [12,13] incorporating surface ionization wave dynamics, surface reaction kinetics, coupled chemical kinetics / transport in the vapor phase, phase transitions, and liquid phase chemistry. The complex kinetic processes involved would never be completely understood without a combined modeling and experimental effort.

- ***Describe the impact of this research on plasma science and related disciplines and any potential for societal benefit.***

These studies would resolve key science challenges listed above, yield accurate quantitative insight into kinetics of liquid-vapor plasmas, and make possible confident prediction of their behavior. These capabilities are critically important for development of a wide range of emerging applications, including (i) generation of reactive nitrogen and oxygen species for biomedical applications; (ii) removal of organic contaminants from water and aqueous solutions; (iii) plasma activation of water for sterilization and disinfection, (iv) wound healing, blood coagulation, and skin cancer therapies; (v) nanoparticle synthesis and materials processing and cleaning in the liquid phase; and (vi) plasma chemical reforming of liquid hydrocarbons and oxygenates.

References

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Figures

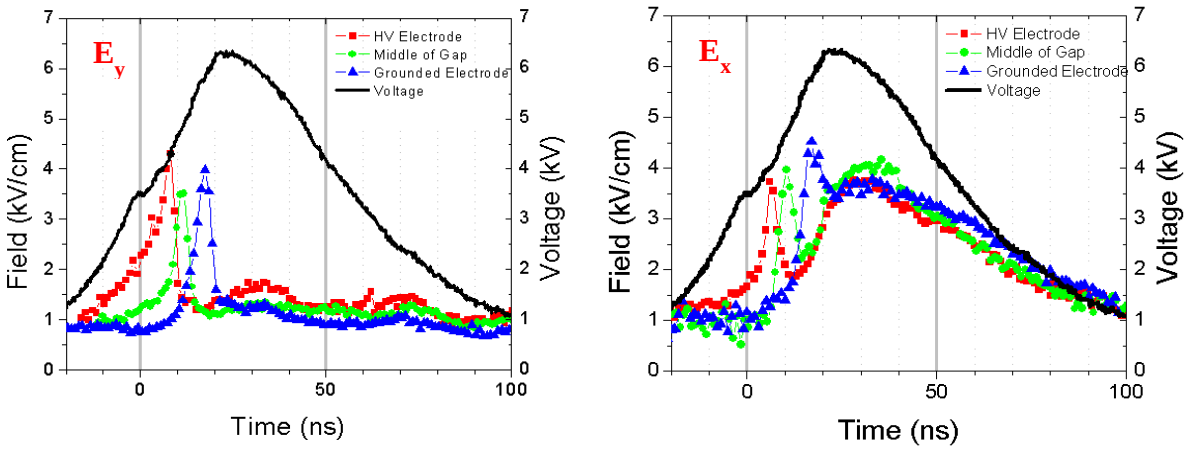

Figure 1. Vertical (E_y) and horizontal (E_x) electric field vector components measured at three axial locations in a ns pulse surface ionization wave discharge in 200 Torr of hydrogen ~100 μm above the alumina ceramic dielectric surface, plotted together with the voltage pulse [5]. Time resolution 1 ns.

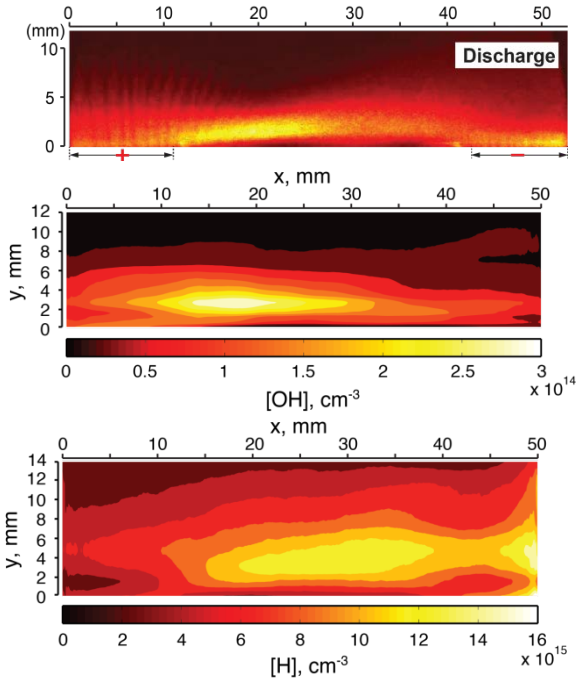

Figure 2. 2-D distributions of plasma emission (top), and OH and H number densities in a double dielectric barrier discharge in H_2O vapor / Ar buffer over distilled water surface (at y=0) [10]. P=30 Torr, locations of electrodes are indicated below emission image.

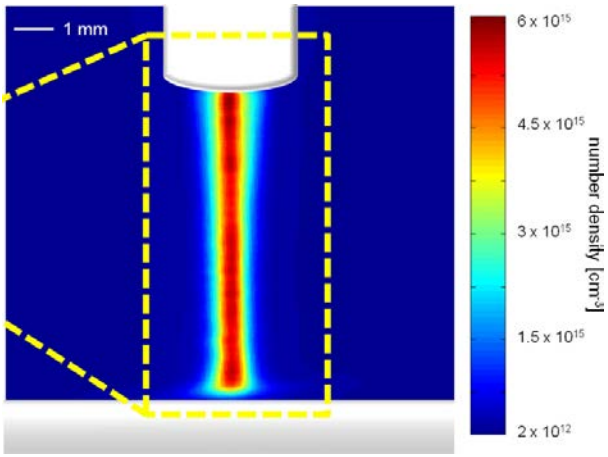

Figure 3. 2-D distribution of O atom number density measured by fs TALIF in an atmospheric-pressure capillary DBD plasma jet in a 2% O_2-He mixture, exhausting to air and impinging on a grounded aluminum surface [11].