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.
Indicate secondary area or areas by placing "S" in right column

	"P", "S"
• Plasma Atomic physics and the interface with chemistry and biology	P
• Turbulence and transport	S
• Interactions of plasmas and waves	
• Plasma self-organization	
• 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:	Probing the interface between plasmas and soft materials
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Describe the research frontier and importance of the scientific challenge

Non-equilibrium processing utilizing low temperature plasmas (LTPs) enables unique surface modification under a variety of conditions. Historically, LTPs have had a substantial impact on solid materials processes for applications including microelectronics and biomedical implants. The extension of controllable non-equilibrium systems to atmospheric pressure using LTPs has transformed the scope of materials functionalization to liquid surfaces, soft polymers, and cellular tissue. The interaction of LTPs and these "soft" material phases represent a new multidisciplinary field with cross cutting fundamentals and applications that by their nature unfortunately fall through the cracks of many basic science funding opportunities that exist in the U.S. Materials directorates see this as a plasma physics challenge whereas plasma physics directorates see this as a materials challenge. In reality this is an area of science that cuts squarely into both areas. Meanwhile, functionalization of soft materials using LTPs is at the forefront of national and international collaborations in Asia and Europe, while there is no comparable program in the U.S., leaving leadership in the field to others.

LTP functionalization of soft materials and liquids is critical to addressing grand challenges and national need. Plasma at the surface of water will enable purification and waste remediation. Functionalization and modification of industrial liquids and soft materials may produce non-equilibrium outcomes at reduced processing temperatures, enabling energy savings. LTPs have the potential for cancer treatment and wound healing, providing new healthcare solutions. Critical to these applications is fundamental understanding of the interface between LTP's and soft materials. Many fundamental scientific challenges remain including (i) second electron emission from soft matter and liquids, (ii) ion exchange at these interface, (iii) the effect of the transfer of large molecules and liquid molecules on the plasma properties, (iv) the transfer of plasma reactivity to the interface, etc.

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

A multidisciplinary, basic science effort built around the existing plasma material interaction (PMI) framework focused on liquids and soft materials would help focus this intellectual diversity to further the science of a highly interdisciplinary field and enable future application research. This could lead to highly impactful applications in critical areas ranging from water treatment and industrial energy efficiency to medicine and managing the nitrogen cycle. The interfacial science of LTPs and soft materials is largely unexplored; the transformative potential is currently unmet. An analogy could be made to the once immature state of understanding of plasma interactions with semiconductor thin films. Fundamental advances in understanding of plasma surface interactions clearly helped enable the 40+ year growth in the microelectronics industry. Similar potential for transformative impact is expected from basic science aimed at probing the interface between plasmas and soft materials.

The fundamental interactions of soft material with photons, charged particles, and non-equilibrium gas phase chemistries produced by LTPs represent a transformative area of science. Soft materials composed of small (e.g. water) and large (e.g. polymers and proteins) molecules interact with this environment in unique photolytic, radiolytic, and electrolytic ways. The multiple spatial and temporal scales associated with these interactions create a uniquely complex environment. Time scales associated with charge transport and chemical reactivity in the gas phase are typically on the order of nanoseconds. When this reactivity is transferred to a liquid, the evolution, particularly with biological entities, continues over hours to days. Likewise,

nanometer-scale structures produced at a soft material interface can impact the transport of species orders of magnitude farther into the bulk. To advance LTP systems for the functionalization of soft materials, a deeper understanding is needed of the underlying plasma-surface science. This will enable detailed interface modelling, in-situ gas phase detection of reactive species, ions and photons, and multi-scale tracking of the material state.

The scale lengths and times for this interface combined with a deeper understanding of how plasmas interact with soft materials require new tools in both computation and experimentation. Computationally, the nanometer-scale interface scale lengths lend themselves ideally to molecular dynamic simulation. These tools have demonstrated utility in both PMI with more traditional materials as well as in the simulation of biological material of interest here. They need to be advanced so that the novel pathways for functionalization of these soft materials via non-equilibrium mechanisms generated by photons, charged particles, etc. to elucidate mechanisms that are not part of the traditional treatment of soft materials. An ideal example of this is the formation of solvated electrons via plasma exposure in water by Rumbach, Bartels, Sankaran, and Go in 2015. How do these impact water chemistry? Do they accelerate or inhibit the uptake or production of reactive species in liquid? Similarly, computational models that incorporate charge equilibration and charge transfer (including surface-hopping and excited state dynamics) into classical interatomic potentials have begun to emerge that once further developed, can reveal mechanisms of complex chemical dynamics in LTPs with unprecedented detail. Experimentally, diagnostics that can probe the soft material directly are needed. Despite the challenges in experimental plasma measurement at atmospheric pressure, this is not the bottleneck in fundamental learning at the soft material interface. Measurement capability at or beneath the surface is needed preferentially in situ during plasma exposure. To achieve this, a multidisciplinary effort that brings together plasma scientists, chemists, biologists, and material scientists that can attack this interface from both directions is needed. Right now the plasma side of this problem struggles with seeing the complete picture of how plasmas interact with soft materials and those who specialize in soft materials aren't fully aware of what the plasma is doing at the surface and near-surface regions. Furthermore, the soft materials themselves will in general affect the plasma structure and dynamics and virtually nothing is understood about this coupling. These gaps in understanding need to be narrowed so that appropriate diagnostics and modelling tools can be developed. In summary, what is required to advance the frontier of plasma interaction with soft materials is a rigorous, multidisciplinary effort that draws not only from the field's current expertise in plasma physics and traditional materials science but also draws in other areas of science that have been largely peripheral in this effort, particularly in the areas of water chemistry, polymers, biology, and medicine.

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

The basic science challenges and breadth of application are well aligned with the basic science mission of several U.S. government agencies most notably NSF, DOE, and 6-1 focused agencies within the DOD; unfortunately the interfacial nature of this research leaves it in a “no man’s land” between basic plasma science, chemistry, biology, and material science. It is hoped that the breadth of applications will attract support from government and industry as these findings enable application level “6-2” development, where a more focused application driven directorate would help to focus this broad spectrum of science to specific needs for specific applications.