White Paper for *Frontiers of Plasma Science Panel*

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	"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	S

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

Title:	**Nonequilibrium processes driven by ultra-short plasma discharges**
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- ***Describe the research frontier*** **and importance of the scientific challenge.**

NONEQUILIBRIUM PROCESSES DRIVEN BY ULTRA-SHORT PLASMA DISCHARGES

Nonequilibrium processes driven by ultra-short plasma discharges is to study the physics and applications associated with volumetric and surface phenomena that are uniquely enabled by ultra-short time plasmas. New technologies are capable of producing plasma discharges that are nanosecond and even sub nanosecond in duration, providing a method for coupling energy into molecular and surface modes more rapidly than thermalization and avalanche arc formation times [1,2]. Much attention has been given to the development and applications of ultrashort laser pulses, however those typically interact with rather small volumes and have very low overall energy efficiencies. Ultra-short pulsed plasmas can be formed throughout volume regions and across surfaces with high efficiency. The reduced electric fields associated with these plasmas can far exceed breakdown and arc formation limits normally associated with long pulse and DC driven discharges and can lead to the formation of nonequilibrium population of atomic and molecular excited states and the production of ions and highly energetic radicals. The rapid deposition of energy into nonequilibrium states can produce reactions that occur without significant background gas or surface heating. Very efficient volume ionization is achievable, enabling magnetic and electric field driven interactions under conditions where such interactions are not normally possible.

Nano- and picosecond discharges at ultrahigh electrical field

High-pressure nonequilibrium plasma has a number of important applications including new areas like medical treatment (sterilization, blood coagulation, wounds healing), biological decontamination, plasma assisted combustion and aerodynamics, and well-known fields such as high power lasers, opening switches, plasma processing, electromagnetic absorbers and reflectors, gaseous pollutants removal, UV and VUV lamps [3-21]. The efficiency of nonequilibrium plasma usage for such applications depends on our ability to control the excitation of different degrees of freedom of the gas during plasma formation, a detailed understanding of fundamental kinetic processes involved, and physics of nonequilibrium discharge development. The precise control of the direction of the energy deposition in the plasma is

possible for relatively short time scales limited by electron multiplication and recombination processes. For high-density media (high-pressure gas in combustion chambers, liquid fuels, bio-liquids) this means sub-nanosecond time scale of the processes. Significant overvoltage and high electron energies can be achieved with a voltage rise time ~1 MV/(cm×atm×ns). Ionization waves propagate with velocity comparable to local speed of light and provide fast and homogeneous excitation of the plasma. Figure 1 demonstrates the maximal discharge time at controllable electric field for discharge in air, P = 1 atm. The critical discharge duration is inversely proportional to the media density and requires picosecond pulses for liquids and high-pressure gases for an efficient selective excitation. Thus, ultra-short pulsed discharges allow the control over electric field in plasma and the direction of energy deposition and media excitation; allow forming pulsed gamma and X-rays, ultra-short e-beams, selective molecular excitation and reactions. Fundamental problems, associated with the high-voltage discharges at extremely high electrical fields, are: non-local electron energy distribution function and formation of run-away electrons of MV energy; unknown differential cross-sections for most of gases; molecular/atomic potential surface modification in ultra-strong external electrical field. For example, in underwater discharge the local electric field reaches the value of 225 MV/cm (Figure 2), which is ~15% from the intramolecular field.

Non-Boltzmann chemically-active systems in ultra-high electric fields

The research will focus on experimental and computational studies of pulsed high-voltage discharges, investigation of electron kinetics, and chemical processes under conditions of strong deviation from Maxwell-Boltzmann equilibrium across translational, vibrational and electronic degrees of freedom of the reactive gases. Two recently discovered kinetic mechanisms demonstrate the importance of nonequilibrium processes in chemically-active systems. The first mechanism includes reactions of "hot" atoms with excessive translational energy. The non-Maxwell translational energy distribution of reagents could lead to significant increase of the rate of radicals production under strong nonequilibrium excitation. Figure 3 demonstrates the efficiency of the "hot" hydrogen atoms conversion into radicals, calculated using Monte-Carlo PIC approach at low gas temperature (T_{gas} = 300 K). The efficiency of radicals production increases twice because of non-Maxwell energy distribution function of H-atoms formed by electron impact dissociation of molecules. The second mechanism takes into account non-equilibrium vibrational excitation of fuel, oxidizer molecules and excitation of molecular nitrogen, which accumulates the major part of vibrational energy in the air-fuel system with plasma excitation. The process of vibrational energy transfer from nitrogen to peroxides and oxygen is responsible for low-temperature ignition and chemical chains development. In combination with radicals production through electronic states excitation this mechanism may decrease a self-ignition threshold down to room temperatures for hydrogen-air and hydrocarbon-air systems. The experimental and theoretical investigations of these thermally-nonequilibrium regimes of chemical reactions will lead to new level of understanding of chemical processes.

Nonequilibrium plasma generation in high-pressure gases and liquids

The proposed study addresses the fundamental mechanisms affecting the design and operation of novel plasma-assisted reactive systems in liquids. The proposed research will lead to deep understanding of generation of plasma near high aspect ratio nanoparticles and sharp tips inside different liquids (oil, liquid fuels, water, bio-fluids) and also in optimizing different applications with in-liquid plasma discharge processes. While underwater electrical discharges have long been used for different applications, such discharges within bulk liquids have recently received renewed interest due to the emergence of several potential application areas. These include high-rate deposition of thin films, biological applications, production of carbon nanotubes, synthesis of nano- and micro-particles, direct excitation/picosecond light sources, in-pipe modification of fuels, and others. For most of these applications, generation and control of a non-thermal discharge in dense liquid media is essential. Fundamental problems, associated with the discharge development in condense media, are: the binary collision approximation cannot be used for electron energy distribution function calculations; electrical fields become comparable with intramolecular fields; electrostriction forces become higher than critical and lead to molecular layers displacement and nano-voids formation.

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

The key approach in advancing the physics of energy transfer and chemical processes in strongly nonequilibrium conditions is a selective, controllable excitation of the media. We will use picosecond and nanosecond discharges at specified electric fields for selective excitation of specified degrees of freedom of the media. The voltage rise rate is on the order of several petavolts per second. Short-pulse discharges allow keeping high electrical fields in the region of maximal discharge energy release, and high plasma homogeneity up to very high media densities. We will measure the rate coefficients for most important processes of radicals' formation in chemically-active systems under non-Boltzmann excitation, including ionization coefficients and quenching of electronically-excited states. Another type of selective nonequilibrium excitation is resonance-enhanced multiphoton ionization and dissociation of atoms and molecules. The REMPI technique typically involves a resonant single or multiple photon absorption to an electronically excited intermediate state followed by another photon which ionizes the atom or molecule. The Raman cell technique combined with the 3J, 5 ns laser will be used for selective pulsed excitation of vibrational degrees of freedom. Different types of plasma discharge cells, reactors and plasma diagnostics are available to achieve the project goals. The experiments will be supported by detailed numerical modeling and theoretical analysis. New research tools required for this work includes FRS, LIF and TALIF diagnostics of single-shot events with nanosecond temporal resolution; analytical and numerical methods for modeling of plasma generation in condense media.

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

Beyond the study of the nonequilibrium physics, the vision for the proposed research activities includes creating and enabling bioelectric technologies for medical and biomedical applications for medical diagnostic and therapeutic engineering, combustion and related engine technologies, for greater efficiencies, reduced emissions from engines, and extended fuels (such as biofuels) for generators, aerospace, and ground and sea-based transportation systems, and agricultural applications, including advanced food processing. The technology will create applications based on previously inaccessible non-equilibrium processes, and represents one of the most important extensions of technology originally developed for the DoD and national laboratories to the civilian sector. The scientific aim of the research is to demonstrate experimentally and theoretically the efficiency of low-temperature pulsed plasma applications, predicting the impact of nonequilibrium plasmas on reactive systems, including new types of engines and combustors. Successful completion of the proposed research will lead to the development of a novel, efficient and inexpensive microfabrication process employing plasma discharges in liquids. The vision will be realized by engineering nano- and picosecond pulsed power systems specifically for biomedical and engineering needs and specifications, and introducing these into important applications in medicine, transportation, and the other areas.

The education and outreach program is driven by the critical need the United States faces attracting people into engineering, and the importance of appreciation for engineering and science by the nation. The goal of the educational component of the proposal is to train the next generation of scientists with the multi-disciplinary background needed to tackle the immensely challenging energy problems, and, specifically, interdisciplinary problem of nonequilibrium plasma assisted processes. Student project participants will have a unique chance to learn from a world-class team of scientists with expertise in low-temperature plasma, non-equilibrium gas discharges, kinetic theory and modeling, and corresponding experimentation. Another important outcome of the Project will be elaboration of completely new teaching courses which will cover the gap between broad range of applications and plasma science on the basis of kinetic theory and detailed physical models of the processes.

A national cross-section is represented with extraordinary experience, creating a unique opportunity for stimulating industry and energizing with pulsed power the national industrial base.

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Figures

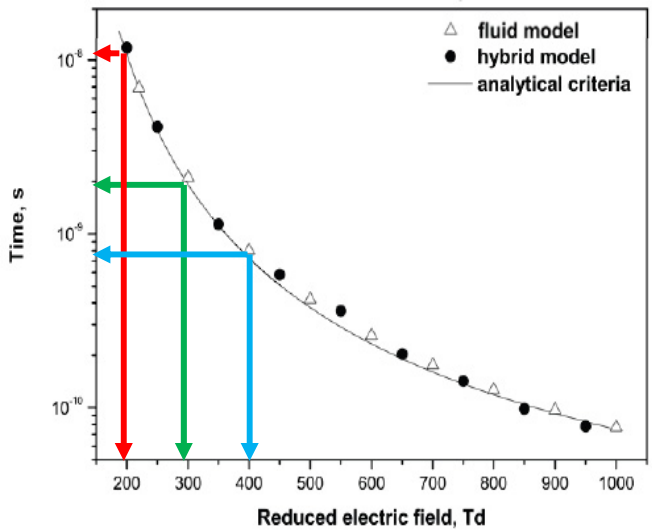

Figure 1 – Critical discharge time at P=1 atm. Air. τ(400Td) ~ 1ns.

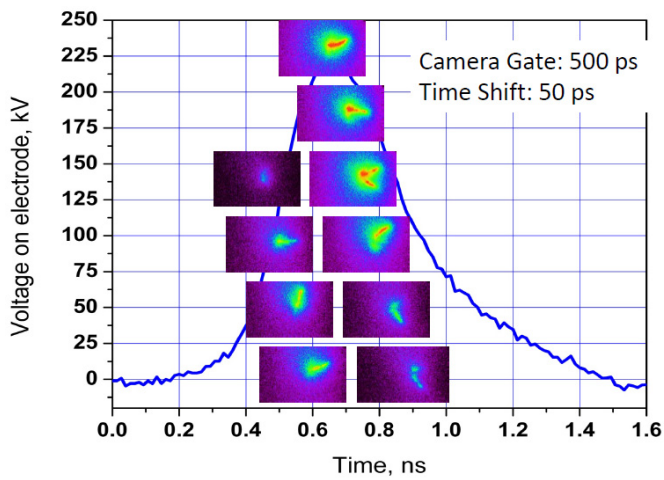

Figure 2 – Picosecond water plasma. Pulse: U = 220 kV; rise time 150 ps; dU/dt = 1.4 MV/ns; Electric field E ~ 225 MV/cm; E/n ~ 670 Td; ionization front propagation speed V = 0.15c.

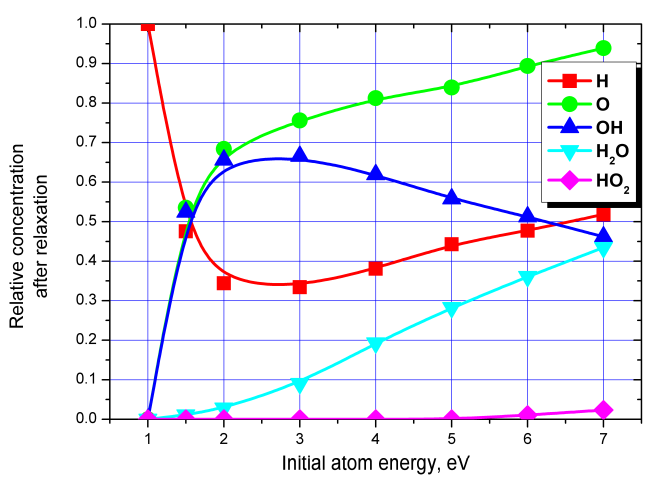

Figure 3 – Relative concentration of particles produced during energy relaxation of one "hot" H atom in the stoichiometric H_2:O_2 mixture at 300 K as a function of initial atom energy.