Frontiers of Plasma Science Town Meeting
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Fundamental Science Challenges in Nonequilibrium Transient Plasmas Sustained in Liquids and at the Liquid-Vapor Interface

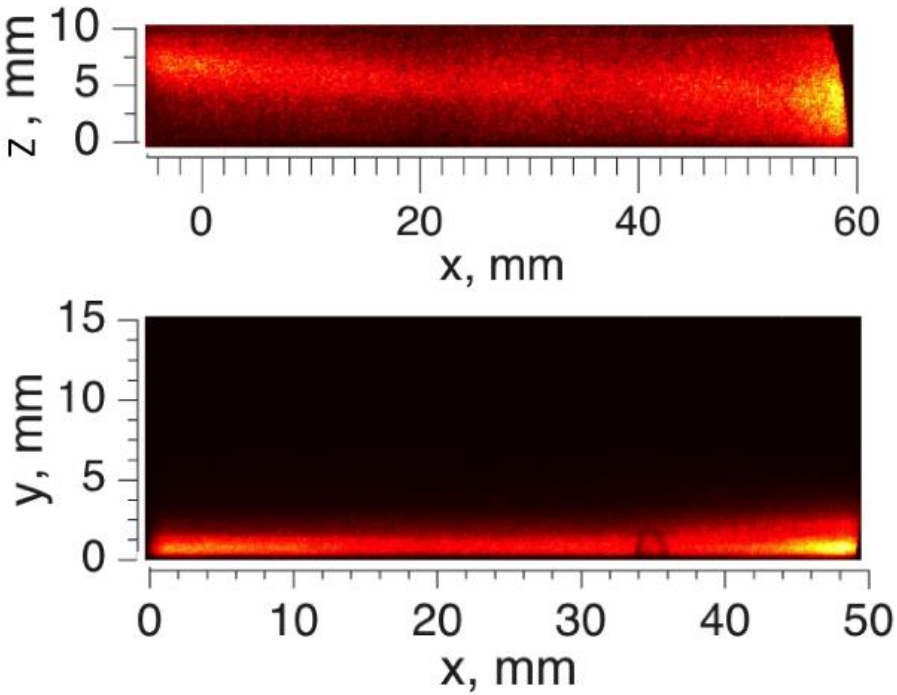
Igor Adamovich (Ohio State University), Edward Barnat (Sandia National Lab), Peter Bruggeman (University of Minnesota), Kraig Frederickson (Ohio State University), David Go (University of Notre Dame), David Graves (UC Berkeley), Vladimir Kolobov (CFD Research Corporation), Mark Kushner (University of Michigan), Michael Lieberman (UC Berkeley), and Sukesh Roy (Spectral Energies)

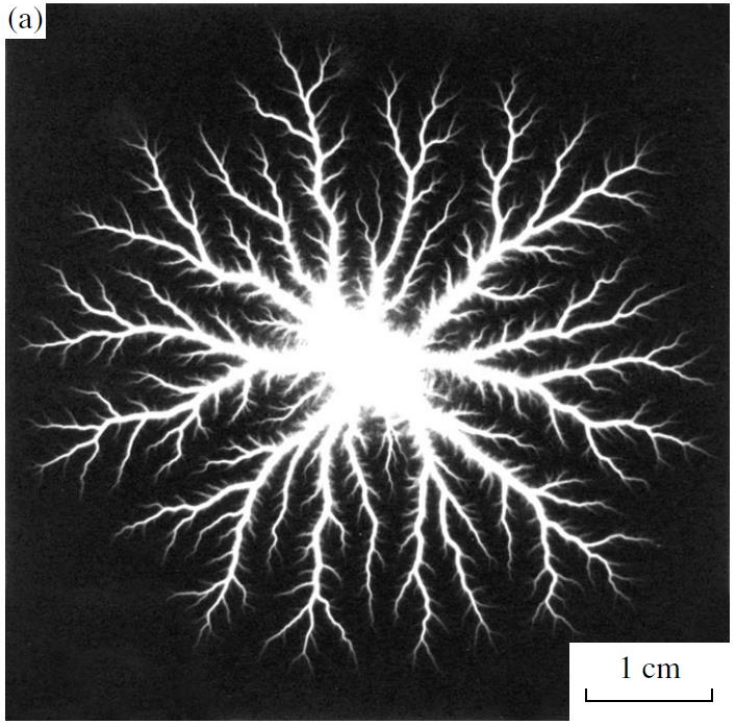
Liquid-vapor plasmas: the frontier

Transient (ns and sub-ns) plasmas at liquid surface, in bubbles, aerosols, or directly in liquid phase: strong coupling of kinetic processes that are poorly understood

- Propagation of surface ionization waves, plasma self-organization, and plasma instability development over a liquid-vapor interface
- Coupled radical species kinetics / transport in the vapor phase
- Transient surface charge accumulation, solvation, decay, and its effect on plasma-liquid interface
- Ionization, charge transport, energy transfer, ion-molecule reactions in dense media: “isolated binary collisions” vs. multi-body collision dynamics
- Effect of vapor and liquid phase kinetics on liquid-vapor phase equilibrium
- Extremely high spatial gradients, short relaxation / quenching times, shock wave generation

Illustration: self-organization in surface plasmas over liquids





Ns pulse surface plasma in low-pressure H_2O vapor / Ar (P=18 Torr) over water:

<u>Very good shot-to-shot reproducibility</u>

Winters et al, J. Phys. D, 2015

µs pulse surface plasma in high-pressure H_2O vapor / air (P=1 atm) over water:

<u>Stochastic, not reproducible</u>

Belosheev, Technical Physics, 2000

Challenges

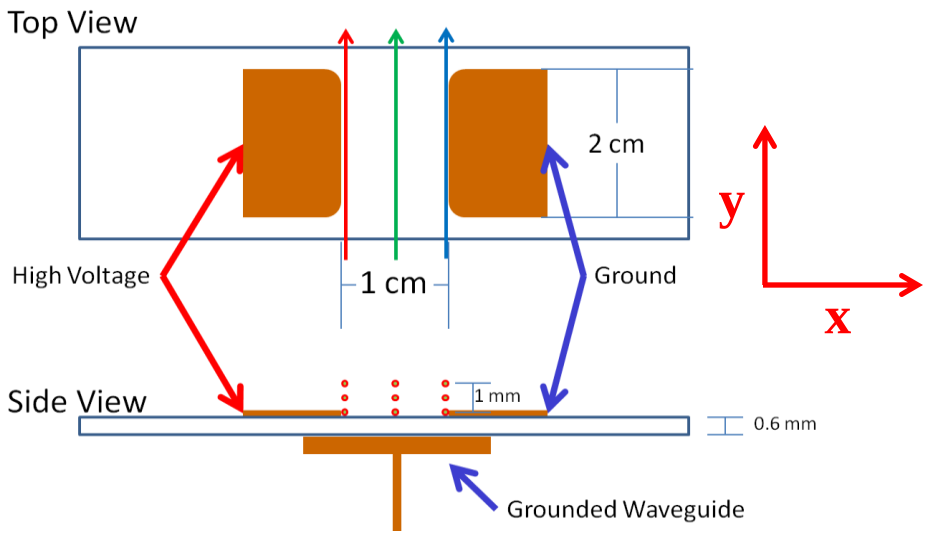
- Sustaining the plasma at controlled and reproducible conditions, in simple geometries with ample optical access, to obtain accurate quantitative insight

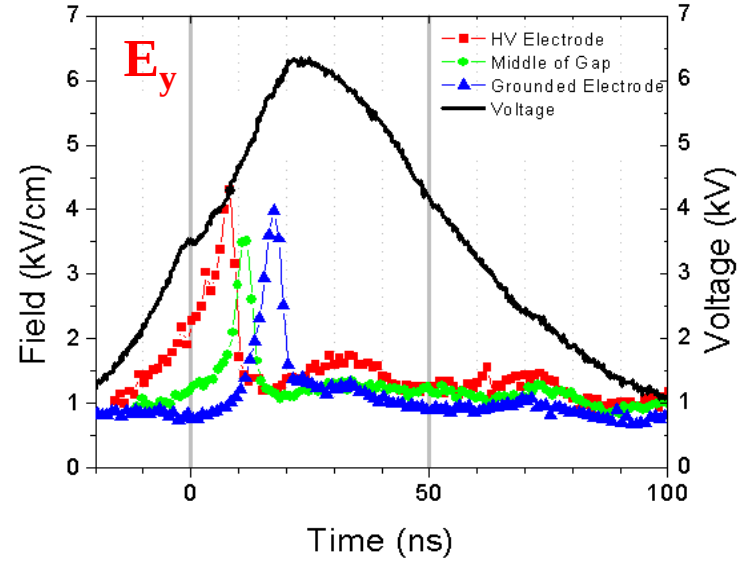
- Pushing diagnostics boundaries: *in situ* optical measurements (i) with sub-ns time resolution, (ii) at high sampling rate (~1-10 kHz) are critical

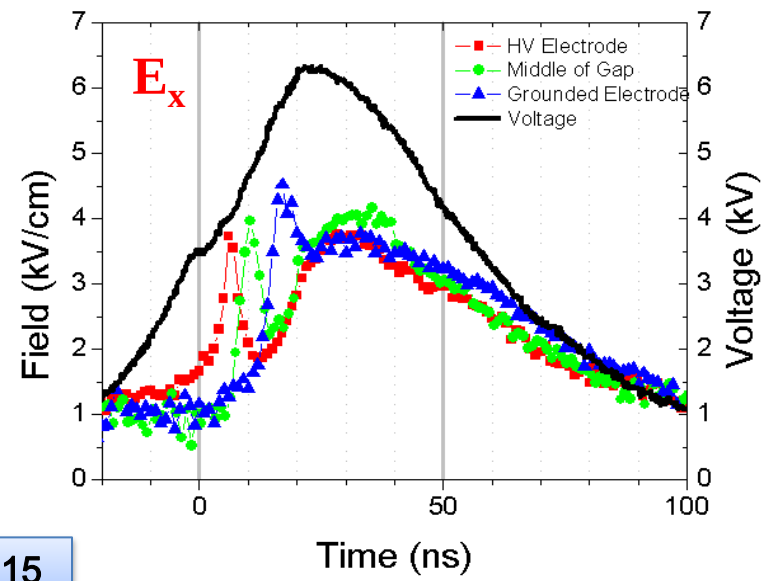
- Pushing theory boundaries: plasma generation directly in liquid phase?

- Pushing modeling boundaries: fully kinetic approach, adaptive mesh refinement, extremely wide range of time scales (~ ps to ~ s) for highly transient, high spatial gradient plasmas (e.g. surface ionization waves)

Recent advances:
$\vec{E}(t)$ in surface plasmas (4-wave mixing)



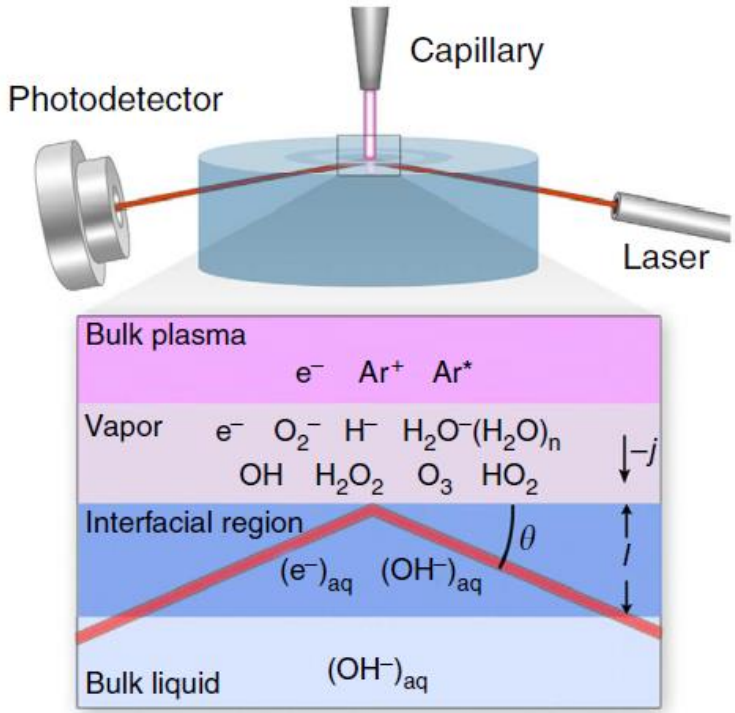


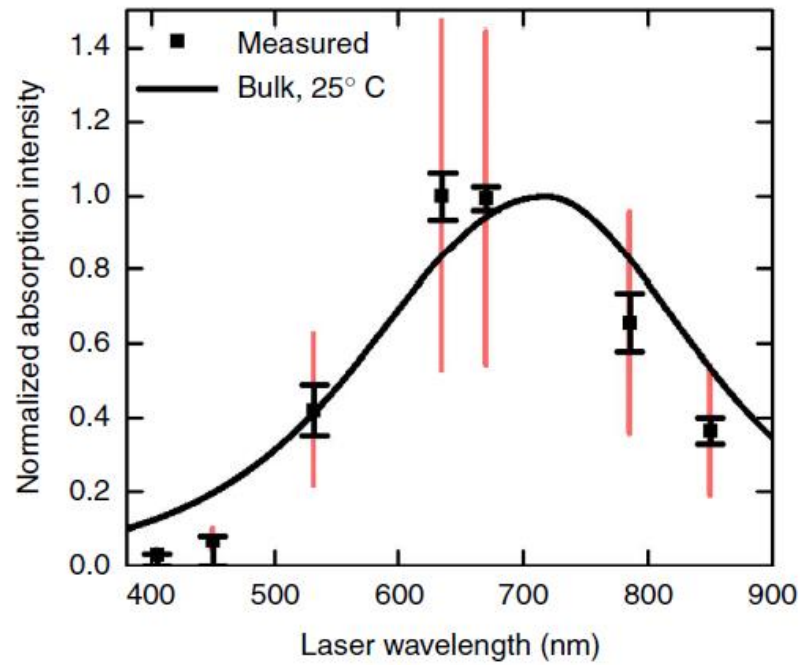


- Surface ionization wave (V=1 mm/ns)
- over solid dielectric (so far)
- Measurements 100 µm from surface
- Both E_y and E_x
- Ps vs. ns: high S/N, time resolution 0.2 ns

Boehm, Goldberg et al, 8th Int. Workshop on Microplasmas, 2015

Recent advances:
Solvated electron measurements (surface absorption)

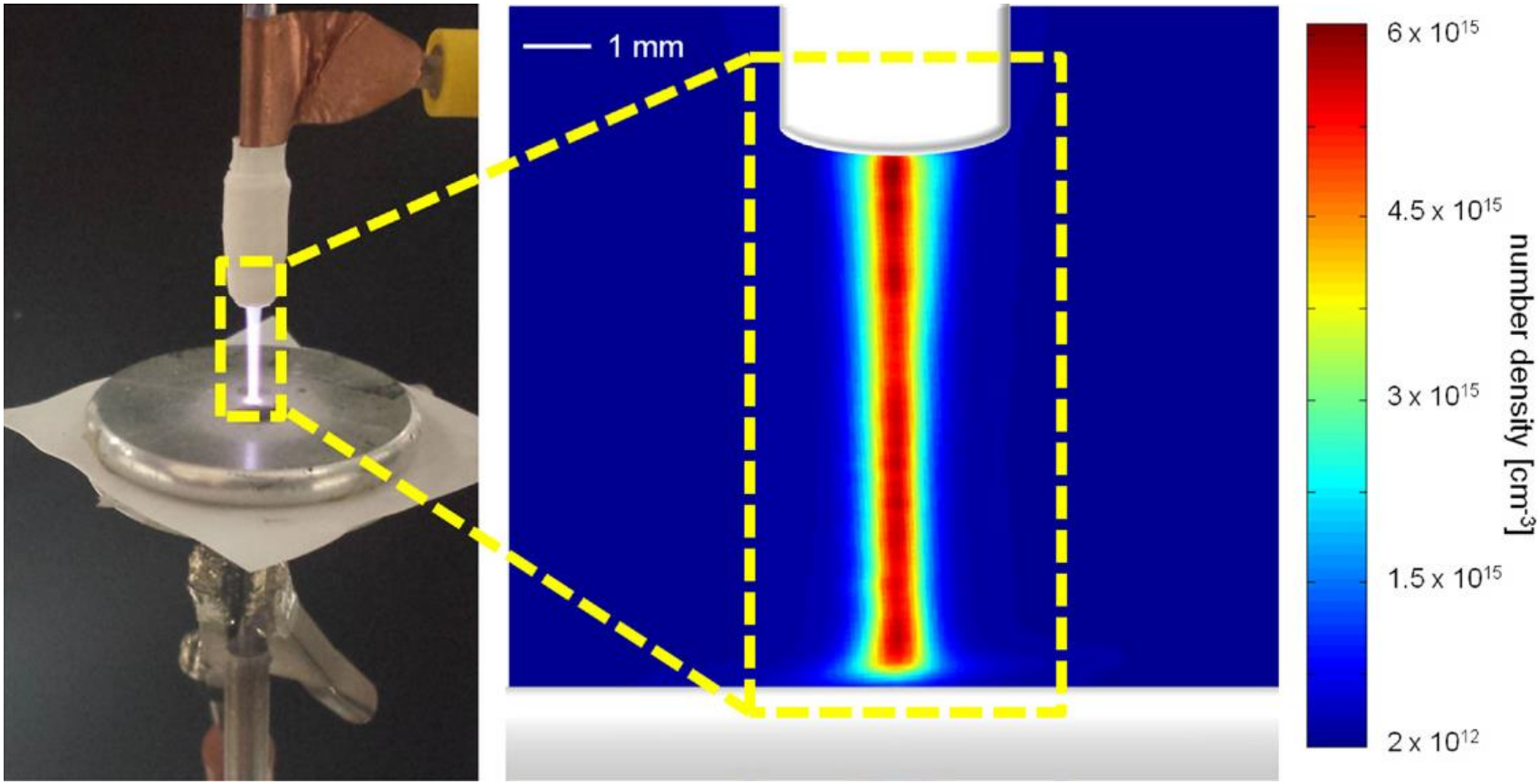




- DC discharge in atmospheric pressure Ar over water
- C.W. laser beam absorption by solvated electrons on the surface
- Potential for highly time-resolved, spatially resolve measurements

Rumbach et al, Nature Communications, 2015

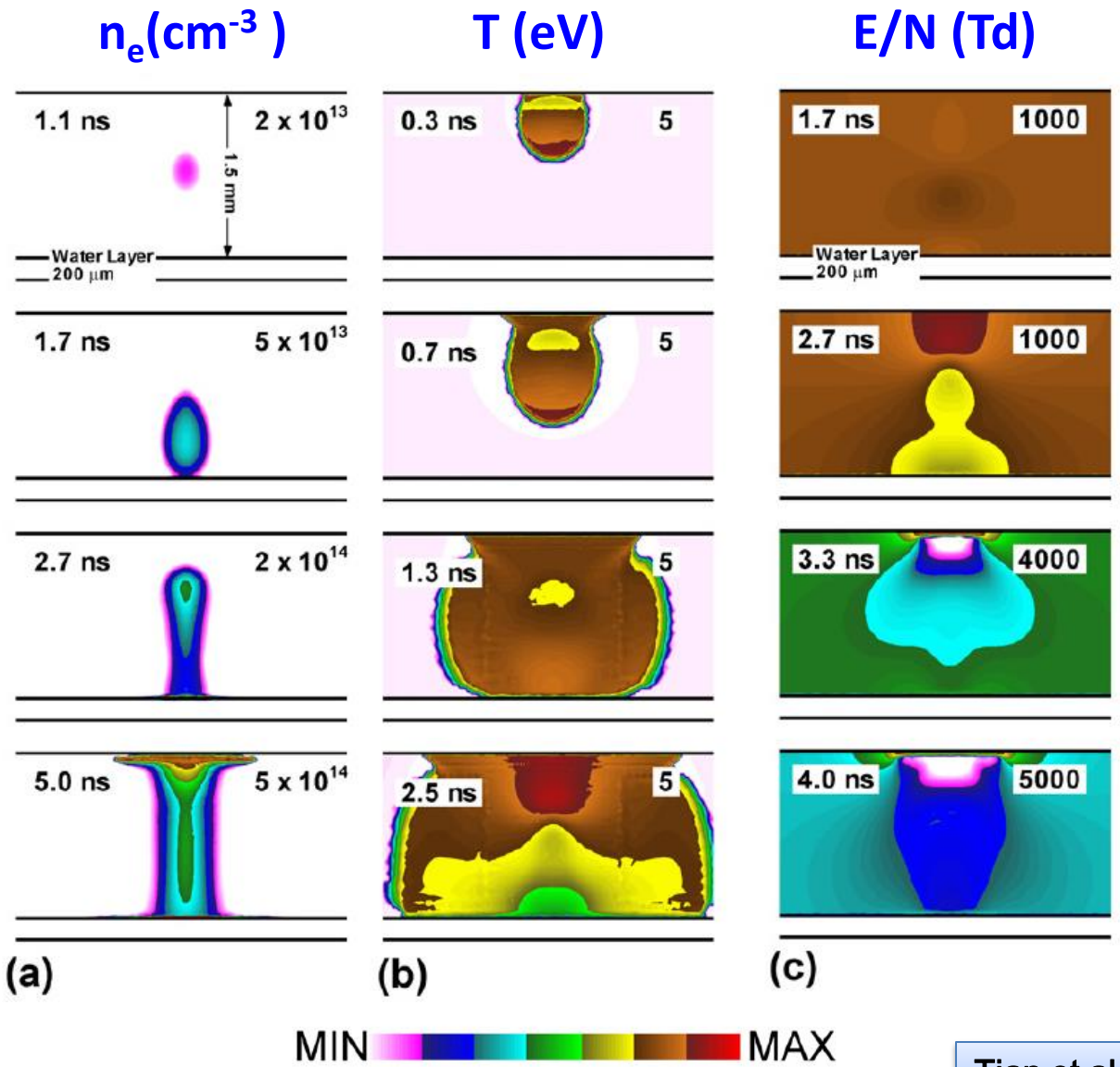
Recent advances:
2-D [O] distribution in atm pressure plasma jet (fs TALIF)



- 2% O_2-He jet in atmospheric air, impinging on a surface
- Fs vs. ns TALIF: photolytic effects minimized, quenching measured directly, 10 kHz sampling rate, 2-D distributions of [O], [H], [N]

Schmidt et al, J. Phys. D, 2015

Recent advances:
Modeling of atm pressure air plasma over water-covered tissue



Tian et al, J. Phys. D, 2014

“Critical mass” of capabilities is here:

(i) non-intrusive plasma diagnostics with high spatial and time resolution,

(ii) advanced theoretical insight

(iii) highly efficient kinetic modeling tools

Unresolved questions

- What are the processes controlling propagation of surface ionization wave plasmas over a liquid-vapor interface (free surface, micro- and macroscopic bubbles, liquid droplets)?
- How do electric field, electron density, electron and photon energy spectra scale with pulse waveform (amplitude and rise time), dielectric constant?
- How do they affect (i) vapor phase chemistry, (ii) kinetics of surface reactions and phase equilibrium?
- What happens with electrons at the plasma-liquid interface, over a wide range of time scales (~ns to ~s)?
- How do charge accumulation on the surface (during the discharge), and current through 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?

State-of-the-art tools: diagnostics

- Electric field vector (ps 4-wave mixing), time resolution 0.2 ns
- Electron density and electron energy: (i) Thomson scattering, (ii) surface absorption, (iii) second harmonic / sum frequency generation at the interface
- Temperature distributions (ps and fs rotationally resolved vibrational and pure rotational CARS)
- Atomic species number density distributions (H, O, and N, ps and fs TALIF)
- Radical species number densities (NO, OH – planar LIF, *in situ* UV absorption; HO_2, H_2O_2 – cavity ring-down spectroscopy)
- Stable product number densities (O_3, NO_x, HNO_3 – *in situ* UV and FT absorption spectroscopy)

State-of-the-art tools: modeling

- Kinetic-fluid and fully kinetic approaches
- Adaptive mesh refinement for transient plasmas, high spatial gradients, and evolving surfaces
- Incorporating extremely wide range of time scales and spatial scales for both phases
- Heterogeneous CPU-GPU computing
- Talk by Vladimir Kolobov, 10:40am

Impact on Plasma Science and Societal Benefit

Advancing fundamental science: quantitative insight into kinetics of plasmas in liquids liquid-vapor interface, confident prediction of their behavior

BUT: plasmas are complex, need insight to design and control, applications must be worth the effort

- Generation of reactive nitrogen and oxygen species for biomedical applications
- Removal of organic contaminants from water and aqueous solutions
- Plasma activation of water for sterilization and disinfection
- Wound healing, blood coagulation, and skin cancer therapies
- Nanoparticle synthesis and materials processing and cleaning in the liquid phase
- Plasma chemical reforming of liquid hydrocarbons and oxygenates

Questions and Comments?