Multiscale Modeling of Plasma Water Interfaces

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Motivation: Plasma-Water Interactions

Applications

- Generation of reactive oxygen and nitrogen species
  - Antimicrobial properties
  - Ammonia production
  - Wound disinfection and healing
  - And more

- Other, domain specific
  - Plasma medicine
  - Synthesize graphene particles and nanosheets
  - Toxic metal detection
  - And much more

Advantages

- Cheap and abundant materials
- "Cold" plasma - useful for thermally sensitive surfaces
  - heat-sensitive equipment
  - bodily wounds

Methods

- **Plasma-in-liquid**
  - Directly ionize water phase with high voltages
  - Requires high voltages, but good source of OH production

- **Bubble plasmas**
  - Gas composition of bubbles may be tailored to adjust chemistry

- **Plasma-liquid interface**
  - Plasma generated in gas phase
  - Transport of reactive species depends on diffusion through water interface
  - Electrons drive RONS production by entering water phase and solvating

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Figure adapted from [3].

Introduction to Zapdos-Crane

- Plasma-liquid interfaces are notoriously nonlinear, multiscale in both space and time, and multiphysics.

- The MOOSE finite element framework was selected as an appropriate platform for development of a general plasma software package:
  - MOOSE applications are natively parallelizable and intended for high performance computing (HPC).
  - All MOOSE apps are able to be coupled together, facilitating multiphysics simulations.

- The MOOSE app Zapdos\(^1\) was developed specifically for modeling plasma transport in 2015-2016:
  - As of 2017, only included support for electron and argon discharges.

- No chemistry capabilities were included in the MOOSE framework, and Zapdos was hard-coded to accept only a handful of reactions.

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Electron density as a function of interfacial loss coefficient in the gas phase (left) and water phase (right). Simulation was performed with Zapdos. Figure adapted from [4].
Model Development

- As of 2017, Zapdos was hard-coded to accept only four species ($e^-$, $Ar^+$ in the gas phase, and $e^-_{(aq)}$ and $OH^-_{(aq)}$ in the water), with 5 total reactions.
- As part of past NSF research, we introduced two new capabilities:

1. Developed Plasma Chemistry Application in MOOSE: “CRANE”
   - https://github.com/lcpp-org/crane
   - Written a model capable of handling an arbitrary number of reactions
   - Reactions can be automatically parsed by code into source and sink terms
   - Coupled to Zapdos to add source terms to drift-diffusion equations

2. Upgraded Zapdos
   - https://github.com/shannon-lab/zapdos
   - Allowed an arbitrary number of user-defined species
   - Included surface charge accumulation
   - Upgraded water model to include neutral transport across interface
**Volumetric Terms:**

Species Density:

\[
\frac{\partial n_s}{\partial t} + \nabla \cdot \vec{\Gamma}_s = R_{st}
\]

Electron Energy:

\[
\frac{\partial (n_e \varepsilon)}{\partial t} + \nabla \cdot \vec{\Gamma}_e = -e\vec{\Gamma}_e \cdot \vec{E} + R_{sj,\varepsilon}
\]

\[\text{Joule Heating}\]

\[
\vec{\Gamma}_s = \pm \mu_s \vec{E} n_s - D_s \nabla n_s
\]

\[
\vec{\Gamma}_e = -\frac{5}{3} \varepsilon \vec{\Gamma}_e - \frac{5}{3} n_e D_e \nabla \varepsilon
\]

Poisson Equation:

\[-\nabla^2 \phi = \frac{\sum_i q_i n_i + q_e n_e}{\varepsilon_0}\]

**Boundary Conditions [6]:**

Electron BC:

\[
\vec{\Gamma}_e \cdot \hat{n} = \frac{1-r_e}{1+r_e} \left[ -(2a_e - 1) \mu_e \vec{E} \cdot \hat{n} n_e + \frac{1}{2} v_{th,e} n_e - \frac{1}{2} v_{th,e} n_{\gamma} \right] - \frac{1}{2} v_{th,e} n_{\gamma} - \frac{2}{1+r_e} (1-a_e) \sum_i \gamma_i \vec{\Gamma}_i \cdot \hat{n}
\]

Ion/Neutral BC:

\[
\vec{\Gamma}_i \cdot \hat{n} = \frac{1-r_i}{1+r_i} \left[ \pm (2a_i - 1) \mu_i \vec{E} \cdot \hat{n} n_i + \frac{1}{2} v_{th,i} n_i \right]
\]

**Reaction Rates:**

\[
R_{sj} = \sum_j \nu_{sj} k_j \prod_{r}^{R} n_r
\]

\[
R_{sj,\varepsilon} = \sum_j \nu_{sj} k_j \prod_{r}^{R} n_r \Delta \varepsilon_j
\]

CRANE: Chemical Kinetics

- **Crane** is a standalone Moose application developed as part of the previous NSF work focused on modeling arbitrary systems of ODEs
- **Source code**: [https://github.com/lcpp-org/crane](https://github.com/lcpp-org/crane)
- **When coupled to Zapdos**, it provides the reaction rate portion of the drift-diffusion-reaction system

\[
\frac{dn_s}{dt} = \sum_{r=1}^{r_{max}} K_{sr}
\]

\[K_{sr} = v_{sr} k_r \prod_i n_i^{r_i}\]

- **Electron-impact reactions** preprocessed with external Boltzmann solver (Bolsig+)
  - Integral of EEDF: \( k_r = \gamma \int_0^\infty \varepsilon f_0 d\varepsilon \)
  - Calculates rate coefficients \( k \) and electron transport coefficients
  - Values stored in look-up tables for a range of mean electron energies

- Developed to allow an arbitrary number of reactions to be added in a human-readable format

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Coefficient</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>( e + Ar \rightarrow e + Ar )</td>
<td>EEDF</td>
<td>( m^2 \text{ mol}^{-1} \text{ s}^{-1} )</td>
</tr>
<tr>
<td>( e + Ar \rightarrow Ar^* + e )</td>
<td>EEDF</td>
<td></td>
</tr>
<tr>
<td>( e + Ar \rightarrow e + Ar )</td>
<td>EEDF</td>
<td></td>
</tr>
<tr>
<td>( e + Ar \rightarrow 2e + Ar^* )</td>
<td>EEDF</td>
<td></td>
</tr>
<tr>
<td>( e + Ar^* \rightarrow 2e + Ar^* )</td>
<td>EEDF</td>
<td></td>
</tr>
<tr>
<td>( Ar^* + Ar \rightarrow e + Ar + Ar^* )</td>
<td>( 3.3734 \times 10^8 )</td>
<td></td>
</tr>
<tr>
<td>( Ar + Ar \rightarrow Ar + Ar )</td>
<td>( 1.807 \times 10^3 )</td>
<td></td>
</tr>
</tbody>
</table>

**How you write it in CRANE:**

```plaintext
[Reactions]
[argon_reactions]
species = 'em Ar+ Ar*'
file_location = 'rate_files'
potential = 'potential'

reactions = '
em + Ar -> em + Ar                : EEDF [elastic] (reaction1)
em + Ar -> em + Ar*               : EEDF [-11.5]   (reaction2)
em + Ar* -> em + Ar               : EEDF [11.5]    (reaction4)
em + Ar -> em + em + Arp          : EEDF [-15.76]  (reaction3)
em + Ar* -> em + em + Arp         : EEDF [-4.43]   (reaction5)
Ar* + Ar* -> em + Ar + Arp        : 3.3734e8'
Ar* + Ar -> Ar + Ar               : 1.807

[]
[]
```

2. Upgrades of Zapdos

Source code: https://github.com/shannon-lab/zapdos

Zapdos required multiple updates to address realistic plasma-water chemistry:

2.1 Accept arbitrary number $s$ of user-defined plasma species

2.2 Add surface charge accumulation for dielectric interfaces

2.3 Include heavy species solvation and evaporation boundary conditions

\[
\frac{\partial n_s}{\partial t} + \nabla \cdot \vec{\Gamma}_s = R_{sr}
\]

\[
\vec{\Gamma}_s = \pm \mu_s \vec{E} n_s - D_s \nabla n_s
\]

\[
-\nabla^2 \phi = \frac{(\sum_i q_i n_i + q_e n_e)}{\varepsilon_0}
\]
2. Upgrades of Zapdos

2.1 Accept arbitrary number of user-defined species

- Existing code was abstracted to include arbitrary species variables
- A new class, ‘HeavySpeciesMaterial’, was added to add species properties (mass, charge, transport coefficients)
- Mobility and diffusivity are by default given by Einstein’s relation (user can change)

```
[gas_species_example]
  type = HeavySpeciesMaterial
  heavy_species_name = Ar+
  heavy_species_mass = 6.64e-26
  heavy_species_charge = 1.0
  diffusivity = 1.6897e-5
[]
```

\[ \mu_s = \frac{Z_s q_e D_s}{k_B T_e} \]
2. Upgrades of Zapdos

2.2 Added surface charge accumulation for dielectric interfaces

- Dielectrics are widely used in plasma discharges, but no interface existed in Zapdos to handle surface charge accumulation

- Surface charge was added to the model in two parts:
  a. ODE at dielectric boundary to describe surface charge accumulation
  b. Interfacial boundary condition for discontinuous electric field

\[ \mathbf{J}_{\text{net}} = \left( \sum_i q_i \mathbf{\Gamma}_i - q_e \mathbf{\Gamma}_e \right) \cdot \hat{n} \]

\[ \frac{d\sigma}{dt} = \mathbf{J}_{\text{net}} \]

\[ (\epsilon_p \nabla \phi_p - \epsilon_d \nabla \phi_d) \cdot \hat{n} = \sigma \]
2. Upgrades of Zapdos

2.3 Include heavy species solvation and evaporation boundary conditions

- A two-way interfacial transport model was added to Zapdos to allow neutral species to transport between gas and liquid phases based on Henry’s law
  a. Henry coefficient, $H$, defines equilibrium concentration of species at interface
  b. Flux equality at the interface allows species to naturally flow in or out of the liquid

- While Henry’s law is an equilibrium relationship, but only a local equilibrium at the interface is assumed - no assumption about bulk concentrations is made

**Henry’s Law (local at the interface):**

\[ H n_G = n_L \]

**Flux Equality:**

\[ D_G \nabla n_G = D_L \nabla n_L \]
Verification of Zapdos-Crane

- Both codes were verified against multiple known problems; two examples:

**Crane vs. ZDPlasKin**
(0D reaction networks)

<table>
<thead>
<tr>
<th>Species</th>
<th>Error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$e^-$</td>
<td>2.19</td>
</tr>
<tr>
<td>$Ar^+$</td>
<td>4.02</td>
</tr>
<tr>
<td>$Ar^{2+}$</td>
<td>2.19</td>
</tr>
<tr>
<td>$Ar^*$</td>
<td>1.79</td>
</tr>
</tbody>
</table>

**Zapdos-Crane vs. Comsol**
(1D Dielectric Barrier Discharge)

- Zapdos-Crane vs. Comsol
Zapdos-Crane was presented at a 2018 APS-GEC Workshop as an open-source plasma tool:


https://github.com/lcpp-org/crane
https://github.com/shannon-lab/zapdos
Plasma-liquid interfaces: a challenge for modern plasma

- Multiscale and multiphysics
  - Electron penetration depth: ~10-100 nm
  - Discharges: mm-m
  - Electron solvation: O(fs)
  - Electron-driven aqueous reactions: O(ns)
  - Chemical reactions: O(us-ms)
  - Species diffusion: O(ms - minutes)

- Strongly coupled behavior between plasma and water
  - Electrons drive chemistry in the interface layer, which change chemical composition of the water
  - Species diffuse in and evaporate out of interface, modifying plasma discharge conditions
  - Electric fields, gas flow can deform water
  - Plasma-induced fluid convection and turbulence is possible
Model of the Plasma-Water Interface in Zapdos-Crane

- Water region assumed to behave as a “dense plasma”:
  - Same drift-diffusion-reaction equations apply
  - Higher background density
  - Relative permittivity of 81

Assumptions:
- Electrons solvate instantly in water phase
  - Solvation time estimated to be O(fs)
- Heat transport is neglected (recently relaxed)
- Electron temperature is not considered in water

Plasma Region:
\[
\frac{\partial n_s}{\partial t} + \nabla \cdot \vec{\Gamma}_s = R_{sr} \\
-\nabla^2 \phi = \frac{(\sum_i q_i n_i + q_e n_e)}{\varepsilon_0}
\]

Water Region:
\[
\frac{\partial n_{s,aq}}{\partial t} + \nabla \cdot \vec{\Gamma}_{s,aq} = R_{sr,aq} \\
-\nabla^2 \phi = \frac{(\sum_i q_i n_i + q_e n_e)}{\varepsilon_0}
\]

Electrons directly drift and diffuse into water:
\[
\vec{\Gamma}_{e,\text{liquid}} \cdot \hat{n} = -\vec{\Gamma}_{e,\text{gas}} \cdot \hat{n}
\]

Heavy Species Solvation (Henry’s Law):
\[
H n_G = n_L \\
D_G \nabla n_G = D_L \nabla n_L
\]

[10] Shane Keniley, Davide Curreli, Corey DeChant, and Steve Shannon, Numerical Modeling of the Plasma-Liquid Interface using the Zapdos-CRANE Open-Source Package, 72nd Annual Gaseous Electronics Conference, College Station, Texas, October 28-November 1, 2019
Case 1: Ar/H₂O plasma on liquid water

A first test of plasma-water interactions was developed in humid argon at atmospheric pressure

- DC circuit with ballast resistor boundary condition was applied
- Grounded wall at x = 1.01 mm
- Plasma-water interface at x = 1 mm

**Water model:**
- 17 species, 67 reactions
- H₂O static background
- Salt included at initial concentration of 10 mM
  - Artificial source term is used to simulate replenishment from bulk for Na⁺ and Cl⁻

**Plasma model:**
- 26 species, 141 reactions
- Humid Argon
- Neutral Ar included as static background
- Reaction network largely adapted from Tian and Kushner [11]

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Results - Ar/H$_2$O plasma on liquid water, species density
Results - Ar/H₂O plasma on liquid water, species density

- Electrons reach high concentrations on the liquid side
- They react quickly, decreasing by a factor of 5 within the first 100 nm
Results - Aqueous Charge Balancing

- Electrons quickly convert to OH\(^-\) through second-order recombination:
  \[2e_{(aq)} + 2H_2O \rightarrow 2OH_{(aq)}^- + 2H_2(aq)\]

- OH\(^-\) accumulation forms highly basic solution at the interface

- Na\(^+\) accumulates at the surface to balance the negative charge injected by the plasma

- This effect was predicted by Rumbach [12] but not seen in previous models [13]

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HO$_2$, H$_2$O$_2$, and OH are the most dominant electron scavengers via reactions:

\[ e_{(aq)} + HO_2 \rightarrow HO_2^- \]
\[ e_{(aq)} + H_2O_2(aq) \rightarrow OH_{(aq)} + OH^-_{(aq)} \]
\[ e_{(aq)} + OH_{(aq)} \rightarrow OH^-_{(aq)} \]

Hydrogen (H$_2$(aq)) reaches high concentrations in the liquid, as expected from electrolysis.

Oxidizing species (O$_2$, O$_3$) are quickly depleted in the interface layer by solvated electrons.

- Increasing solvated electron concentration in the liquid phase should decrease the concentration of oxidizing agents in the liquid.
I. Aqueous Chemical Pathways

- Solvated electrons have been shown to play a dominant role in the plasma-water interface.

- While solvated electrons clearly cause a decrease in oxygen species in the thin interface region (< 1 micron), they also open up additional pathways in the water.

Based on the model results we expect that:

Increasing electron current density will decrease delivery of O$_3$ and H$_2$O$_2$ due to aqueous chemical reaction pathways with solvated electrons.

\[ e_{(aq)} + O_3_{(aq)} \rightarrow O_3^-_{(aq)} \]

\[ e_{(aq)} + O_3^-_{(aq)} \rightarrow O_2_{(aq)} + 2OH^-_{(aq)} \]

\[ e_{(aq)} + H_2O_2_{(aq)} \rightarrow OH^-_{(aq)} + OOH^-_{(aq)} \]
Case 2: Air/H₂O (humid air) plasma on liquid water

- This case involves an atmospheric pressure mixture of nitrogen, oxygen, and water
  - 1D DC discharge, two region model
  - Grounded wall at liquid boundary \( (x = 1.01 \text{ mm}) \)
  - \( V_{\text{appl}} = -3 \text{ kV} \)
  - Both air and liquid chemistry models are adapted from Tian’s 2015 thesis and Buxton et al [4] [7]

- Humid air plasma model \((\text{N}_2/\text{O}_2/\text{H}_2\text{O})\)
  - 32 species, 187 reactions
  - Nitrogen, water, and hydrogen: Itikawa database
  - Oxygen: TRINITI database; both at: www.lxcat.net
  - Water introduced with vapor pressure BC at liquid interface (amounts to ~1% humidity)

- Water model
  - 29 species, 93 reactions
  - Permittivity: \( \varepsilon_r = 81 \)
  - Initial pH of 7 \( ([\text{H}_3\text{O}^+_{\text{aq}}] = [\text{OH}^-_{\text{aq}}] = 5 \times 10^{-11} \text{ cm}^{-3}) \)
  - Solvation occurs instantly upon entering water phase

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Case 2: Air/H₂O (humid air) plasma on liquid water, density

\[ R = 0.55 \text{ M}\Omega \]
\[ j_e = 6.1 \text{ kA m}^{-2} \]
Case 2: Air/H$_2$O (humid air) plasma on liquid water, density
Solvated Electrons, Penetration Depth

- In all cases the solvated electrons quickly react within the first 100 nm
- Penetration depth* slightly decreases with electron current density
- 75 nm at 4 kA m\(^{-2}\) to 69 nm at 33 kA m\(^{-2}\)

\[n(x) = n_0 e^{-x/l}\]

*PD is here defined as 10% of the surface value, not classical “l”
What is happening in the first 80 nm?

- The thin electron layer is very chemically active
- Electrons react significantly with all other radicals in the liquid phase
- Second order recombination rate increases quickly with electron concentration
- The terminal product of most reactions is hydroxide OH⁻

\[ e_{(aq)} + HO_2(aq) \rightarrow HO_2^-(aq) \]

\[ e_{(aq)} + HO_2^-(aq) + H_2O \rightarrow OH_{(aq)} + 2OH_{(aq)}^- \]

Dominant reactions with \( e_{(aq)} \) averaged over first 80 nm

- \( 1 \text{ M} = 1000 \text{ mol m}^{-3} \)

- Reaction also includes \( H_2O \)
Recently Started Validation of Plasma-Water Interaction Model

- The model presented in this work must be validated to ensure that it is accurately simulating plasma-liquid chemistry

- Experiments carried out by Prof. Sankaran’s group (UIUC) are measure aqueous conditions (reactive oxygen species concentrations, pH) after plasma treatment

- The aqueous chemistry and plasma-water interaction model is compared to experimental measurements of aqueous species and pH

- Parametric scan of plasma parameters are performed to observe changes in reactive species production

Conclusions

- Crane and Zapdos are two new, open-source, software applications available to the LTP community, which can be used for the simulation of Low Temperature Plasmas with complex Plasma Chemistry.

- Crane and Zapdos were used to study Plasma-water interactions, allowing innovative features, such as:
  - Gas and liquid phases dynamically and implicitly coupled
  - Water affects discharge, and vice-versa

Future Work:

- Experimental validation of plasma-water model
  - Qualitative and semi-quantitative validation of the plasma-water model
  - Comparison to experimental measurements (Sankaran) of a plasma-water interface electrolytic cell

- Tackle the challenge of solving the coupled nature of plasma-water interface
  - Develop physically meaningful definition of solvated electron penetration depth, compatible with observations
  - Determine how solvated electrons affect the generation of selected reactive species in the water
References (1)


References (2)


