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Structural, Thermophysical, and Dynamic Properties of Hydroxylammonium Nitrate (HAN) Water Mixtures at the Liquid-Vacuum Interface

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- **Background**
- **Computational Methods**
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  - Test Matrix
- **Results**
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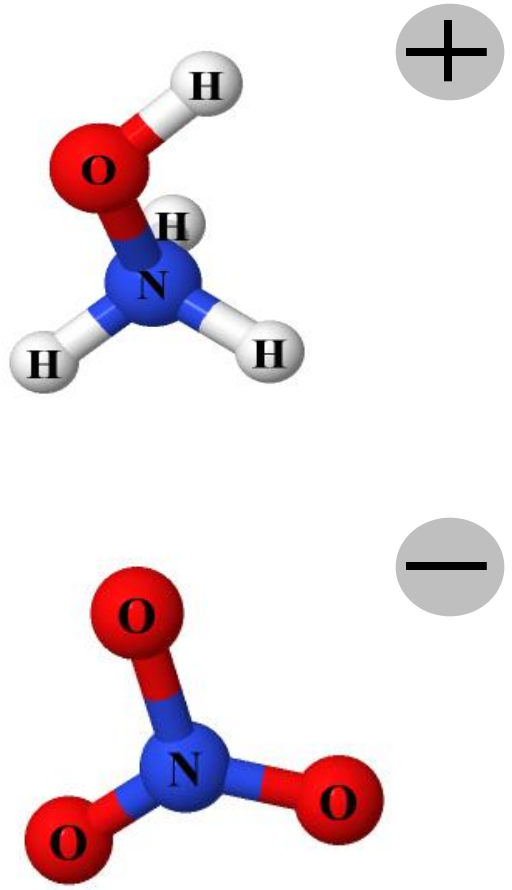
    - HAN-H_2O Liquid Vacuum Interface
- **Future Work**



Cations and Anions for hydroxylammonium nitrate (HAN)

Introduction

Ionic Liquids as Green Propellants

- Hydrazine, a heritage in-space mono-propellant, is highly toxic and results in expensive manufacturing and handling procedures
- ASCENT (Advanced Spacecraft Energetic Non-toxic) propellant is an alternative being developed by the AFRL
  - Composed of **HAN** (Hydroxylammonium Nitrate) and **HEHN** (Hydroxyethylhydrazinium Nitrate) [1]
  - Demonstrated in a 1-N chemical mono-propellant catalytic thruster in the 2019 GPIM mission
- Resolving basic (1) **<u>thermophysical properties</u>** and fundamental (2) **<u>thermal and catalytic decomposition mechanisms</u>** remain an active area of research.

https://mediaarchive.ksc.nasa.gov/#/Detail/8998

https://www.wpafb.af.mil/News/Article-Display/Article/1433869/afrl-green-monopropellant-licensed-to-nevada-small-business/

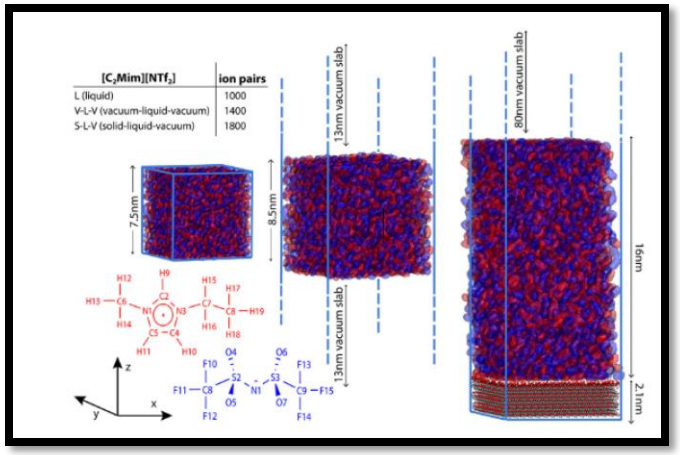
Properties	Hydrazine	LMP-103S	AF-M315E	GEM
Theoretical Specific Impulse I_{sp} (s)	236	252	266	283
Density ρ (g cm^{-3}) (@ 20 °C)	1.0	1.24	1.47	1.51
Volumetric Specific Impulse ρI_{sp} (g s cm^{-3})	236	312.48	391	427
Vapor Pressure P_V (kPa) (@ 25 °C)	1.91	15.1	1.4	<1
Toxicity	High	Moderate	Low	Low

Summary of performance and physical properties of green and traditionally used monopropellants [2]

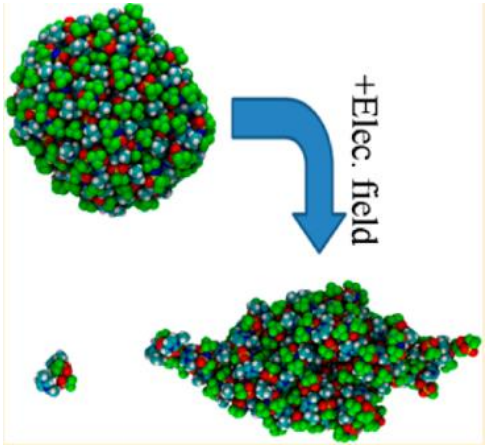
[1] Auman, Kerstyn. "Non-Catalytic Microwave Ignition of Green Hydrazine Replacements." Master's Thesis, Pennsylvania State University, 2019., and Fortini, A. J., J. R. Babcock, and M. J. Wright. "Self-adjusting catalyst for propellant decomposition." United States patent US 20080064913A1 (2008). [2] A. E. S. Nosseir, A. Cervone, and A. Pasini, "Review of State-of-the-Art Green Monopropellants: For Propulsion Systems Analysts and Designers," Aerospace, vol. 8, no. 1. 2021, doi: 10.3390/aerospace8010020.

Investigating Fundamental Properties of ILs

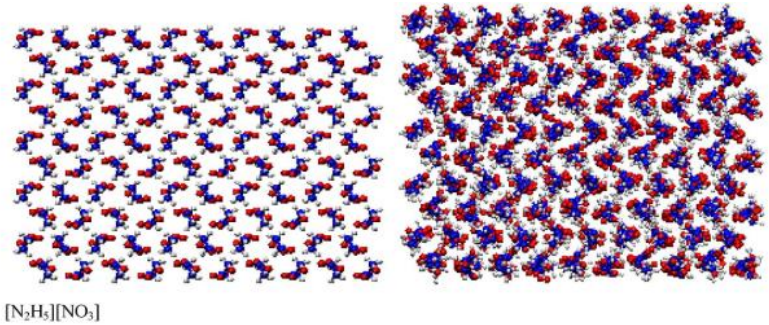
- Previous Studies have…
  - Quantified density, condensed-phase structure, viscosity, surface tension, conductivity, etc.
  - Investigated aprotic ionic liquids (e.g., EMIM NTf_2) both fundamentally and for exploratory simulation conditions (i.e., electric fields, surface interactions, etc.)
  - Ab initio and DFT calculations have investigated protic ILs such as HAN and HEHN
- **<u>Research Objectives</u>**:
  1. Resolve fundamental thermophysical and structural properties of HAN-based IL mixtures
  2. Investigate thermal decomposition pathways for HAN-based IL mixtures



Fundamental study of EMIM NTf_2 in the bulk, liquid-vacuum interface, and liquid-solid interface [1]



Classical MD simulations of EMIM NTf_2 nano-sized droplets under electric fields [2]



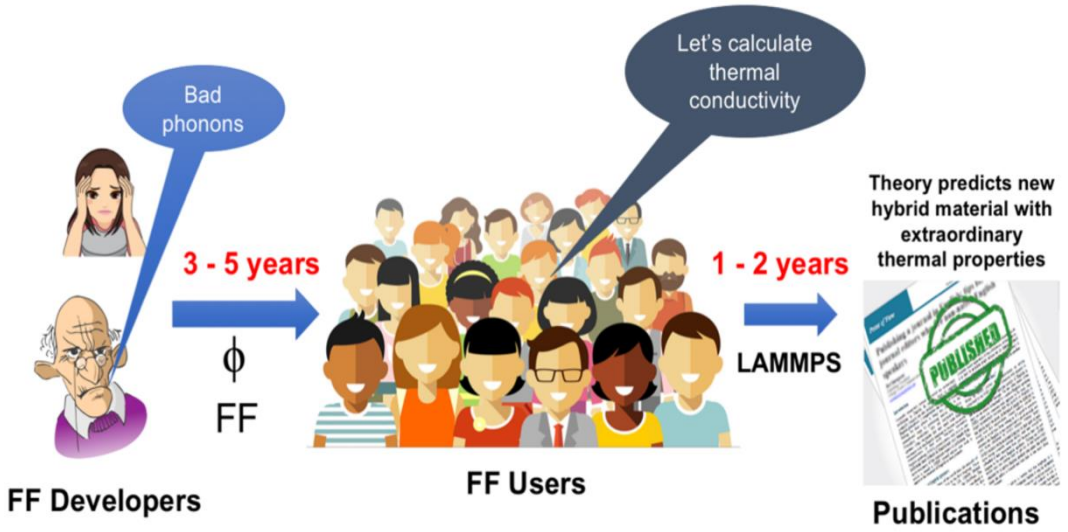
Bulk-phase simulation of hydrazine derivatives [3]

[1] N. Vučemilović-Alagić *et al.*, "Insights from molecular dynamics simulations on structural organization and diffusive dynamics of an ionic liquid at solid and vacuum interfaces," *J. Colloid Interface Sci.*, vol. 553, pp. 350–363, 2019, doi:10.1016/j.jcis.2019.06.017. [2] B. D. Prince, P. Tiruppathi, R. J. Bemish, Y.-H. Chiu, and E. J. Maginn, "Molecular Dynamics Simulations of 1-Ethyl-3-methylimidazolium Bis[(trifluoromethyl)sulfonyl]imide Clusters and Nanodrops," J. Phys. Chem. A, vol. 119, no. 2, pp. 352–368, Jan. 2015, doi:10.1021/jp507073e. [3] K. E. Gutowski, B. Gurkan, and E. J. Maginn, "Force field for the atomistic simulation of the properties of hydrazine, organic hydrazine derivatives, and energetic hydrazinium ionic liquids," Pure Appl. Chem., vol. 81, no. 10, pp. 1799–1828, 2009, doi:10.1351/PAC-CON-08-09-24.

Background

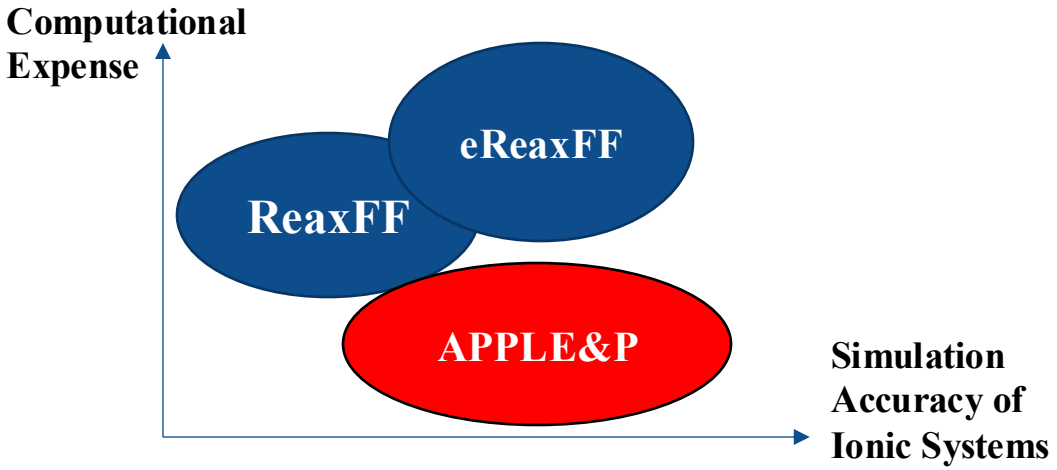
Molecular Dynamics Force Fields

- Choosing the force field (FF), or set of empirically-determined parameters that define the system's interatomic potential, is a crucial aspect of conducting molecular simulations
  - FF development can be a long, difficult process!



Cartoon representation of force field development life cycle [1]

- FFs can be characterized into multiple categories based on
  - Material properties
  - Underlying physics and chemistry (i.e. functional form)
    - All-atom vs. coarse grained
    - nonreactive vs. reactive
    - **Polarizable vs. nonpolarizable**



[1] H. Chan et al., "BLAST: Bridging Length/time scales via Atomistic Simulation Toolkit," CoRR, vol. abs/2002.1, 2020, [Online]. Available: https://arxiv.org/abs/2002.10401.

Polarizable Force Fields: APPLE&P

Non-Polarizable MD Force Field

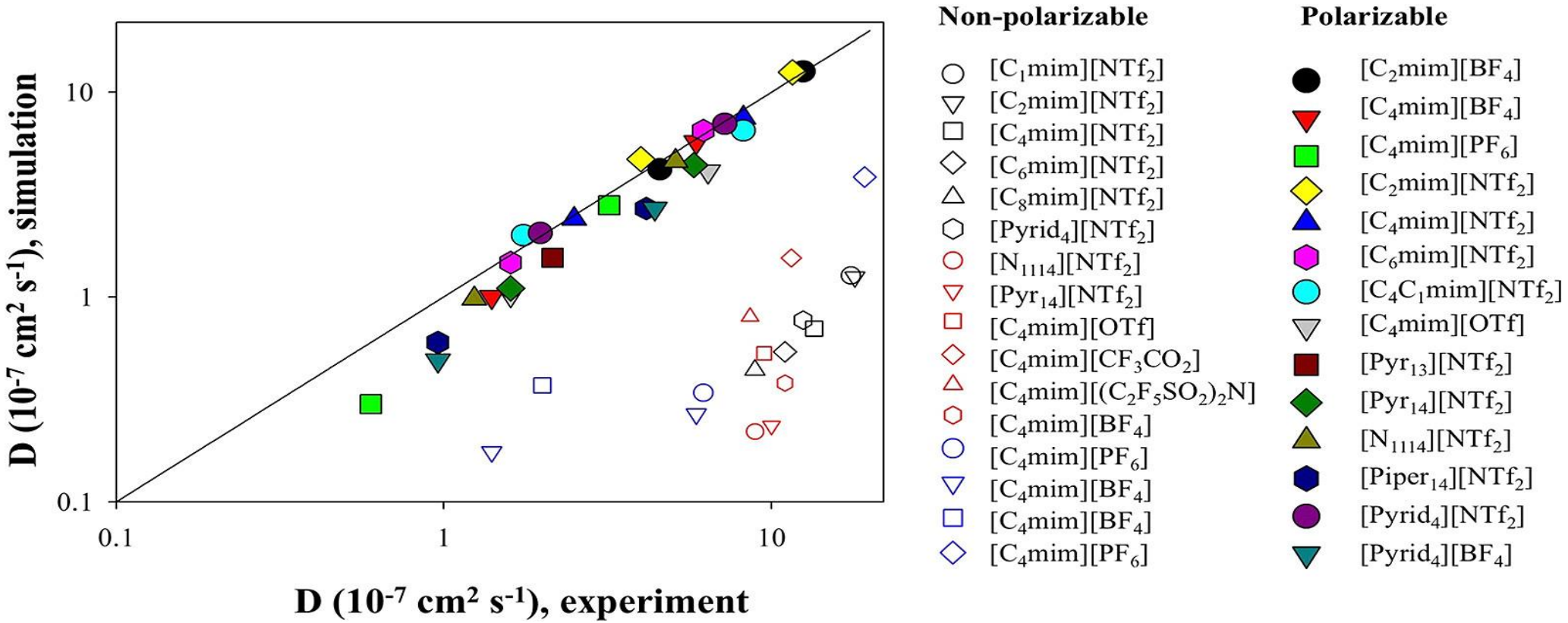
$$U_{ij}(r_{ij}) = \sum_{bonds} \frac{1}{2} \boldsymbol{k_b}(r - r_0)^2 + \sum_{angles} \frac{1}{2} \boldsymbol{k_a}(\theta - \theta_0)^2 + \sum_{torsions} \boldsymbol{k_\phi}[1 + \cos(n\phi - \delta)] + \frac{1}{4\pi\epsilon_0} \sum_{i \neq j} \sum \frac{\boldsymbol{q_i q_j}}{r_{ij}} + 4\boldsymbol{\epsilon_{ij}} \sum_{i \neq j} \sum \left[\left(\frac{\boldsymbol{\sigma_{ij}}}{r_{ij}} \right)^{12} - \left(\frac{\boldsymbol{\sigma_{ij}}}{r_{ij}} \right)^{6} \right]$$

Polarizable MD Force Field

$$U_{ij}(r_{ij}) = \sum_{bonds} \frac{1}{2} \boldsymbol{k_b}(r - r_0)^2 + \sum_{angles} \frac{1}{2} \boldsymbol{k_a}(\theta - \theta_0)^2 + \sum_{torsions} \boldsymbol{k_\phi}[1 + \cos(n\phi - \delta)] + \frac{1}{4\pi\epsilon_0} \sum_{i > j} \left(\frac{\boldsymbol{q_i q_j}}{r_{ij}} \right) + \sum_{i > j} \left(\boldsymbol{A_{\alpha\beta}} \exp(-\boldsymbol{B_{\alpha\beta}} r_{ij}) - \boldsymbol{C_{\alpha\beta}} r_{ij}^{-6} + \boldsymbol{D} \left(\frac{12}{\boldsymbol{B_{\alpha\beta}} r_{ij}} \right)^{12} \right) + \frac{1}{2} \sum_i \vec{\mu}_i \cdot \vec{\mathrm{E}}_i^0$$

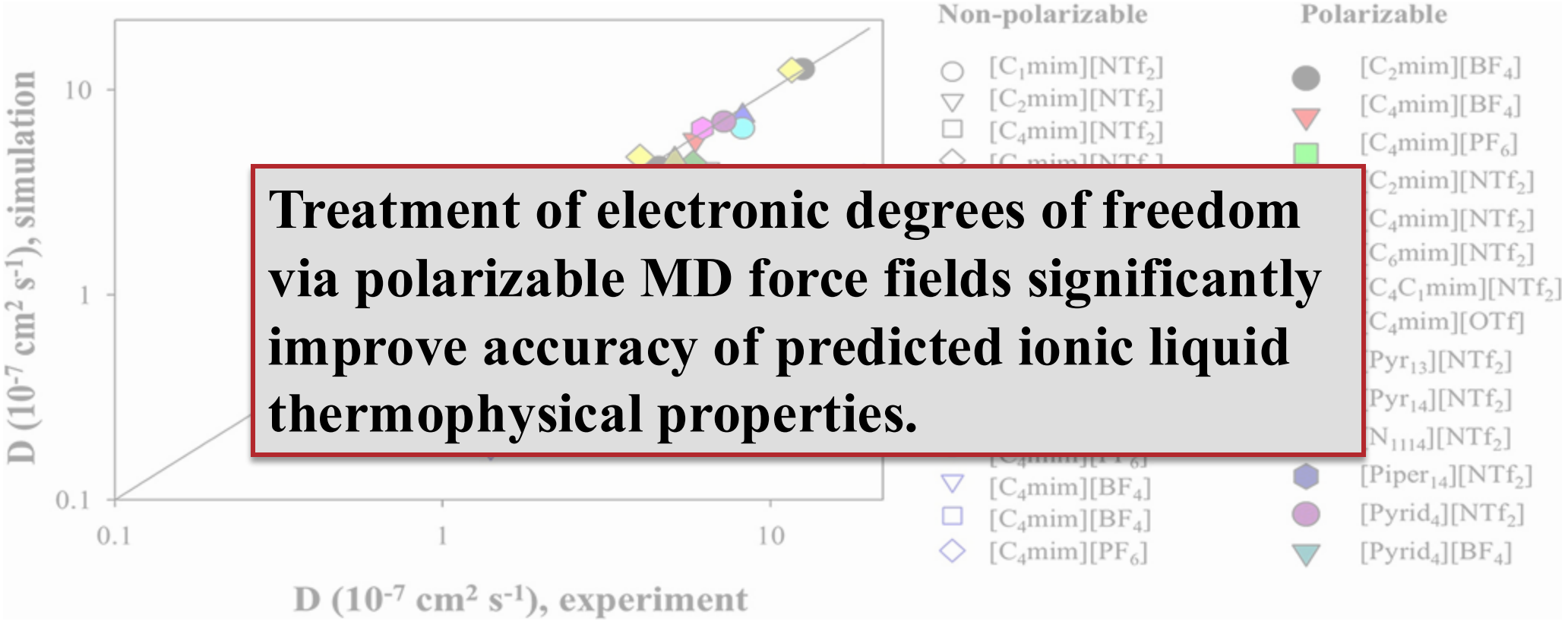
$U_{ij}(r_{ij})$: total potential energy
k_b, k_a, k_ϕ: bonded term coefficients
q_i: permanent atomic charge
$\vec{\mu}_i$: induced dipole at force center i
$\vec{\mathrm{E}}_i^0$: electric field due to fixed charge
$A_{\alpha\beta}, B_{\alpha\beta}$: repulsion parameters
$C_{\alpha\beta}$: dispersion parameters
α, β: atom types

Polarizable Force Fields: APPLE&P



Comparison of polarizable and non-polarizable force fields based on self-diffusion coefficients obtained by MD simulations and experimental results.

Polarizable Force Fields: APPLE&P



Treatment of electronic degrees of freedom via polarizable MD force fields significantly improve accuracy of predicted ionic liquid thermophysical properties.

Comparison of polarizable and non-polarizable force fields based on self-diffusion coefficients obtained by MD simulations and experimental results.

Computational Methods

Methods—Molecular Dynamics Force Fields

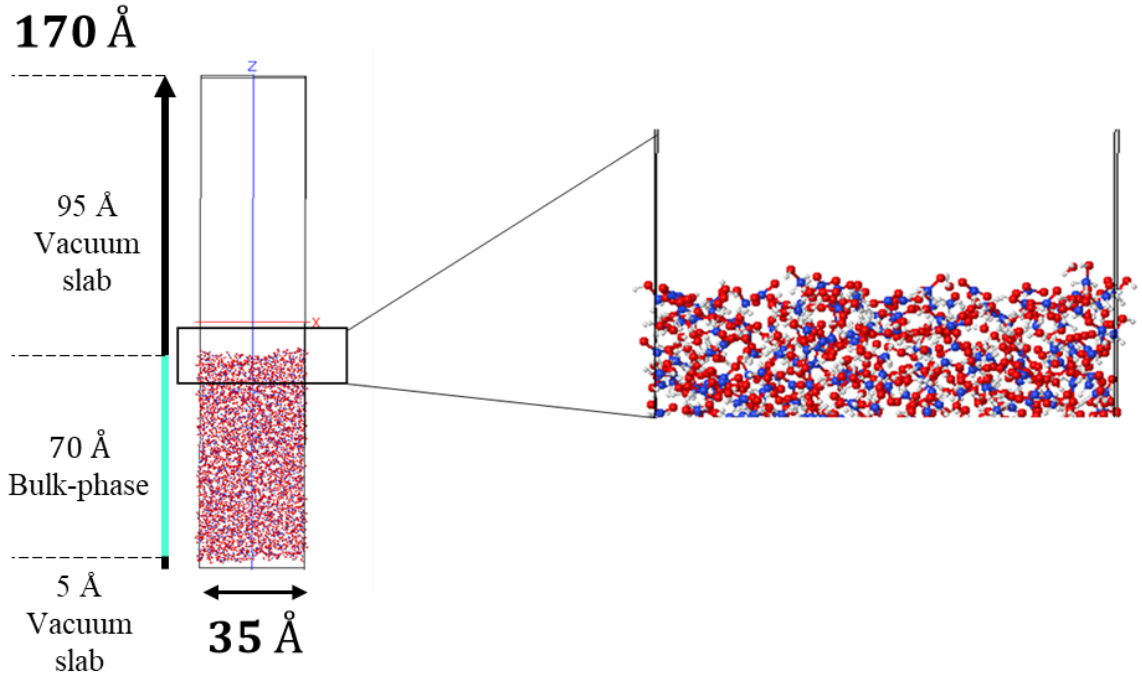
- In this work, we are interested in fundamental properties of HAN-based IL mixtures in the bulk phase and at the liquid-vacuum interface
- Starting with simpler systems allows for ease in analysis for primary AF-M315E constituents

Investigated Simulation Test Matrix

Conditions	Composition	Analysis
Bulk Condensed Phase (Separate Work)	ASCENT	• Structural Properties • Dynamics and transport properties
Liquid-Vacuum Interface	**HAN-H_2O**	• **Structural Properties** • **Evaporative Mechanisms**
Droplet-Vacuum Interface (Future Work)	HAN-H_2O HEHN	• Structural Properties • Evaporative Mechanisms

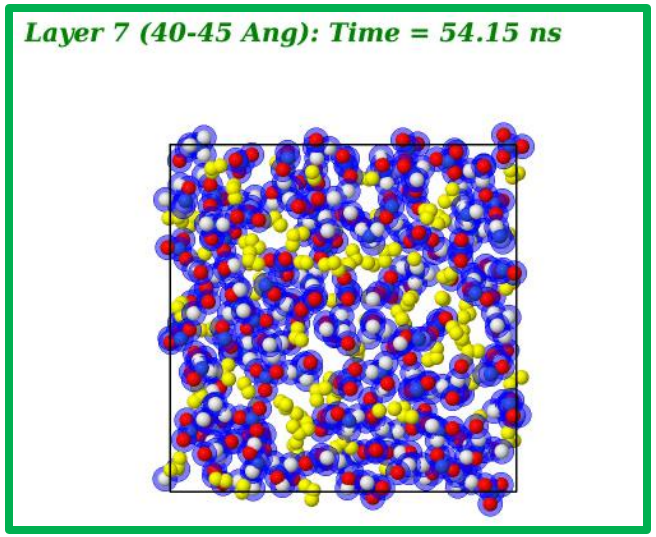
Simulation Setups

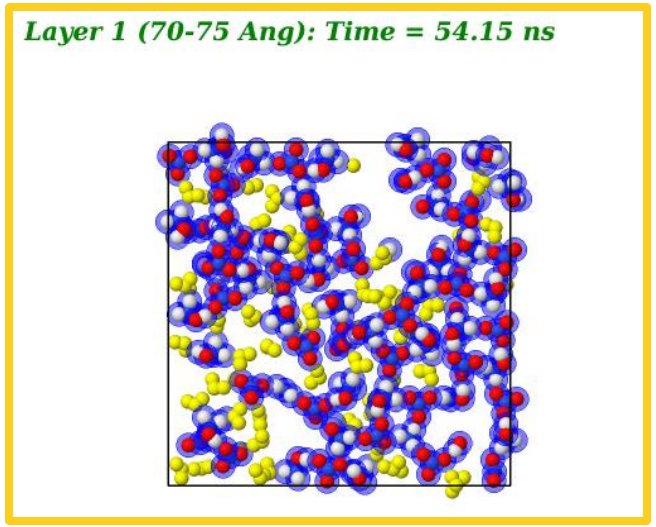
- **Liquid-Vacuum Interface Simulations**
  - Periodic system
  - Long, NVT runs for ~100 ns
  - 80% HAN, 20% Water by wt. %
    - 660 HAN / 880 Water Molecules
  - Required ~900 core hours / nanosecond of simulation time → nearly *4 weeks* of total run time

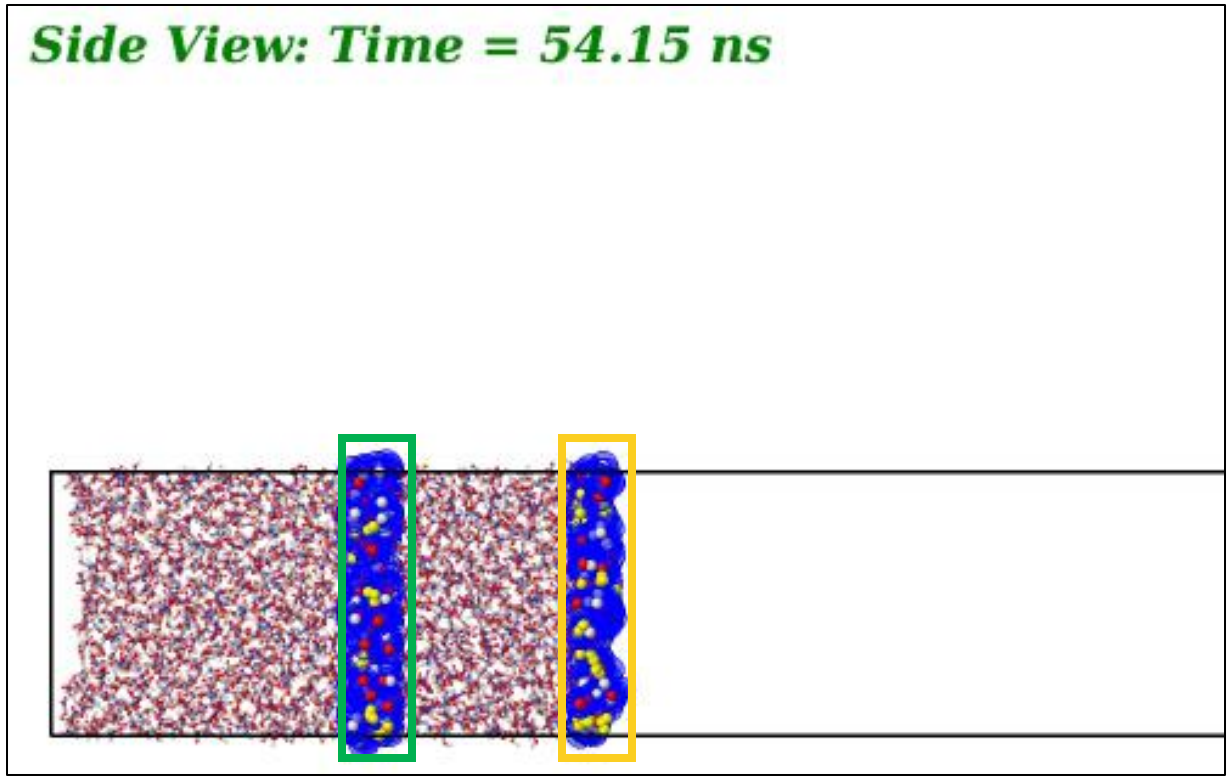


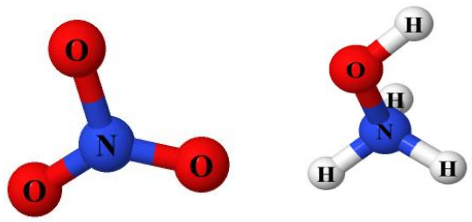
Results

L-V Interface Simulations – Visualization







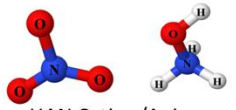


HAN Cation/Anions

Water Molecules

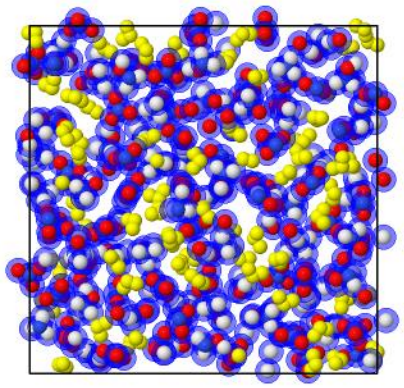
Evaporated Water Molecules

L-V Interface Simulations – Visualization

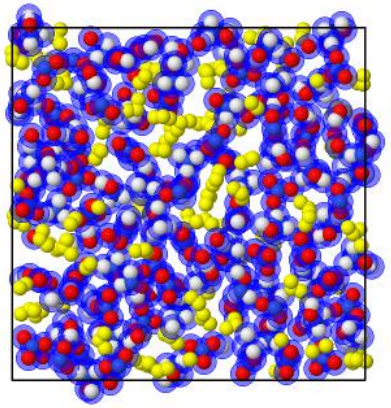


Water Molecules

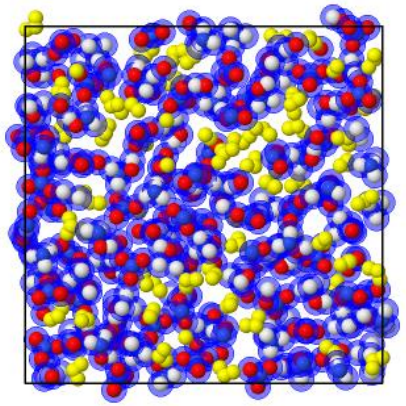
Layer 7 (40-45 Ang): Time = 55.50 ns



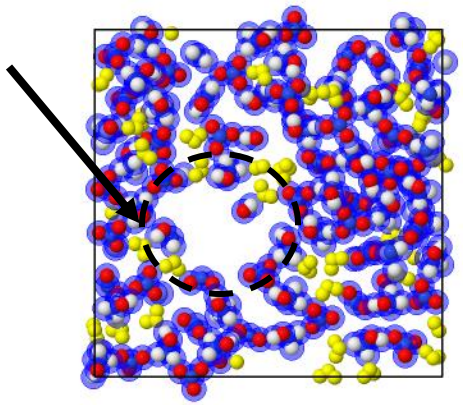
Layer 7 (40-45 Ang): Time = 59.10 ns



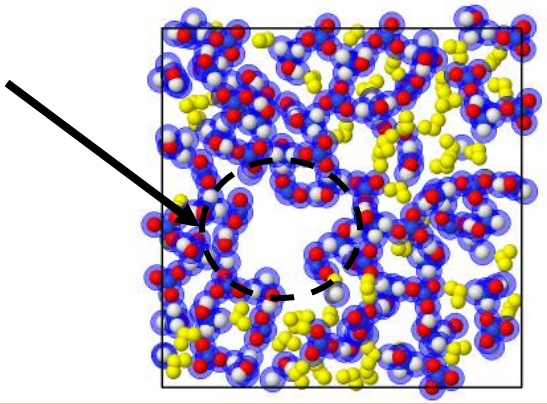
Layer 7 (40-45 Ang): Time = 69.60 ns



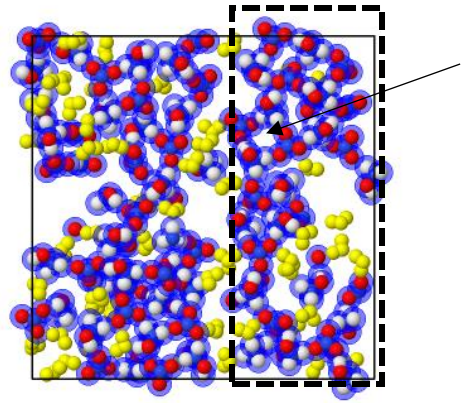
Layer 1 (70-75 Ang): Time = 55.50 ns



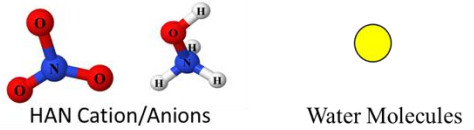
Layer 1 (70-75 Ang): Time = 59.10 ns



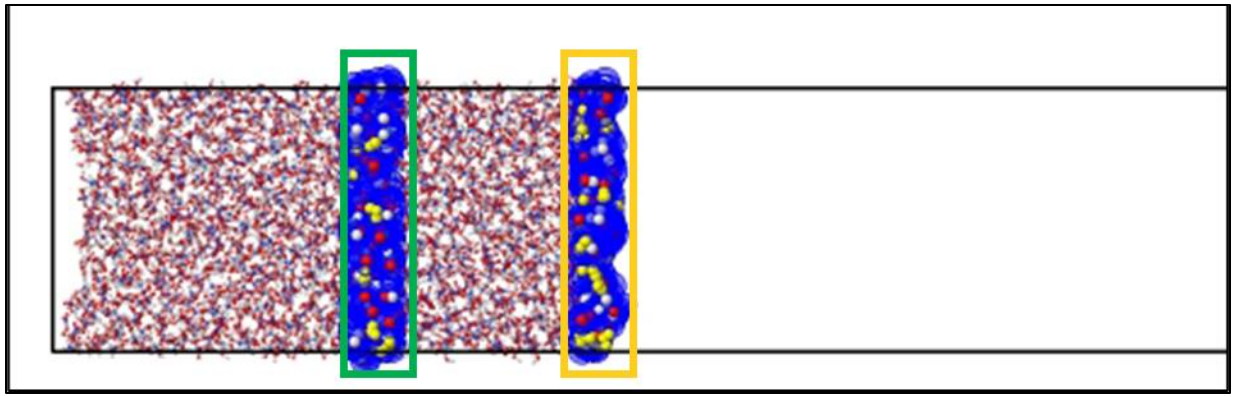
Layer 1 (70-75 Ang): Time = 69.60 ns

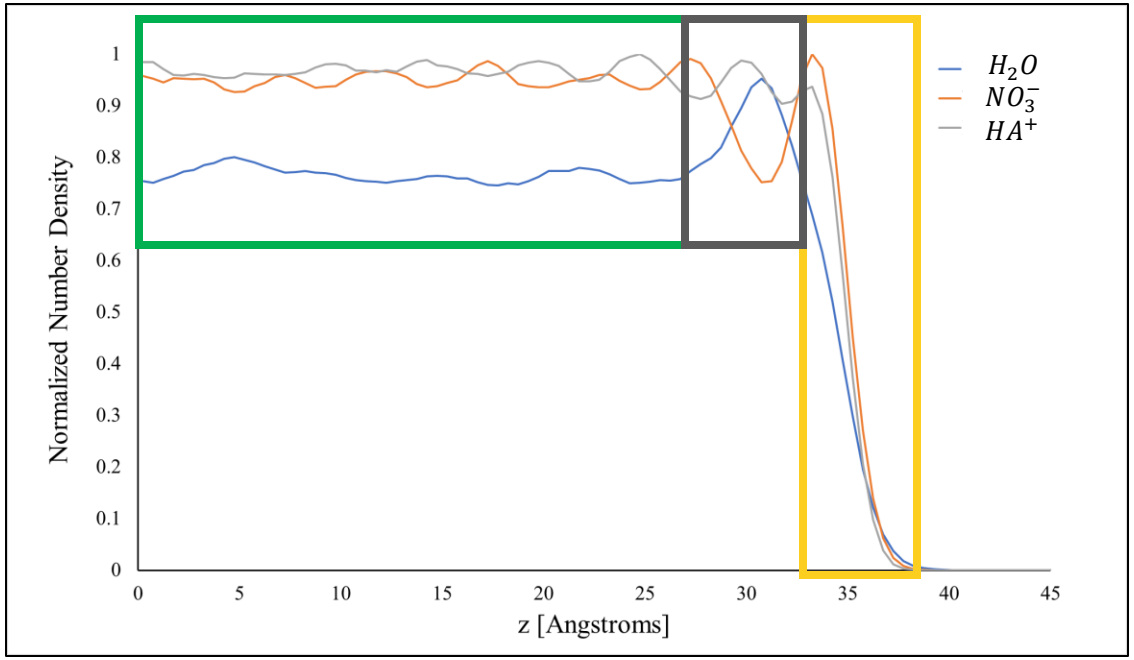


L-V Interface Simulations – Number Density



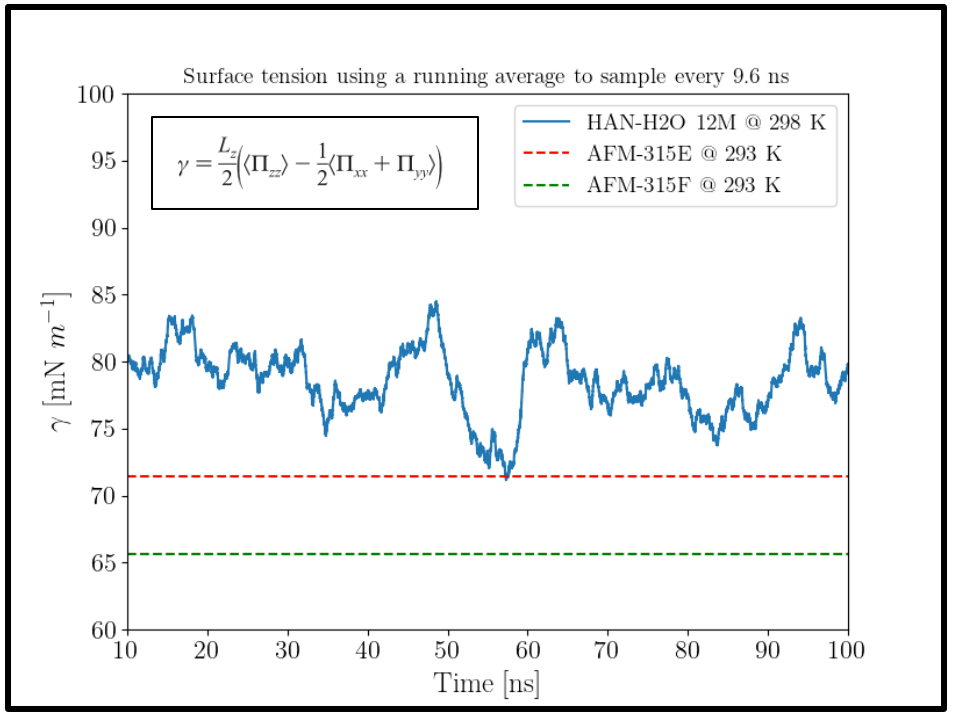
- Normalized number density can be quantified along the HAN-Water system
  - A drop in HAN cation/anion density results in an increased density of water molecules near the interface
- Two regions can be identified, both the bulk region with a mixed state and the interfacial region, where the number density falls off dramatically





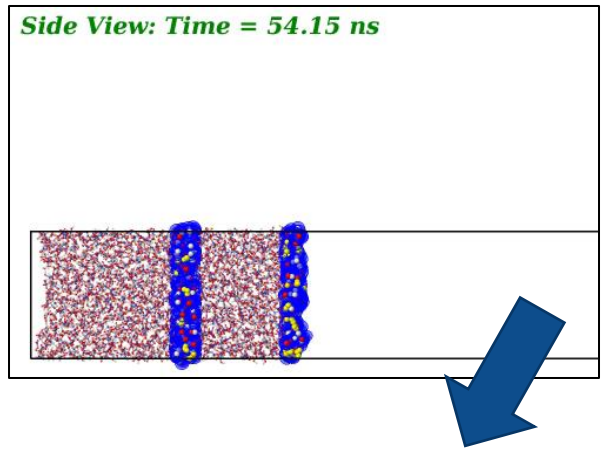
L-V Interface Simulations – Surface Tension

- Surface tension is calculated based on the pressure tensor
- Results are within orders of magnitude for similar systems
  - Uncertainties are quantified based on Gaussian behavior in fluctuating surface tension values
- Polarizable results have been reported to be more reliable for surface tension calculations
  - Molecules are more mobile, self-diffusion is higher
  - Larger cations have led to lower surface tension—difficult to ascertain which variables lead to variance in surface tension

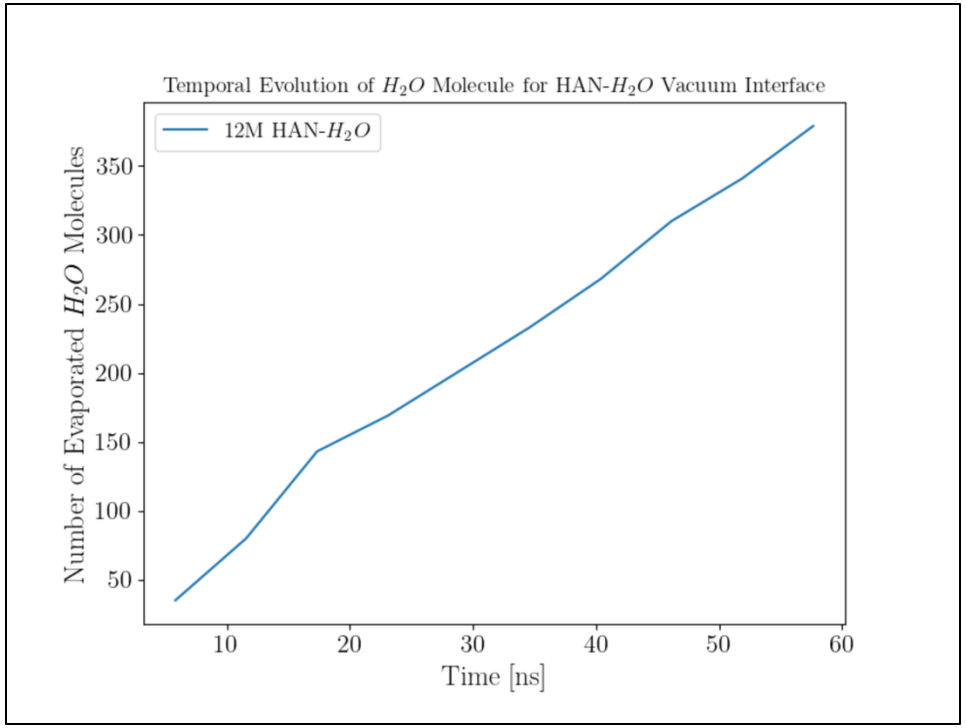


Mixture	γ [$mN\ m^{-1}$]
HAN-H_2O	78 ± 3
HAN-HEHN mixture 1	**71.4**
HAN-HEHN mixture 2	**65.6**
H_2O	**72**

L-V Interface Simulations – Evaporation



- Evaporation mechanisms can be quantified by using cumulative distribution functions (CDFs)
  - Periodic boundary conditions are imposed (i.e., concentration does NOT change over time and "evaporated" water molecules are sent to opposite end of domain)
- Estimated flux of $\sim 10\ kg \cdot s^{-1} \cdot m^{-2}$ suggests high rates of outgassing as has been shown in recent experimental observations
- Theoretical comparison is left for future work



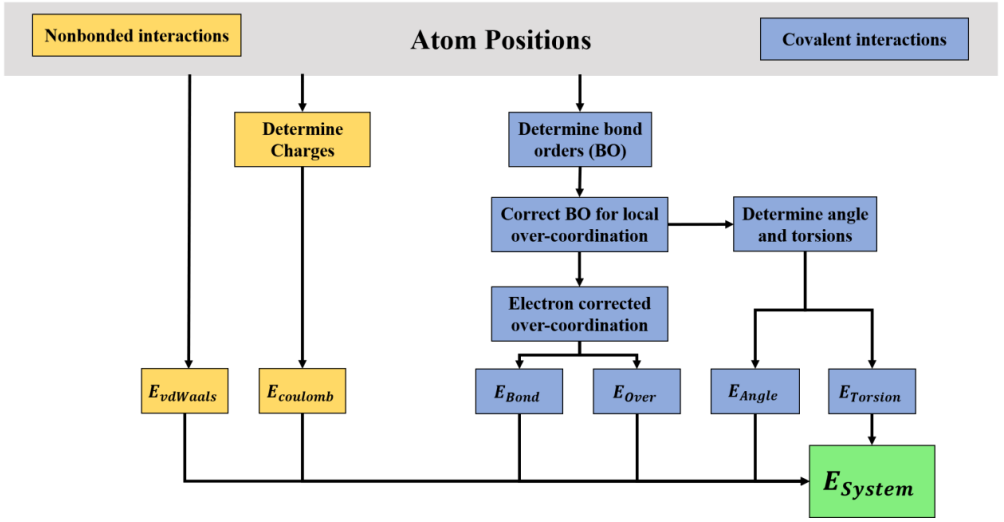
Conclusions & Future Work

Conclusions & Future Work

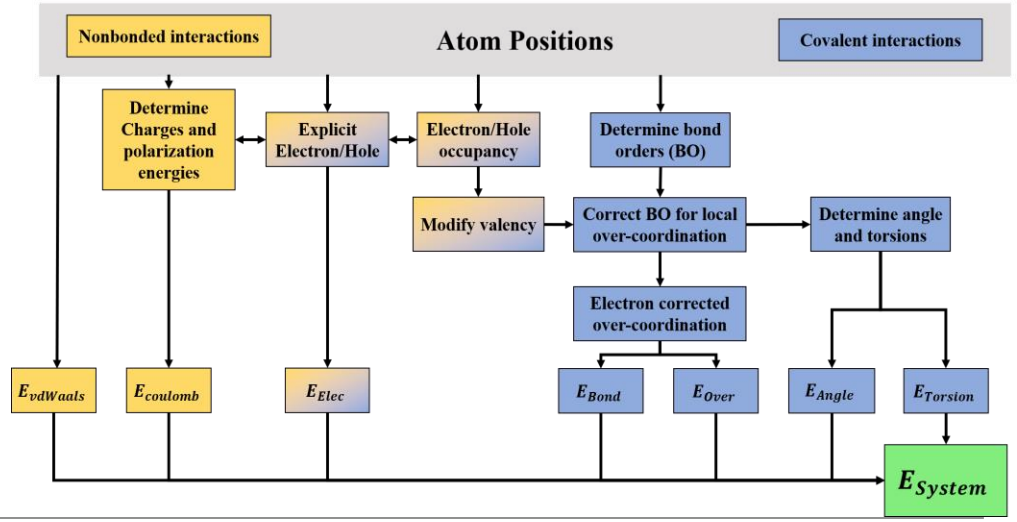
- A polarizable force field, APPLE&P, was used to investigate fundamental properties of HAN-based ionic liquids mixtures
- A HAN-water system was investigated at the liquid-vacuum interface.
- Future Work:
  - Use APPLE&P for HAN-HEHN mixtures
  - Compare results with eReaxFF Simulations
    - Critical chemical effects, such as proton transfer mechanisms, must be included to investigate propulsion system performance implications
  - Investigate more complex environments of interest for propulsion applications (thermal or catalytic reactions, electric fields, etc.)

[1] K. Chenoweth, A. C. T. van Duin, and W. A. Goddard, "ReaxFF Reactive Force Field for Molecular Dynamics Simulations of Hydrocarbon Oxidation," J. Phys. Chem. A, vol. 112, no. 5, pp. 1040–1053, Feb. 2008, doi: 10.1021/jp709896w.

Reactive MD Force Field



Reactive + Polarizable MD Force Field



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- The presenter would like to thank mentors and colleagues at USC, UCLA Plasma & Space Propulsion Laboratory (PSPL), and AFRL.

Questions?

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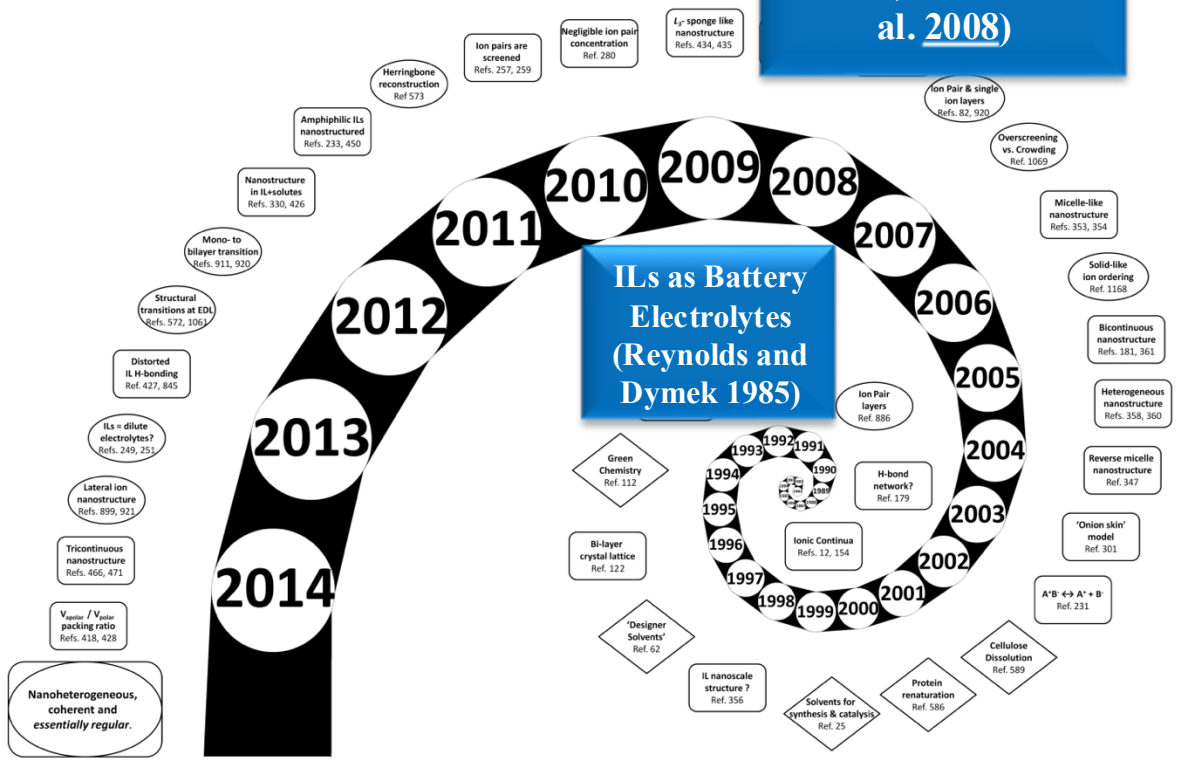
Introduction to Ionic Liquids

- Ionic Liquids (ILs) are molten salts composed of cations and anions that result in numerous advantageous thermophysical properties, such as…
  - room temperature melting points
  - high energy density
  - negligible vapor pressure
  - high electrical conductivities

- ILs have gained significant interest over the past 2 decades for a variety of applications pertinent to the AFRL
  - Batteries & fuel cells
  - Electrically-controlled solid propellants
  - In-space refueling
  - Propulsion management devices

ILs as Hypergolic Fuels (Schneider et al. 2008)

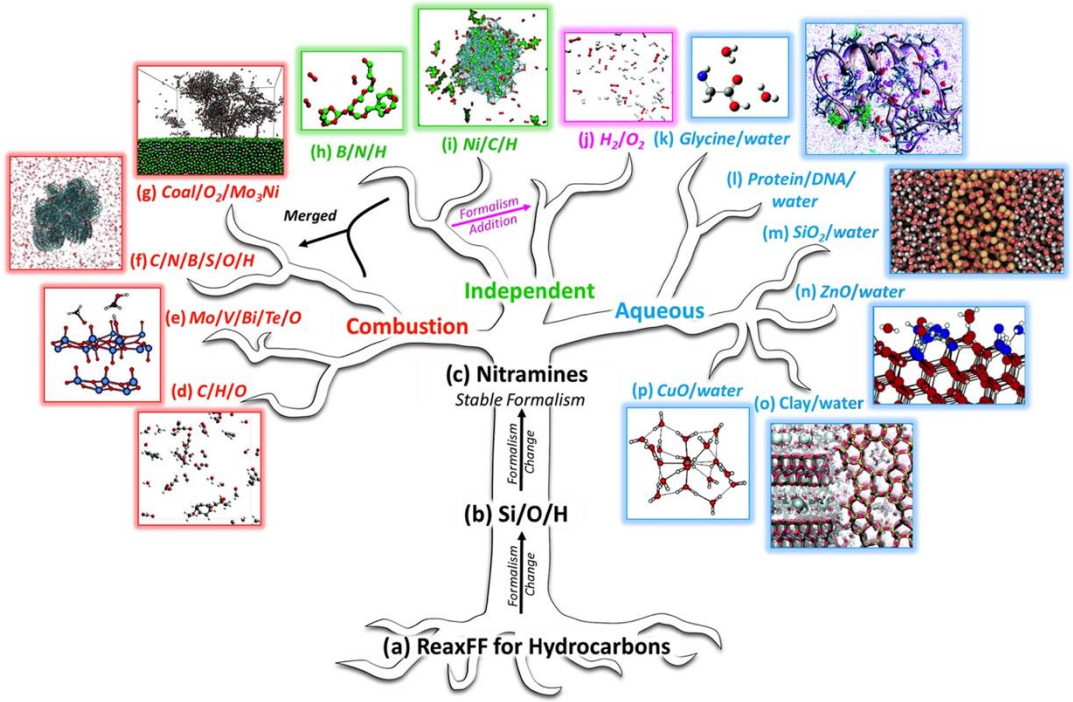


IL-propellant Demonstration on-board GPIM Mission (2019-2020)

*The area of each year's circle is proportional to the number of "ionic liquid", or "ionic liquids" publications based on an ISI web of science search.[1]

[1] R. Hayes, G. G. Warr, and R. Atkin, "Structure and Nanostructure in Ionic Liquids," Chem. Rev., vol. 115, no. 13, pp. 6357–6426, Jul. 2015, doi: 10.1021/cr500411q.

BONUS: ReaxFF



Iterative methodology of ReaxFF force field MD simulations (left) and ReaxFF development tree, where each branch represents a transferable set of parameters for hydrocarbon applications (right) [1]

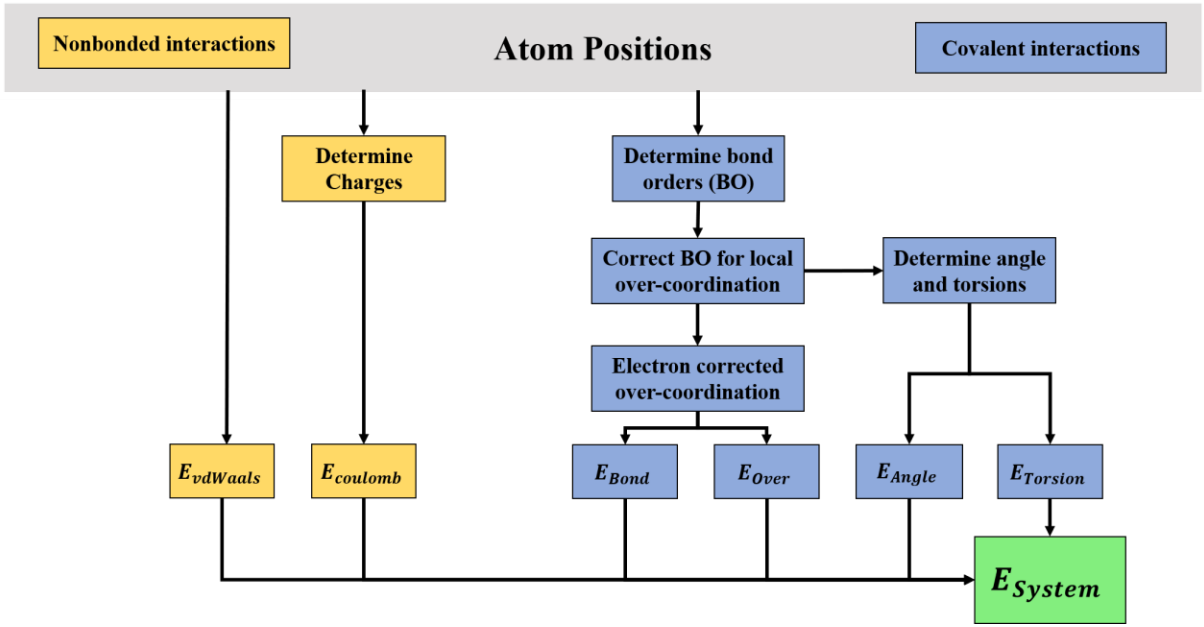
Reactive MD Force Field

$$BO_{ij} = \exp\left[p_{bo,1}\left(\frac{r_{ij}}{r_0^{\sigma}}\right)^{p_{bo,2}}\right] + \exp\left[p_{bo,3}\left(\frac{r_{ij}}{r_0^{\pi}}\right)^{p_{bo,4}}\right] + \exp\left[p_{bo,5}\left(\frac{r_{ij}}{r_0^{\pi\pi}}\right)^{p_{bo,6}}\right]$$

Single (Sigma) bond

Double (first pi) bond

Triple (second pi) bond



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BONUS: HAN-H2O Interface—Surface Tension Results

- Gaussian shape at large window for the running average (m = 1000) for last 50 nanoseconds
- To quantify proper uncertainties, simulated surface tensions are continuously calculated until Gaussian behavior is achieved—non-Gaussian behavior may indicate additional required simulation time