Understanding Ionic Liquid Structure via Polarizable Molecular Dynamics Simulations

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Motivation

- Ionic liquids (ILs) are low-melting point ($\leq$100 °C) organic salts with favorable properties for **gas separation** (e.g., CO_2 capture), **energy generation and storage**, or even **in-space propulsion**.
- **Polarizable force fields are essential** for accurate electrostatic and transport property predictions (*Bedrov et al. Chem. Rev. 2019 119 (13), 7940-7995*).
- **Investigating local nanostructure serves as an instrumental step** towards understanding and tuning macroscopic properties for optimal technology design.

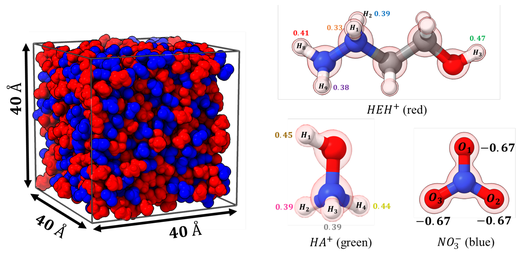


Figure 1. Computational domain and molecular/charge structure of **hydroxyethylhydrazinium nitrate (HEHN)**. Production simulations conducted using the **APPLE&P** software for **400 cation-anion pairs** in the *NPT* ensemble for ∼10 **ns**.

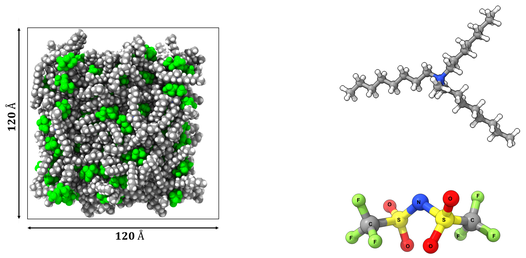


Figure 2. Domain and molecular structure of methyltrioctylammonium bis(trifluoromethylsulfonyl)imide ([N_{1888}][TFSI]). Production simulations conducted using the **OpenMM** software for **1600 (!!) cation-anion pairs** in the *NPT* ensemble for ∼50 **ns**.

Theory and Methods

Induced Dipole Moment Method

$$\vec{\mu}_{i\beta}^{\,\text{ind}}(t) = 4\pi\epsilon_0 \hat{\alpha}_{i\beta} \cdot \vec{E}_{i\beta}(t) \tag{1}$$

atomic polarizability tensor

local electric field ($\vec{E}^{q}_{i\beta} + \vec{E}^{\mu}_{\beta}$)

Classical Drude Oscillator Model

$$\vec{\mu}_{i\beta}^{\,\text{ind}}(t) = q^{D}_{i\beta} \cdot \vec{d}_{i\beta}(t) \tag{2}$$

Drude particle partial charge

Drude displacement from nucleus

polarizable atom β of molecule i

Scattering (S_{NN}) and Charge-correlation (S_{ZZ}) Structure Factors

$$S_{NN}(\mathbf{k}) = \frac{1}{V} \langle \hat{\rho}_N(\mathbf{k}) \hat{\rho}_N(\text{-}\mathbf{k}) \rangle$$

ensemble average

volume

momentum transfer variable

number of atoms in system

position of atom i

$$\hat{\rho}_N(\mathbf{k}) = \sum_{i=1}^{N} f_i(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{r}_i}$$

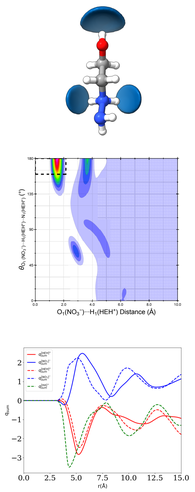
atomic form factor

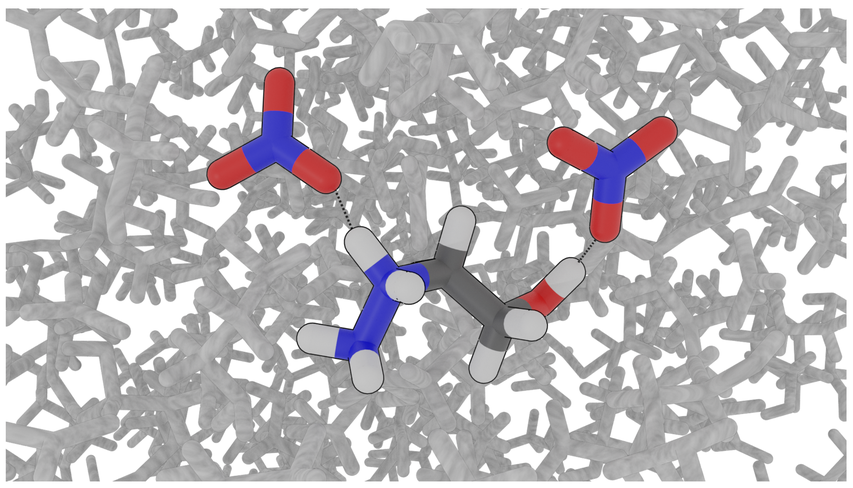
charge-correlation structure factor

$$\frac{4\pi}{k_B T} \lim_{|\mathbf{k}|\to 0} \frac{S_{ZZ}(\mathbf{k})}{\mathbf{k}^2} = 1 - \frac{\epsilon_\infty - 1}{\epsilon_\infty} \tag{3}$$

infinite frequency dielectric response

Results: HEHN

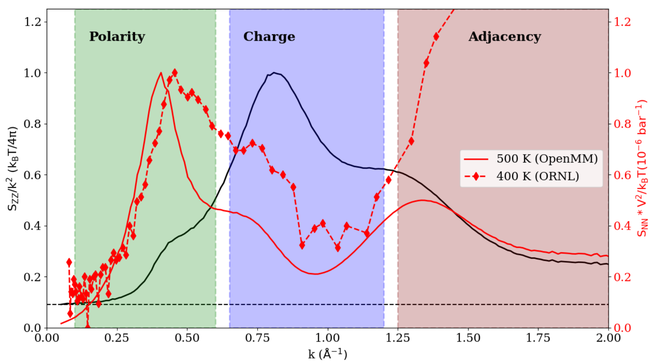


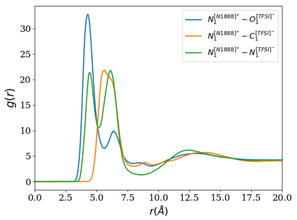


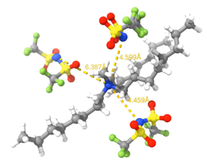
Summary of Results

1. Spatial distribution functions (SDFs) indicate the hydrogens of **amine** and **hydroxyl** groups as hydrogen bond **donor sites**.
2. N – H···O and O – H···O H-bonds are **strong** ($\leq$2.2 Å) and **linear** ($\sim 20 - 30°$).
3. Electrostatically, HEHN resembles a **"disordered lattice"** (*Roy et al. J. Phys. Chem. B . 2010, 114, 8410–8424*).

Results: [N1888][TFSI]







Summary of Results

1. **Two dominant spatial motifs manifest**, where [TFSI] N and O preferentially coordinate with the cationic N.
2. N_{1888} **apolar chains produce polarity domain formation**, as evidenced by low wavevector S_{NN} peaks.
3. Charge-correlation structure factor indicates the length scale, $k \sim 0.75$ Å^{-1}, of important Coulombic interactions.

Future Work & Acknowledgements

- HEHN is a potential rocket propellant constituent → **reactive force field simulations**
- Unexplained data on [N_{1888}][TFSI] at charged gold surface → **interfacial simulations**
- Developing polarizable MD force fields is challenging → **machine learning** to improve simulation turnaround for new systems

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