

Ionic Liquids as High-Temperature Electrolytes for PEMFCs: A Multiscale Computational Study.

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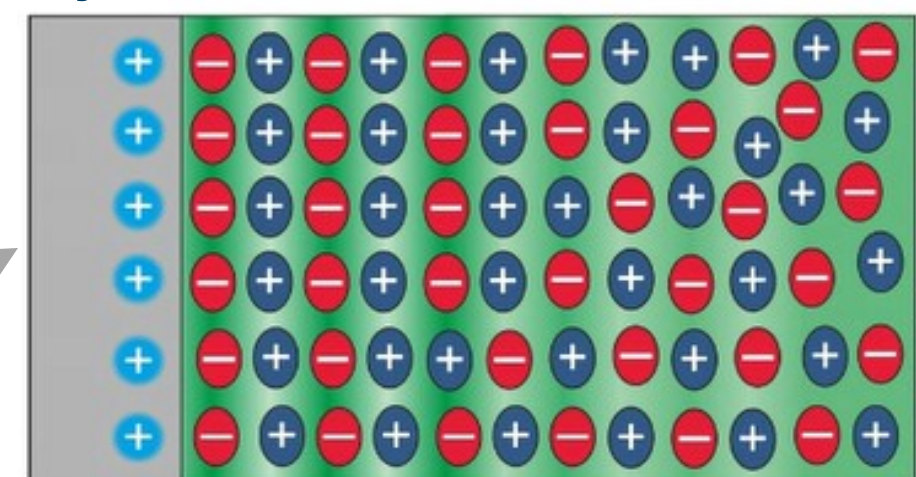
Efficient ways of energy conversion and storage are needed for a successful energy transition. Massively produced hydrogen will be a crucial energy carrier in the future and related technologies for its production, conversion and storage are therefore widely investigated. In that respect, we investigate novel electrolytes for Proton Exchange Membrane Fuel Cells (PEMFCs). Current PEMFC technology relies on proton conduction in water-swollen organic membranes, leading to complex water management systems and, thus, limiting the working temperature to below 90 °C [1]. To remove these limitations and lower the cost of the device, membranes doped with protic ionic liquids (PILs) are considered as novel fuel cell electrolytes. PILs have good proton conduction properties, as well as high thermal stability, gas conductivity and good mechanical properties under non-humidified conditions [2]. Many studies have been carried on for this type of PEMFC, demonstrating good responses to the presence of water, which is unavoidable during fuel cell operation [3]. We investigate how the interfacial and bulk properties are affected by the temperature and the presence of water.

PROTIC IONIC LIQUIDS AND PEMFC

Aim: increasing the working temperature to > 120 °C

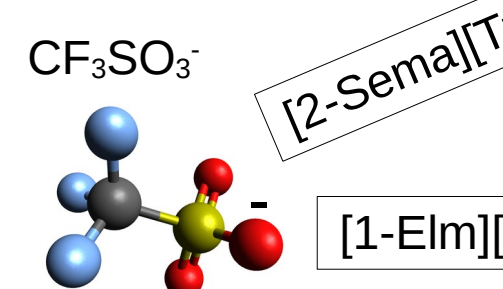
Approach: proton transport by using a **non-aqueous protic ionic liquid (PIL)**.

Double layer structure is formed at the interface^[4]



$pK_A=0.94^{[5]}$ $C_3H_{10}O_3SN^+$

$\rho = 1.645 \text{ g/cm}^3$

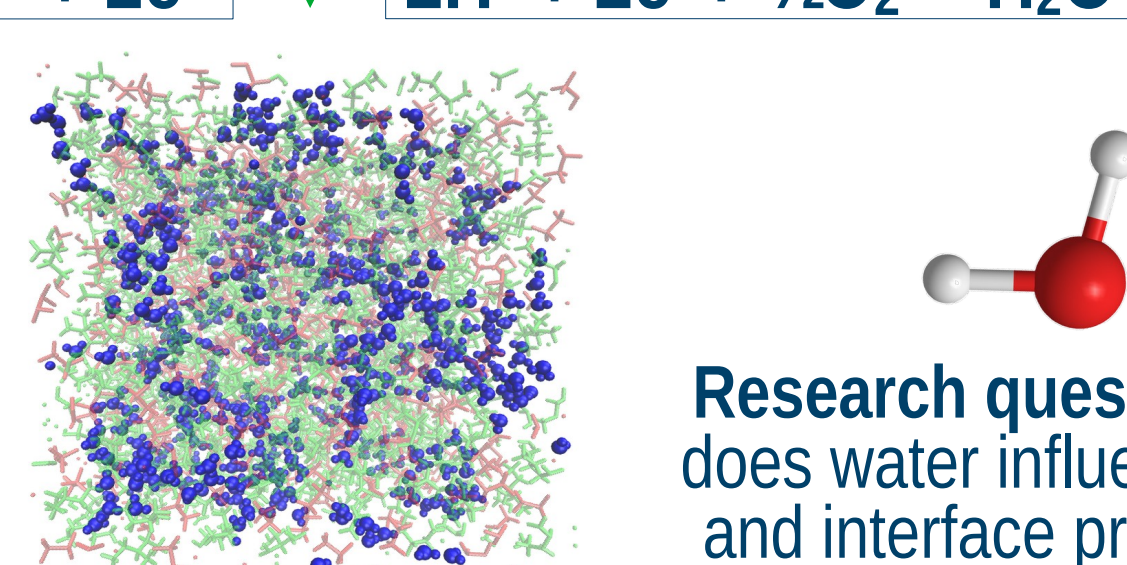
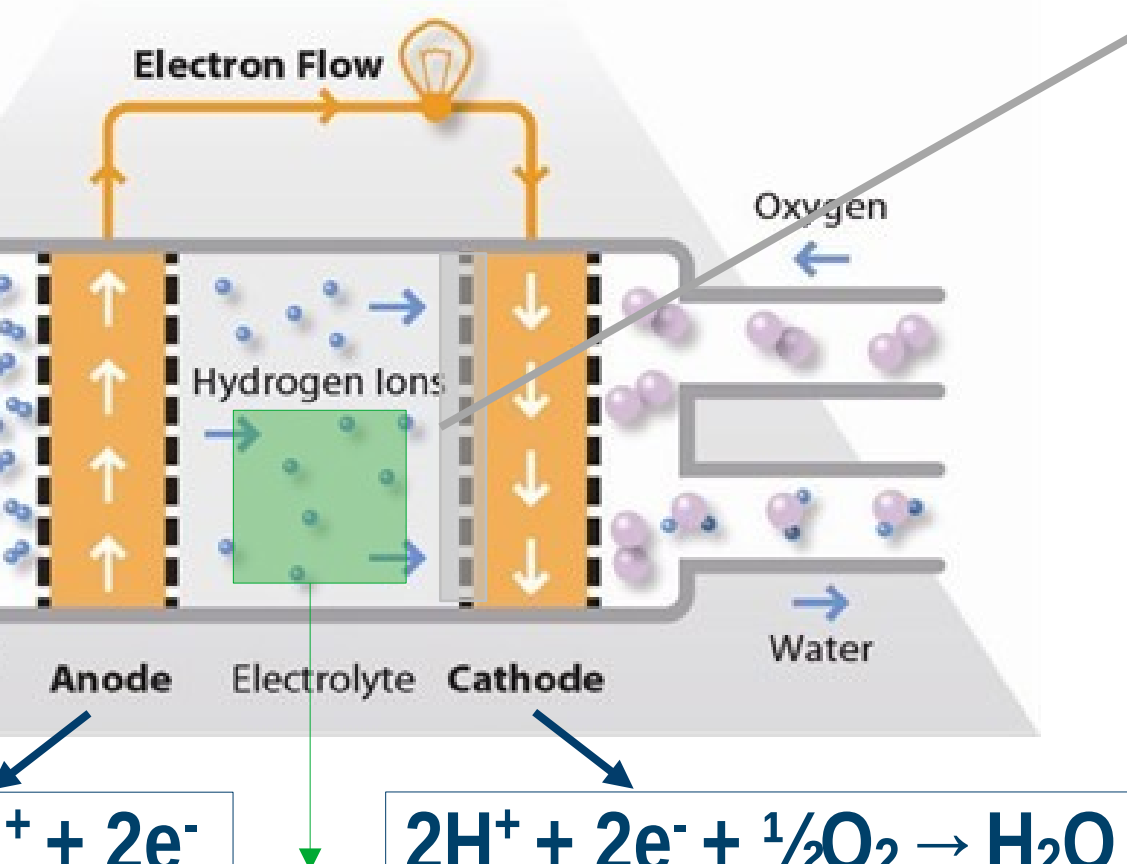
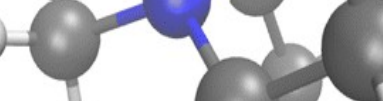
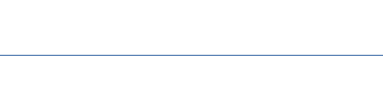
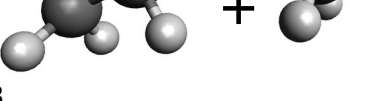
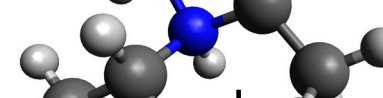
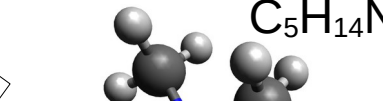
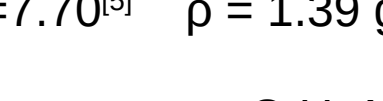
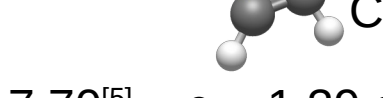
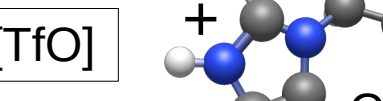
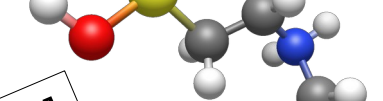
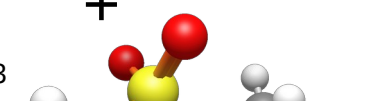
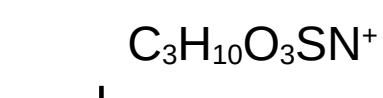


$pK_A=7.70^{[5]}$

$\rho = 1.39 \text{ g/cm}^3$

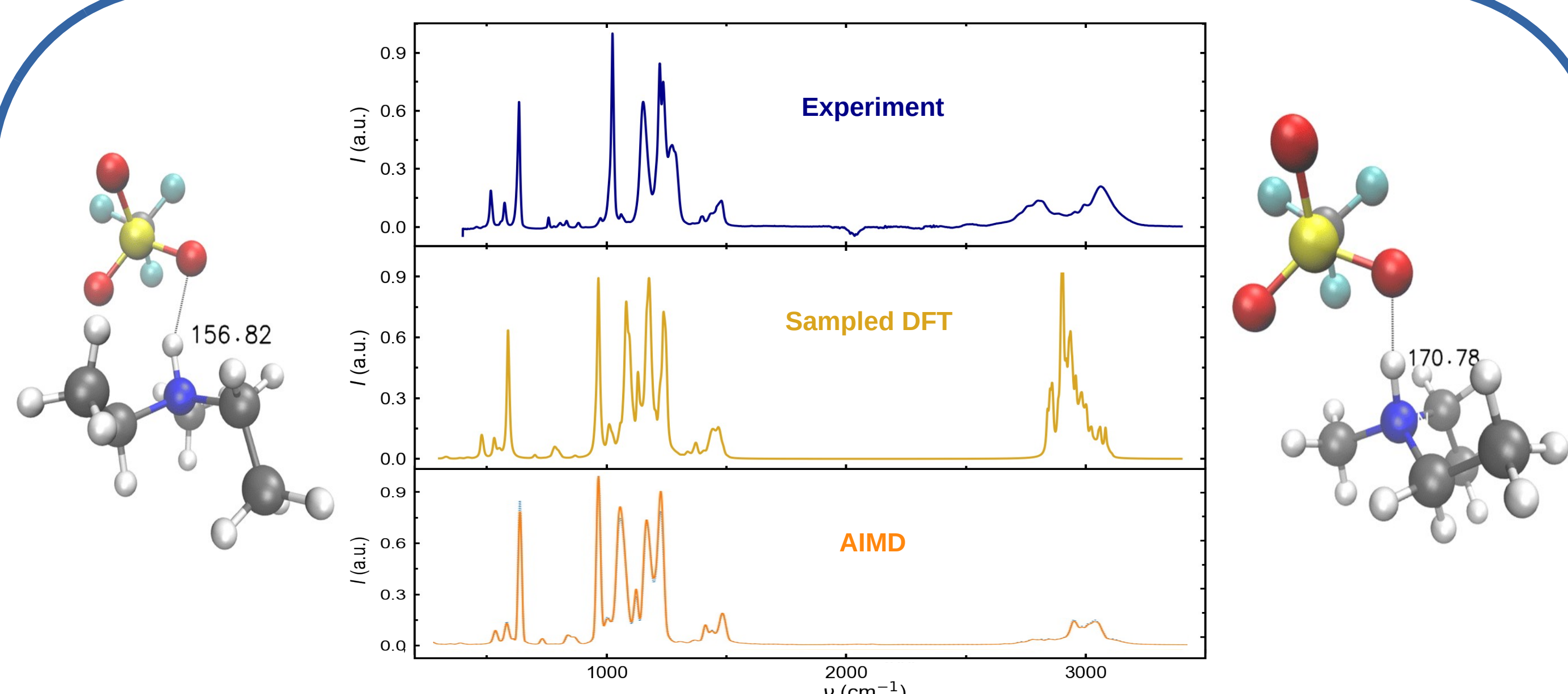
$pK_A=10.55^{[5]}$

$\rho = 1.29 \text{ g/cm}^3$



Research question: how does water influences bulk and interface properties?

Analyzing ion vibrations



Comparison of spectra obtained with different computational techniques, with the experimental spectrum of the protic ionic liquid [DEMA][TfO].^[6]

By using different computational techniques and comparison with experiments, we analyze the infrared spectrum of the protic ionic liquid [DEMA][TfO]. Low-frequency vibrations stem from triflate anions and their interactions, while high-frequency N-H stretching broadens due to dynamic hydrogen bonding and its frustrated motion between two neighbouring oxygens of the same anion.^[6]

SUMMARY AND OUTLOOK

A combination of MD, DFT and AIMD simulations was used to analyze the behaviours of protic ionic liquids (PILs) in the context of mid-temperature fuel cells applications.

Ion vibrations have been analyzed and described^[6] assigning vibrational modes to each peak and understanding the broadening of the double peak in the H-F region. The bulk phase phenomena were correctly reproduced, both in case of varying temperature and water content. We managed to compute the main dynamic properties in an accurate way, providing good structure for the interface simulation. In the results on interfacial structuring of PILs, we observe some layering of ions at the interface. In the next step the effect of voltage will be investigated.

Further investigation:

BULK PHASE

- Quantification and characterization of water cluster in the 3 different PILs.
- Analysis of ions clusters formation (triples) and compute viscosity.

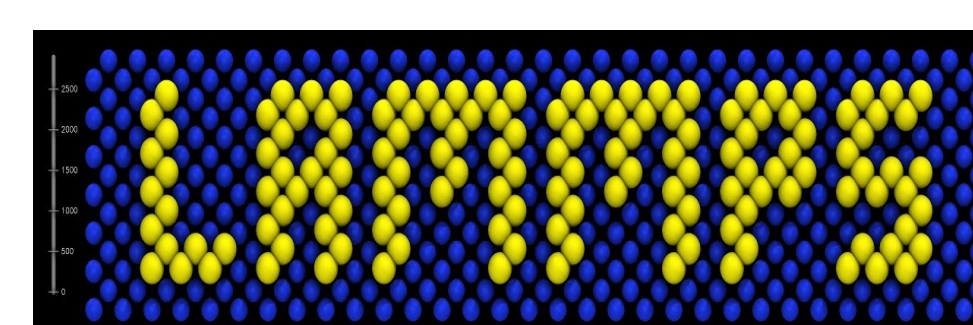
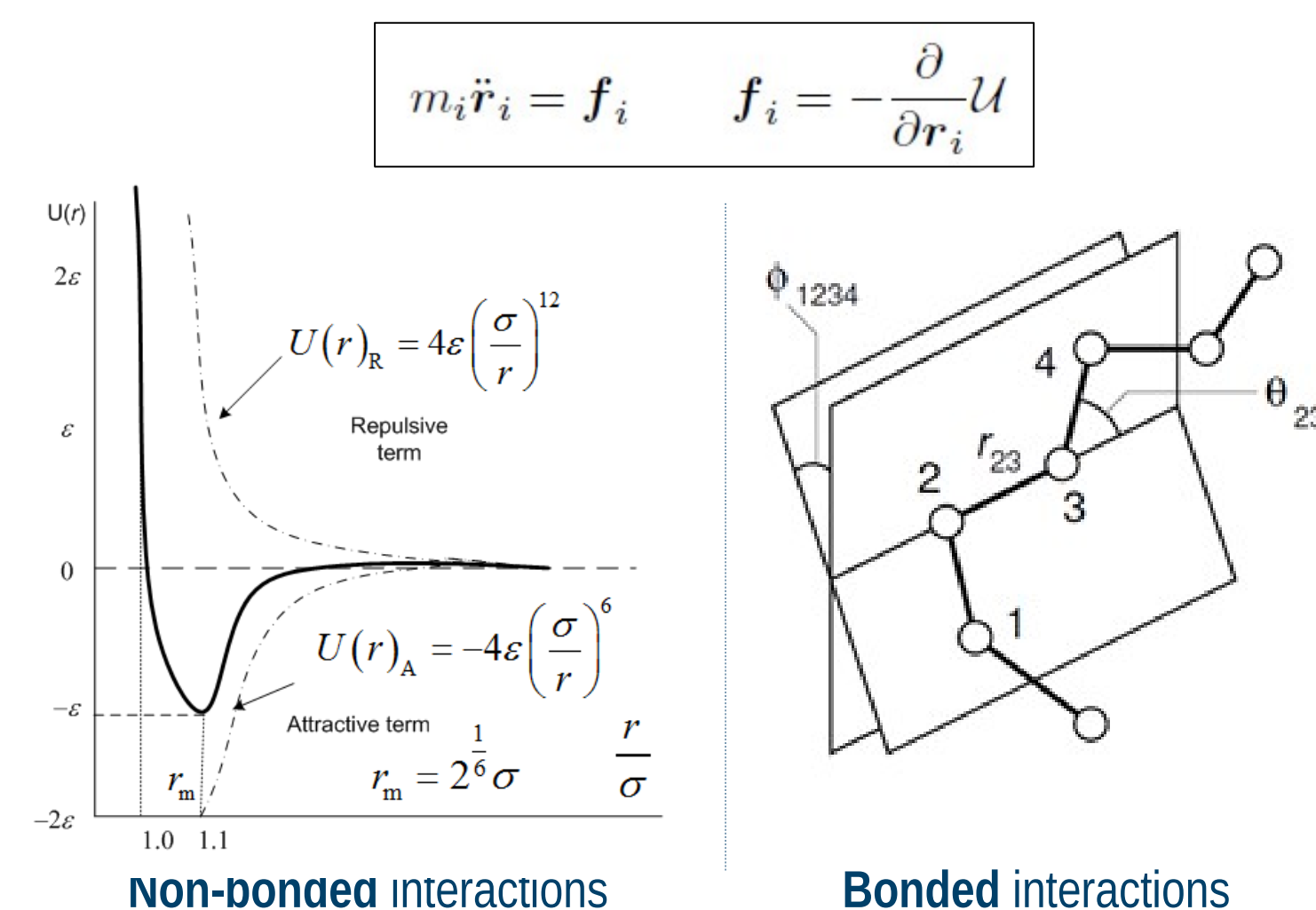
INTERFACE

- Application of electric field due to the potential difference between electrodes with the electrode package of LAMMPS.
- Analysis of the EDL structure at the interface as a function of temperature and water content.

METHODOLOGY

Classical Molecular Dynamics (CMD)

- based on solving Newton's equation of motion, it takes into account the dynamics of the system.
- allows for the simulation of larger systems.



Density Functional Theory (DFT)

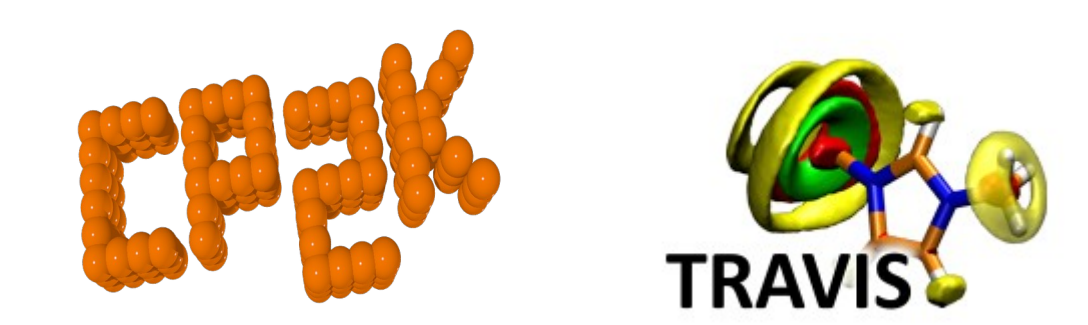
- based on quantum mechanics, static approach.

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) + V_H(\mathbf{r}) + V_{XC}(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}).$$

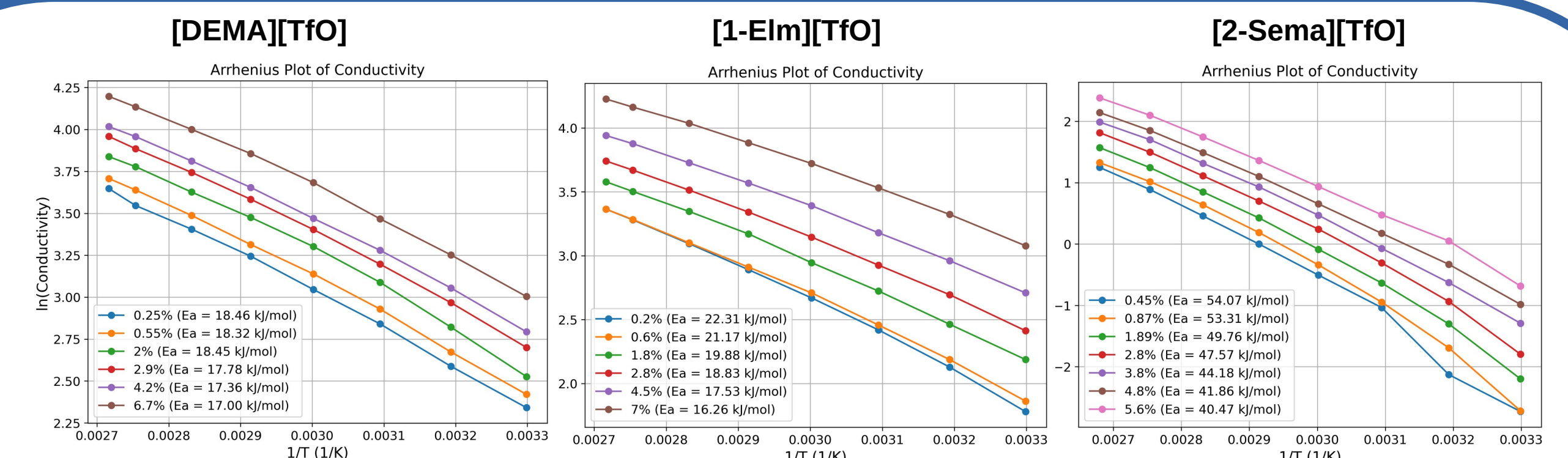


Ab Initio Molecular Dynamics

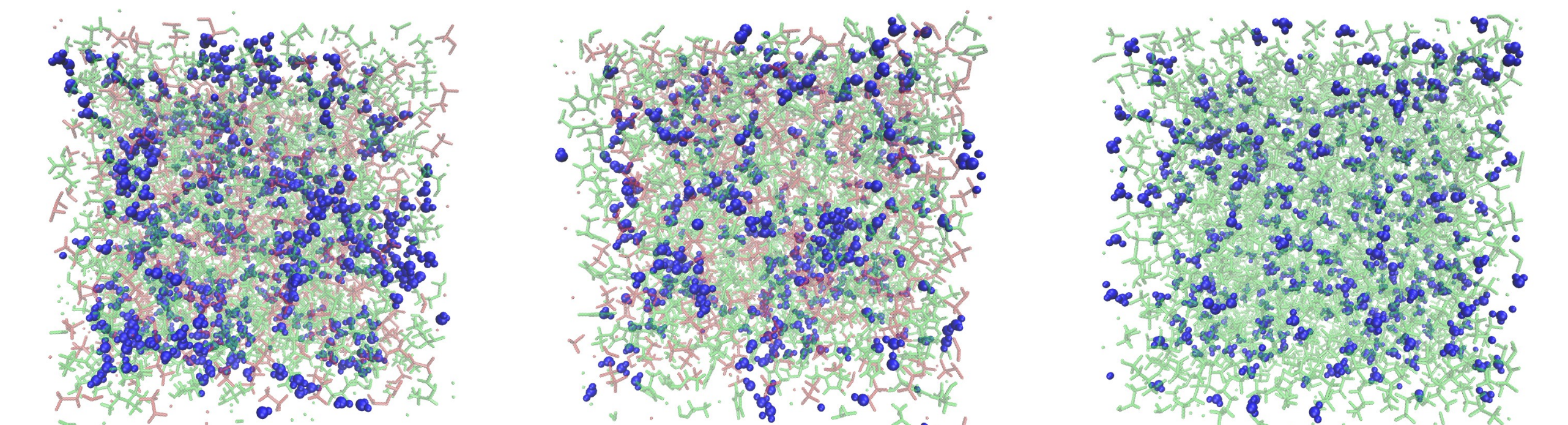
- compute forces acting on the nuclei at each time step with DFT.
- short trajectories (5 ps) and small system (300 atoms) with respect to CMD.
- high computational cost.



Collective transport phenomena in periodic systems



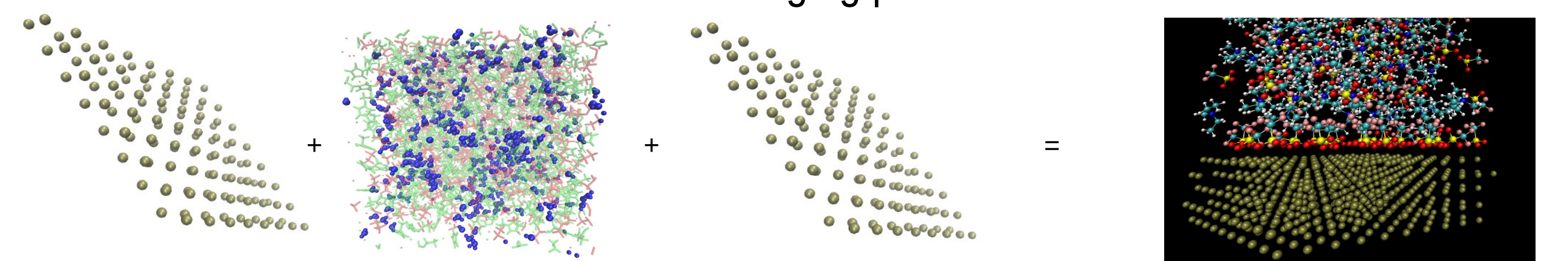
Measured conductivity of the 3 PILs as function of water and temperature in bulk phase.^[5]



The higher the acidity of the cation, the more the water tends to create a network with the ion pairs. We want to investigate the viscosity for understanding the implications of water clustering.

Properties of electrolyte - electrode interface

The accurate results from the bulk phase are necessary for the interface simulation. We use them as input to have an equilibrated system between the electrodes before the charging process.



We are interested in the arrangement of ions and water molecules at the interface. We can see layering of the ions at the interface but we only have point charges applied on the electrodes. In the next step, the electric field will be applied.

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