Molecular simulation of ionic liquids confined inside nanoporous carbon CMK-3

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Abstract

A fundamental understanding of the structural and dynamical properties of ionic liquids (ILs) inside nanoporous materials is crucial for applications in electrochemical double layer capacitors (EDLC), batteries and solar cells. We performed classical molecular dynamical simulations of the IL [emim$^+$][NTf_2^-] inside the ordered mesoporous carbon CMK-3. The confined IL forms different layers around the carbon surfaces in CMK-3, and these layers of ions have different mobilities depending on their distance from the carbon surface. The structure of the IL inside the nanopores is related to the capacitance (how much energy can be stored), and the dynamics of the IL is related to the electrical resistance in electrochemical double layer capacitors, batteries and solar cells.

Background

ILs are organic salts with a melting temperature below the boiling point of water. ILs have electrochemical and thermal stability, low vapor pressure, low flammability, high viscosity, and non-volatile behavior. We use classical molecular dynamic (MD) simulations, based upon Newton's laws of motion, to study the IL [emim$^+$][NTf_2^-] inside the ordered mesoporous carbon CMK-3. We used an atomistic representation of our IL. CMK-3 has uniform pore size, large surface area, and regularly interconnected pores.

Simulation Details

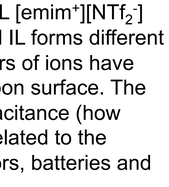
Ionic liquid:

1-ethyl-3-methylimidazolium, [emim$^+$]

bis-(trifloromethylsulfonyl) imide, [NTf_2^-]

CMK-3: CMK-3 models of Jain *et al.* (GCMC of adsorption of fictitious ideal gas of C atoms in a silica nanopore) (S. K. Jain, PhD Thesis, NCSU, 2008)

A material composed of hexagonally-packed carbon nanorods with uniform diameter, 4.5 nm, and uniform pore size, 1.4 nm



Force field: take from Kelkar and Maginn
The Journal of Physical Chemistry B 2007, *111*, 4867-4876

Software:
GROMACS (Groningen Machine for Chemical Simulations)
VMD (Visual Molecular Dynamics)

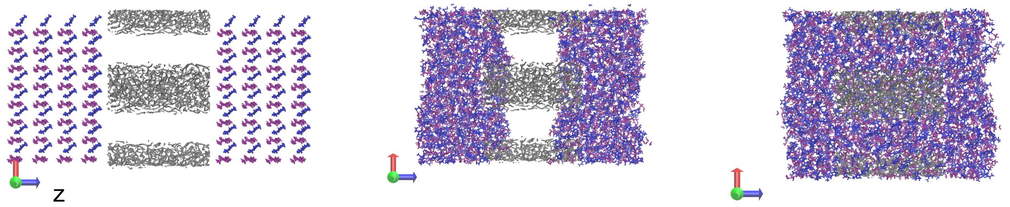
Simulation Procedures

Step 1: Ions are arranged in an arbitrary lattice, outside of the pores
Step 2: Minimize energy of the system
Step 3: Simulation is started with melting at *T= 500 K*
Step 4: Once IL is fully inside the pores, temperature is reduced to 333 K. Run for at least 10 ns more for equilibration and averaging

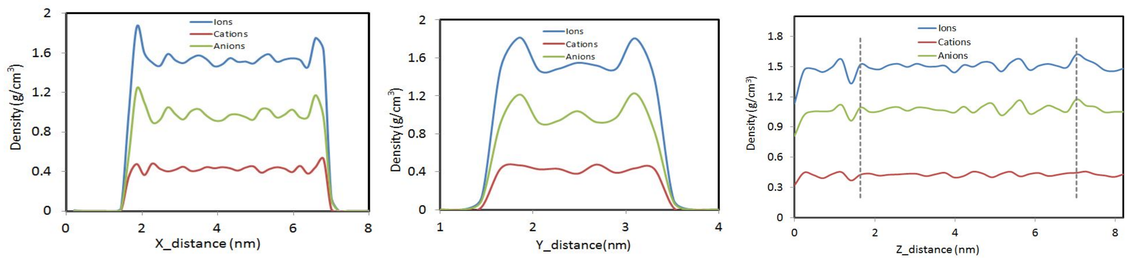
Also ran simulations for IL in the bulk, for comparison with the confined system.

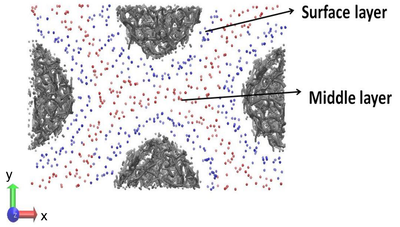
Results and Discussion

Snapshots of the process of filling the nanopores



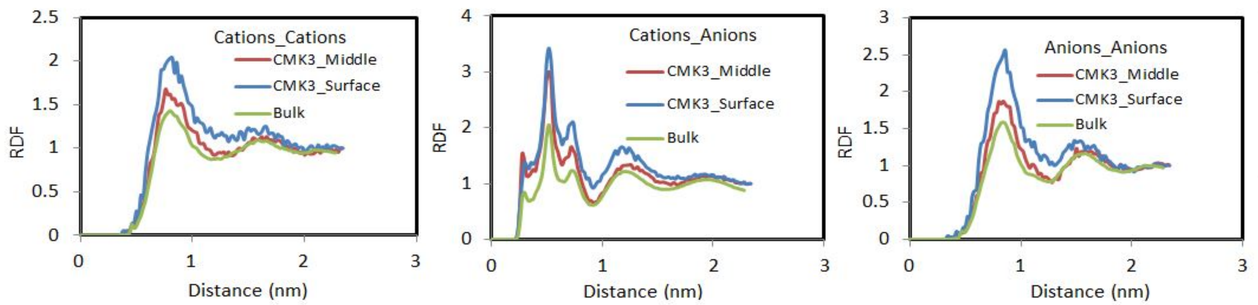
Density of the ions, cations and anions at 333 K





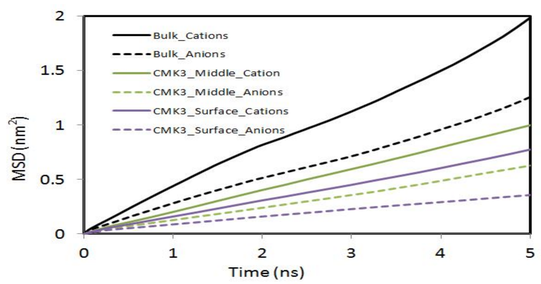
- The ions inside CMK-3 have the same density as the ion outside CMK-3
- Larger density of ions near the surface of CMK-3
- Anions have higher density than cations.

Radial distribution function of IL in different layers



- The positions of the peaks of RDF for the ions in different layers and bulk system don't change.
- The height of the peaks of RDF is higher for the ions near the surface.

Mean square displacement of IL in different layers



- The ions in the center of CMK-3 have faster dynamics than the ions near the carbon surfaces
- Cations have faster dynamics than anions.
- The confined ions have slower dynamics than the bulk ions

Conclusions

- IL forms layers of fluid around the carbon surfaces of CMK-3; larger density of ions near carbon surfaces
- Layer of ions near carbon surfaces have slower mobilities than ions that are farther away; IL inside CMK-3 have slower dynamics than bulk IL

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