# Molecular Dynamics Simulation of the Ionic Liquid [DMIM+][Cl-] Confined Inside Multi-Walled Carbon Nanotubes

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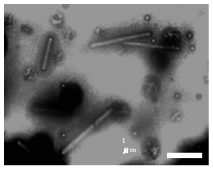
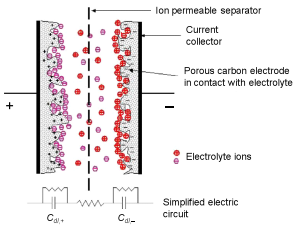
## MOTIVATION



- Warner *et al.* (ACS Nano **2009**) *synthesized* nanoparticles from ionic liquids (ILs) that are *frozen at room temperature* (GUMBOS = ***G***roup of ***U***niform ***M***aterials ***B***ased on ***O***rganic ***S***alts)
- It might be possible to develop frozen IL-based nanomaterials with desirable properties:
  - Magnetic, fluorescent nanoparticles for medical imaging, magnetic hyperthermia cancer treatment
  - Nanomaterials could be prepared from FDA-approved compounds (vitamins, aminoacids, drugs) → could eliminate toxicity effects
- 1D-nanomaterials recently prepared using hard-templating materials with cylindrical nanopores (multi-walled carbon nanotubes, anodic aluminum oxide membranes)
  - Magnetic, optical properties depend on crystalline nanostructure
  - Melting points, crystalline structure inside nanopores significantly different from bulk
  - Fundamental understanding of properties of ILs inside nanopores essential to tune/optimize properties of GUMBOS-based 1D-nanomaterials
- ILs inside nanopores also relevant for energy storage devices, such as electrochemical double-layer capacitors (EDLCs) (Pandolfo and Hollekamp, J. Power Sources **2006**)




- Use molecular simulation to understand how pore size, pore loading, wall-IL interactions affect structural, dynamical properties of confined ILs

## SIMULATION DETAILS

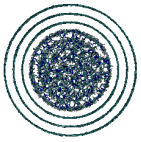
- Ionic Liquid -

  - 1,3-dimethylimidazolium chloride, [DMIM+][Cl-]
- Molecular dynamics (MD) simulations, NVT ensemble, GROMACS MD package
- All-atom force field of Lopes *et al.* (JPCB **2004**)
- Hard template: multi-walled carbon nanotubes (MWCNTs) diameters: 2.0 nm, 2.5 nm, 3.0 nm and 3.7 nm
- Other Software: VMD, RasMol

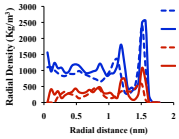
## SIMULATION PROCEDURE

1. Insert given amount of IL into the MWCNT, relax system so that it reaches a local energy minimum (energy minimization procedure)
2. Melt system at 600 K for 0.3 ns
3. Anneal the system from 600 K to 425 K in 1.5 ns
4. Equilibration + production run at 425 K for 30 ns

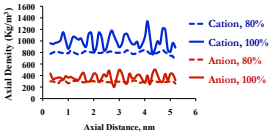
## RESULTS AND ANALYSIS



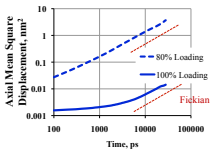
Diameter-3.7 nm

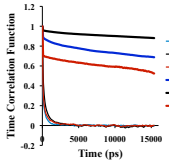



- Layering observed in radial density profile
- Radial structure varies with pore size, pore loading (expressed as a % of $\rho_{bulk}$)

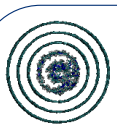



- No particular structure observed in axial density profile; slight variations due to pore size, pore loading

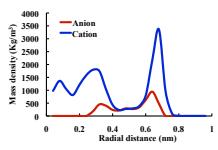


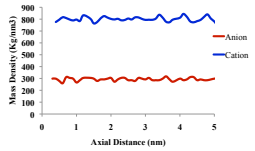



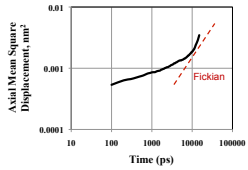

- MSD = measures mobility of cations vs. time
- Lower pore loadings → cations move faster, diffusive regime reached faster
- Time correlation functions of rotation of cations = a measure of how the rotational motion at time t is correlated with the same motion at t=0
- Rotational motion of cations around different symmetry axes decorrelates faster at lower pore loadings

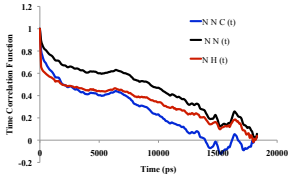


Diameter-2.0 nm
100% loading




## CONCLUSIONS

- Layering effects observed in radial density profiles, but order is lost for larger pore sizes near center of pore. Peaks for cations, anions observed at same values of r; maximum density observed close to the carbon surface
- Imidazolium rings of cation ($DMIM^+$) close to pore walls arrange parallel to them (results not shown)
- No particular structure observed in axial direction
- MWCNT diameter determines stacking and distribution.
- Faster dynamics observed at (1) lower pore loadings, same pore size; and (2) larger pore sizes, similar pore loading

## FUTURE DIRECTIONS

- ILs in solid state
- Other nanoporous materials (different materials, pore geometries)
- Other force fields:
  - Polarizable force field APPLE&P (Borodin, JPCB **2009**)

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