Molecular Simulation Studies of the Ionic Liquids

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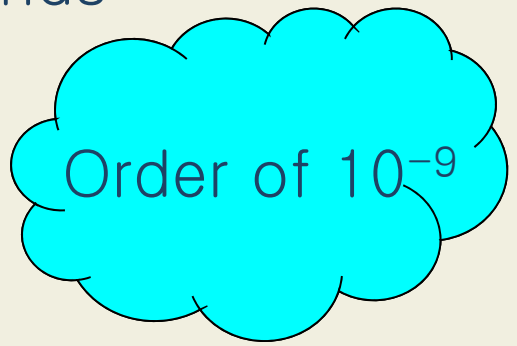
Themodynamics & properties lab

Why molecular simulation?

- Possible ILs compounds



- Thermophysical properties related to chemical structure and constitution

Application to the commercial process

Monte Carlo Simulation

- Major components of a MC
  - Probability distribution function
  - Random number generator
  - Sampling rule
  - Scoring (or tallying)
  - Error estimation
  - Variance reduction techniques
  - Parallelization and vectorization

- Solvation of small molecules in imidazolium ILs

  Dimethylimidazolium chloride

  C.G.Hanke et al.(2002)

- Thermodynamic properties of

  1-n-butyl-3-methylimidazolium hexafluorophosphate

  Jindal K.Shah et al.(2002)

- Effect of potential model (united atom force field)

  1-n-butyl-3-methylimidazolium hexafluorophosphate

  Jindal K. Shah et al. (2003)

Solvation of small molecules in ILs

Dimethylimidazolium chloride

- Cations and anions of the liquid

  Rigid charged molecules with fixed geometry

- Intermolecular potential

  Two-body term interaction

- Methyl group & methylene group

  Single sites (united atom force field)

- Electrostatic part of interaction

  Fixed point charge on each sites (partial charges)

Short range interaction (repulsion & dispersion)

Site-Site interaction

- Interaction between ions (partial charge on atom)

  site-site Buckingham potential

- Solute-solvent short range interaction

  Lennard-Jones site-site interaction

  (C.F.Hanke et al. 2001)

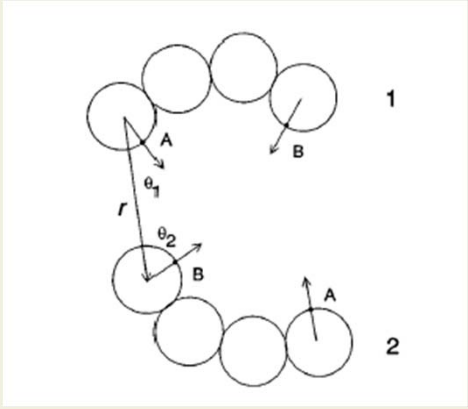
- Long range electrostatics

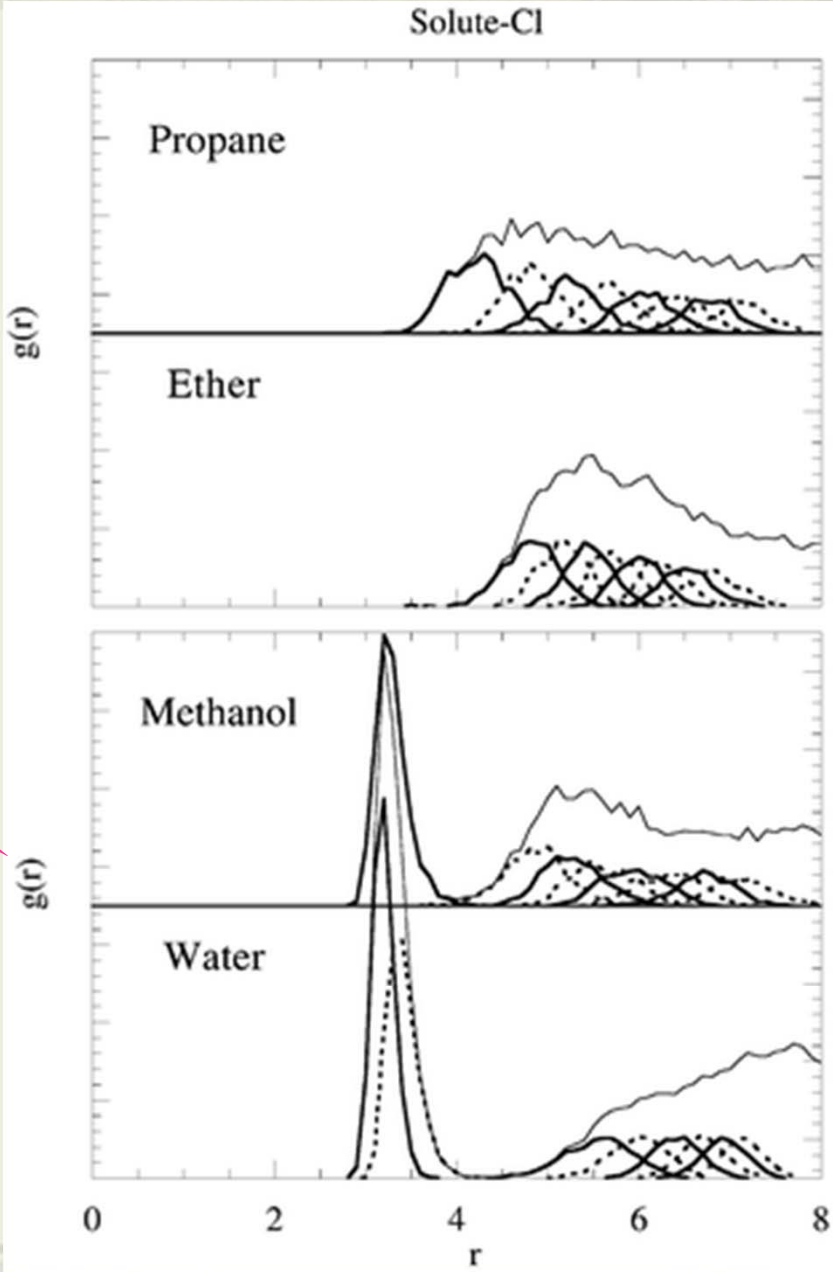
  Ewald summation – surrounding medium equal vacuum (($_s$ = 1).

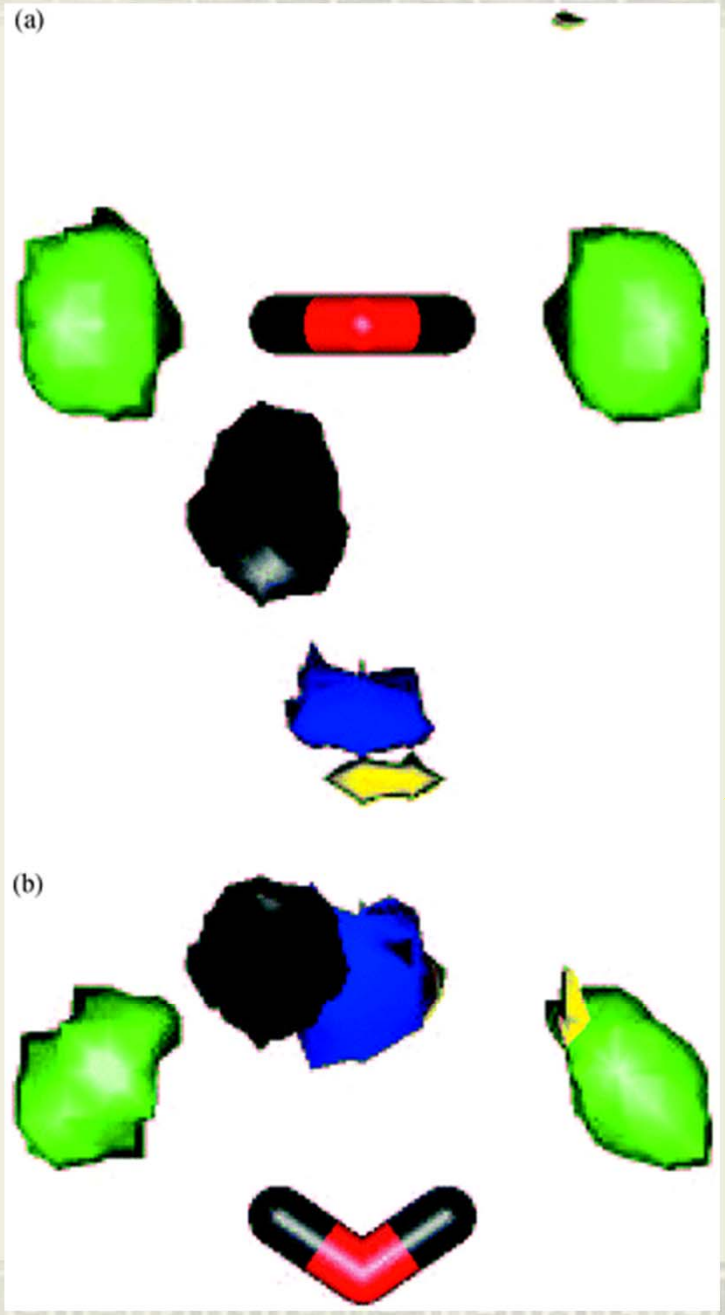
Local structure

- examined the local environment around the solutes

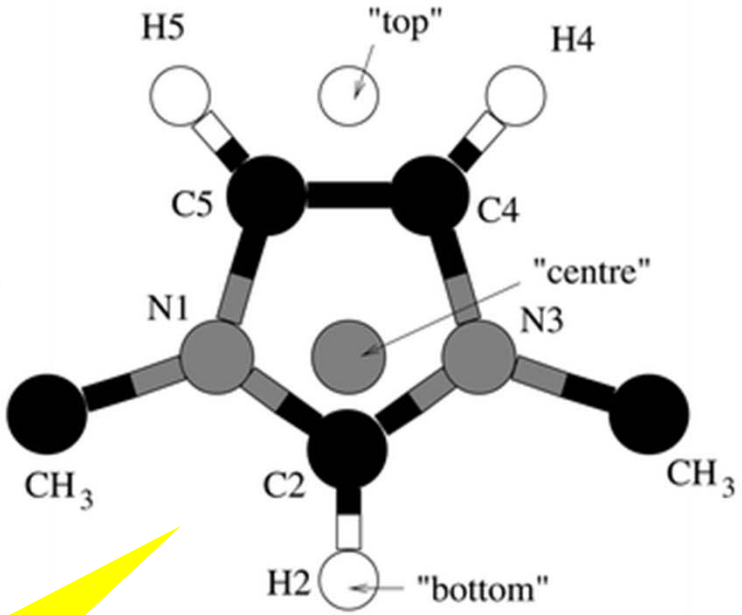
Ranked distribution function



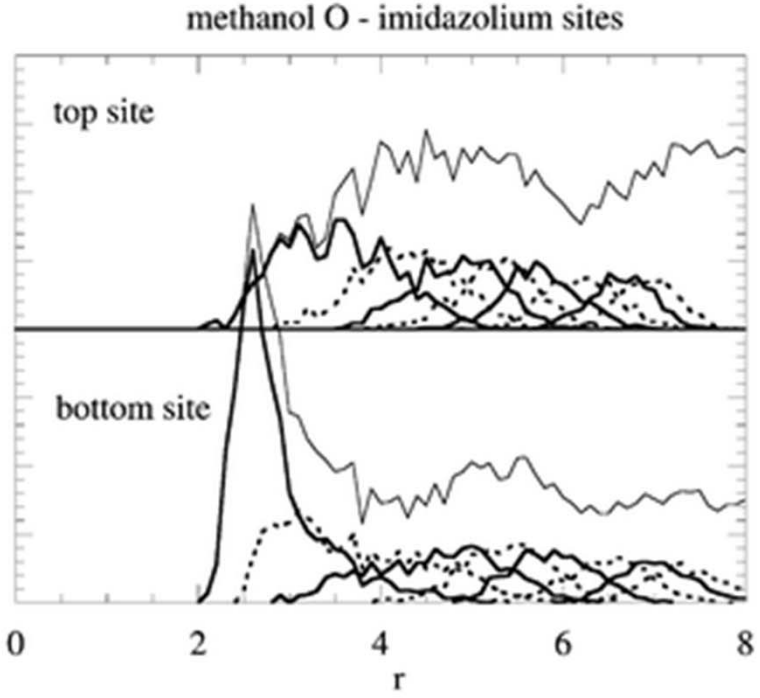


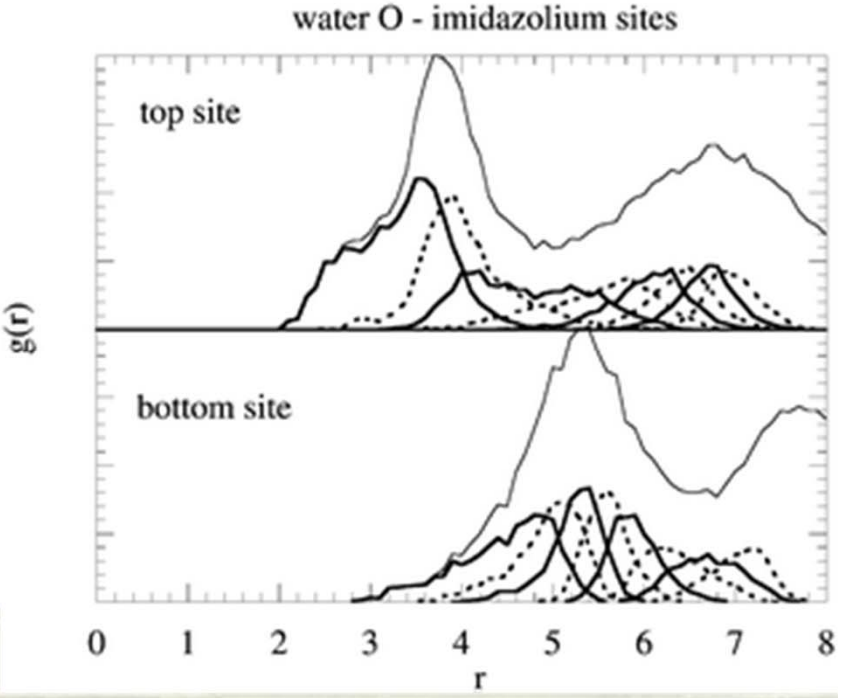


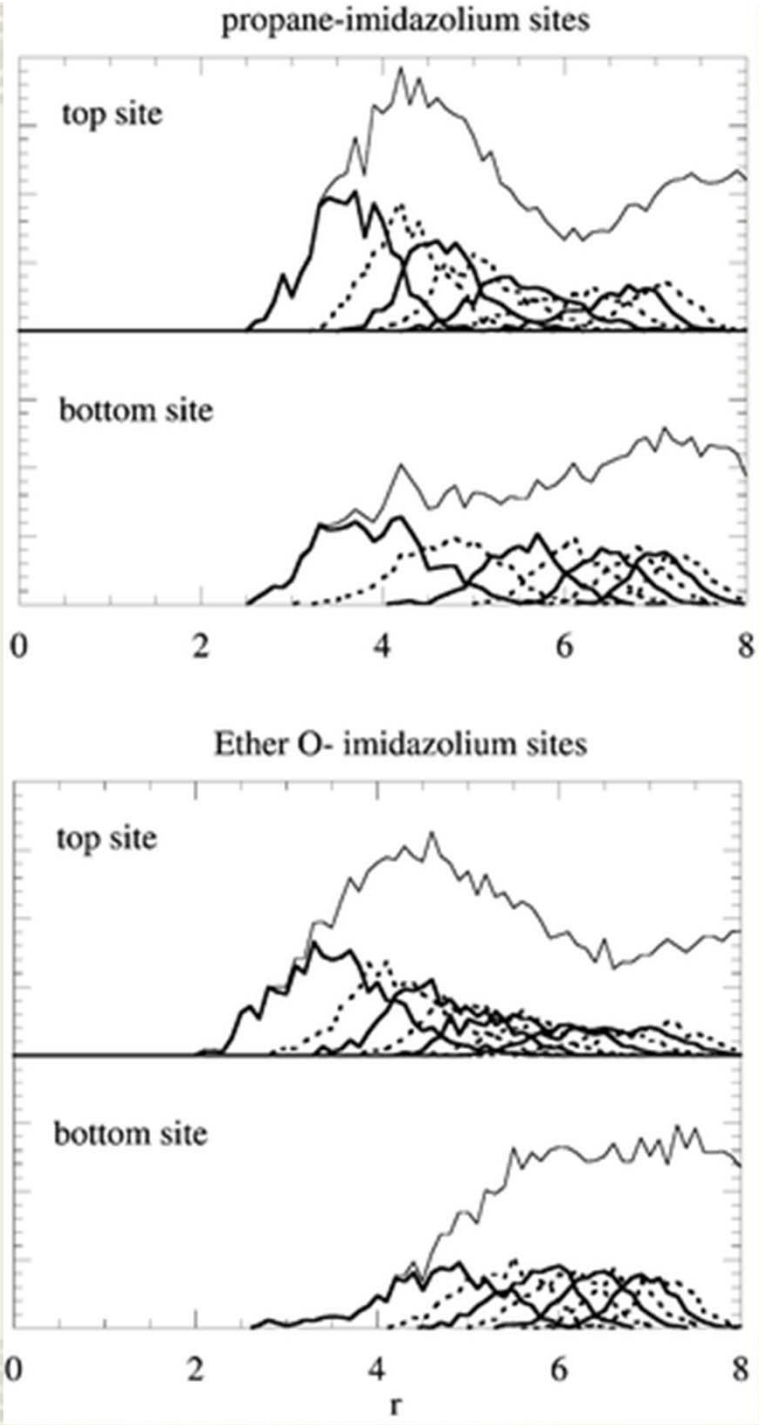
Three dimensional probability distribution



Structure of imidazolium ion






propane-imidazolium sites
top site
bottom site
0
2
4
6
8
Ether O- imidazolium sites
top site
bottom site
0
2
4
6
8
r

Pure properties of [bmim][PF_6]

- Inter- and intra-molecular potential function
  - Functional form of the force field

$$v_{tot} = 1/2 \sum_{ij} \left[4\varepsilon_{ij} \left(\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right) + \frac{q_i q_j}{r_{ij}} \right] + v(\phi)$$

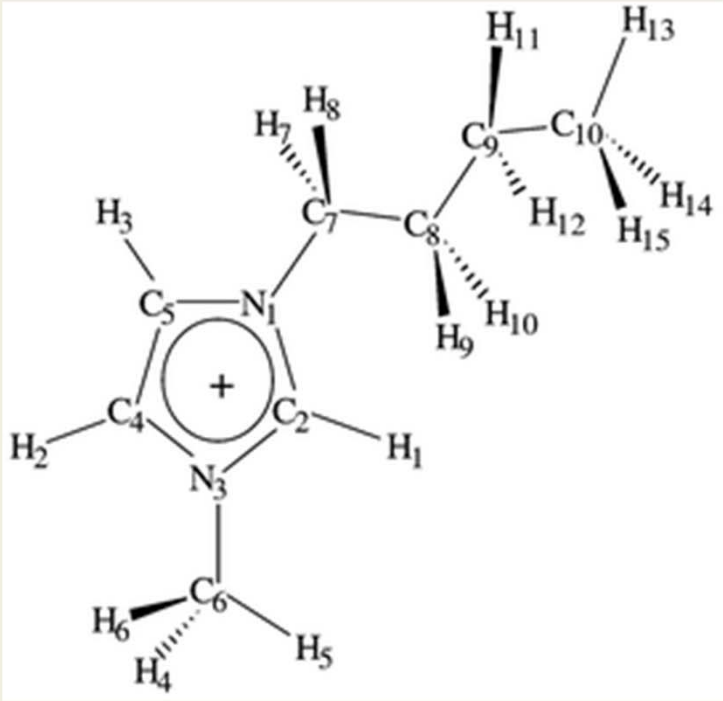
Jindal K. Shah (2002)

$$v(\phi) = v_0 + \frac{v_1}{2}(1 + \cos(\phi)) + \frac{v_2}{2}(1 - \cos(2\phi)) + \frac{v_3}{2}(1 + \cos(3\phi))$$

  - Lennard-Jones
  - Coulombic term
  - Torsional potential of dihedral angles

Ab initio calculation

- To determine the minimum geometry
- Bond length, angle, ring geometry (Cartesian coordinates)



CHELPG scheme

- Partial charges on each atoms

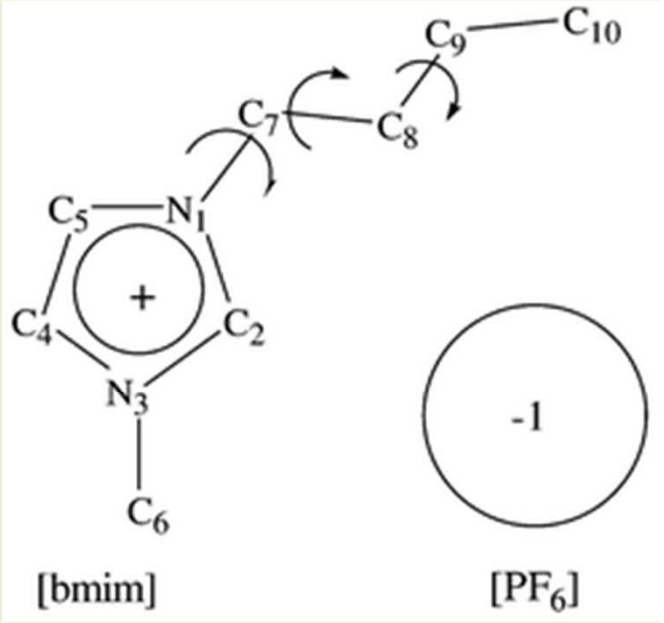
C.M.Breneman (1990)

United atom approximation

- Carbon atoms and PF_6 anion
- Carbon and hydrogen atom bond as single site located at the center of the carbon atom
- Partial charges are equal calculated carbon and hydrogen

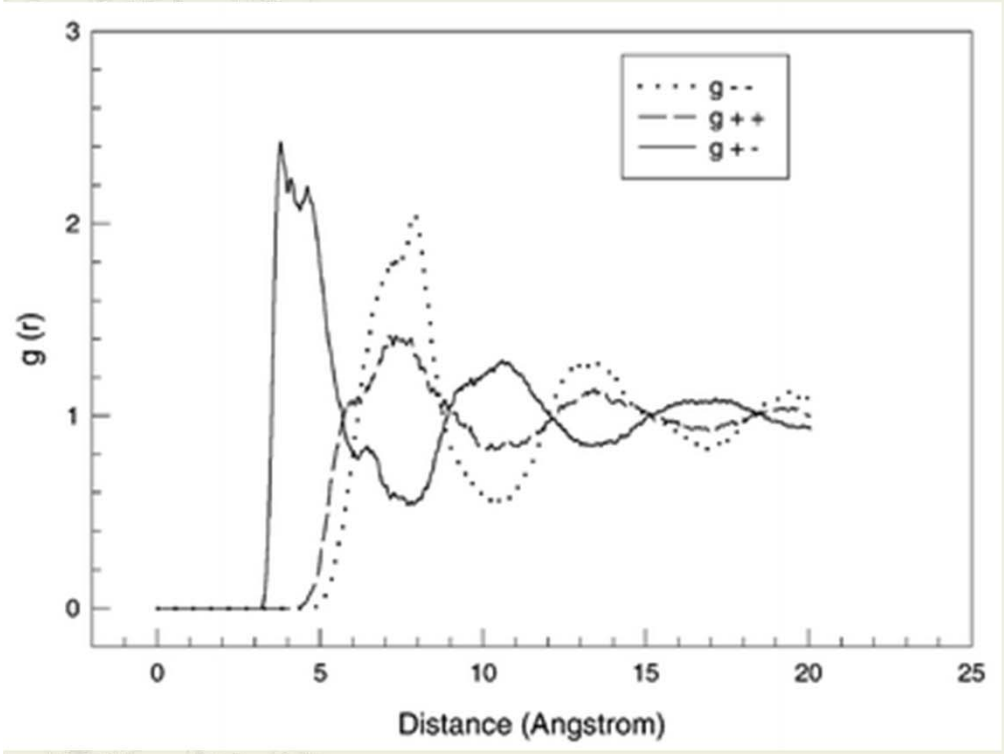
UA approximation

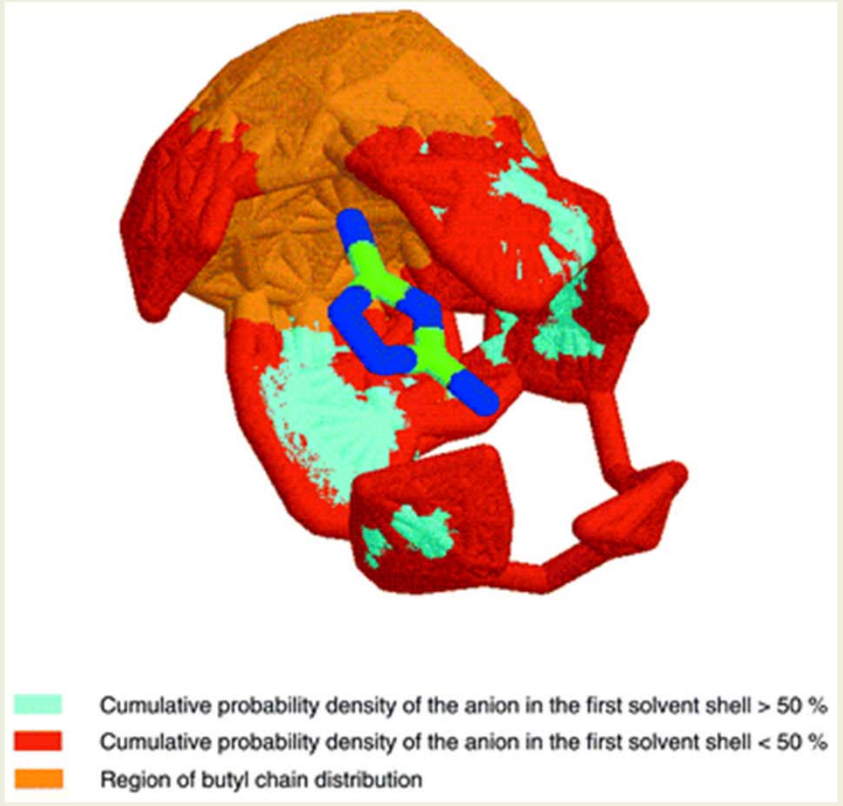
- Reducing computational costing



Simulation details

- Isobaric-isothermal (NPT) ensemble
- Each 192 cations and anion in periodic boundary
- Type of Monte carlo move
  - Translation of COM
  - Rotation about randomly chosen axis through cation COM
  - Dihedral angle rotations
- Volume change were attempted by adding two move (maintain pressure)
- Spherical potential truncation & long range correction


g (r)
Distance (Angstrom)
g - -
g + +
g + -
0
1
2
3
0
5
10
15
20
25


Cumulative probability density of the anion in the first solvent shell > 50 %
Cumulative probability density of the anion in the first solvent shell < 50 %
Region of butyl chain distribution

Effects of potential models

- Effect of the accuracy of the force field
  - Untied atom force field vs. all atom force field

- Required correct force field Jindal K. Shah (2003)
  - Understanding properties of ILs mixtures
  - Lack of experimental data
  - Sensitive properties with atom force field

- UA1 UA2 AA

Modeling vs. Simulation

- Density
  - UA1 : 3-5% over predicts
  - UA2 : 3-5% under predicts
  - AA : less than 1%

Comparison simulation with model

- Simulation
  - According to the composition and molecular structure, one can predict the thermodynamic properties
  - Need not the experiment
  - Calculation is quite costly
  - Accuracy of potential model is required to guarantee the value

- Model
  - Simplicity and quick calculation
  - To have accuracy result in explicit system
  - Some experimental data is required
    - To new or complex molecule (cannot explore), it is impossible to apply without other experiments

References

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