Coarse-grained Force Field Development of Room Temperature Ionic Liquids

Presenter: Alireza Moradzadeh, PI: Narayana R. Aluru

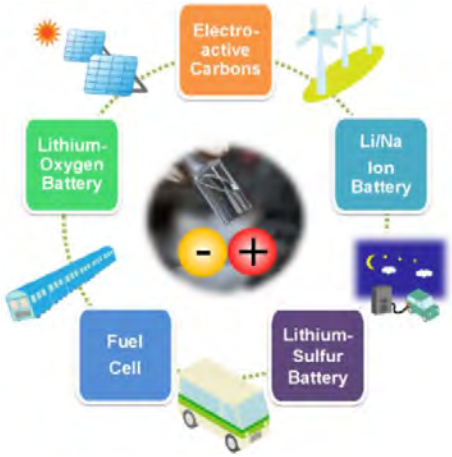
University of Illinois at Urbana-Champaign

Introduction and Background

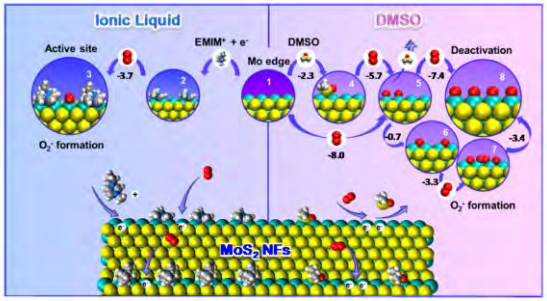
- Room Temperature Ionic Liquid (RTIL) are a new class of solvents
- Future chemistry demands its own solvents, RTILs are known as ‘green solvent’ and ‘designer solvent’
- Potential applications are hindered by lack of fundamental understanding like their heterogeneous structure and dynamics but still in liquid phase

- Current applications include but not limited:
  1. Energy storage
  2. Gas separation
  3. Lubrication
  4. CO2 Reduction

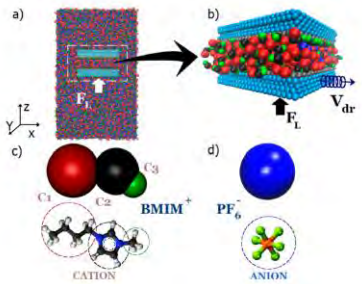
Watanabe et al. 2017 Chemical Review



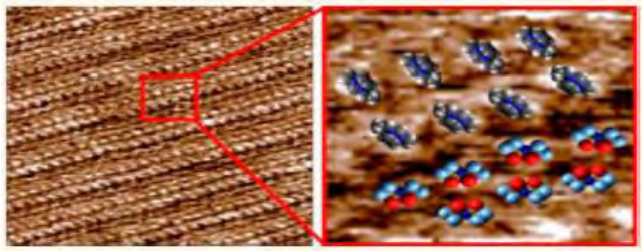
Assadi et al. 2016 ACS Nano



Fajardo et al. 2015 JCPL



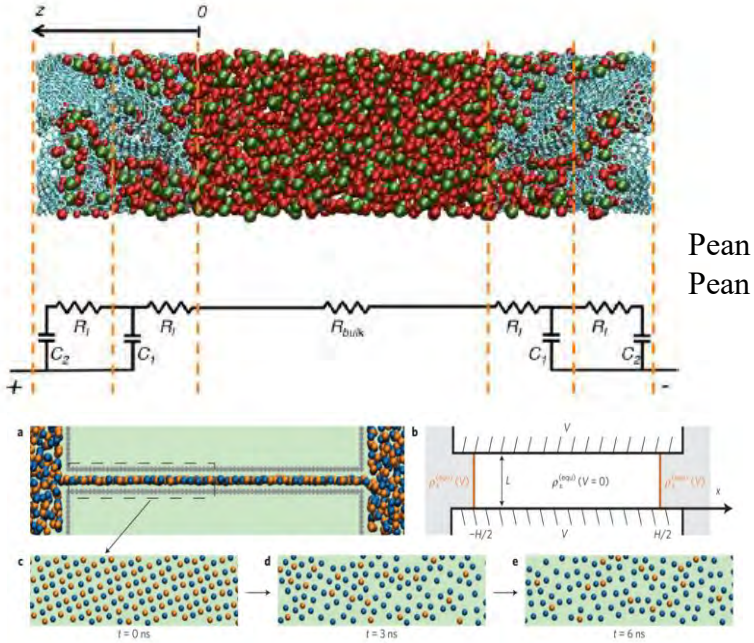
Elbourne et al. 2015 ACS Nano



Why: Coarse-graining

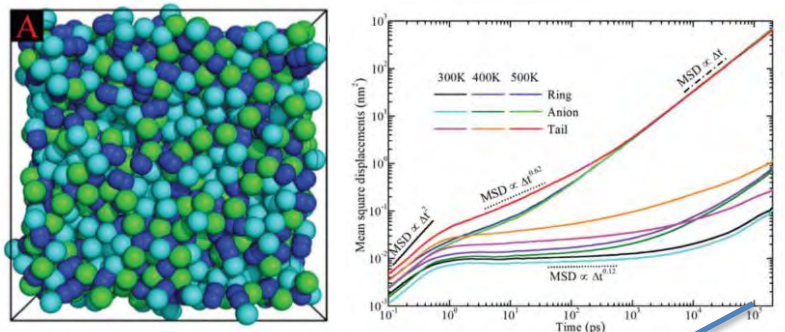
- Coarse-grained Simulation

To obtain the physical phenomena occurring in large time and size scale, hundreds of computationally intensive simulations are need to be carried out. All-atom MD simulation is not an option. Initial study used toy model, systematically parametrized coarse-grained model can bring a breakthrough.



Kondrat et al. 2014 Nature Materials

Pean et al. 2014 ACS Nano
Pean et al. 2015 JACS



Wang et al. 2018 Soft Matter, ~100 ns

System: Coarse-Grained and All-atom Simulations

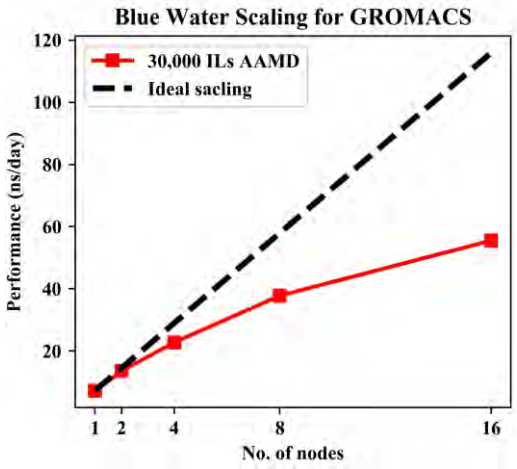
- System size for all-atom (AA) and coarse-grained (CG) simulation and cases, without computational cost of force field optimization!
- Package

1. GROMACS (MD) (Parallel)

2. VOTCA (data analyzing, Los Alamos National Laboratory)

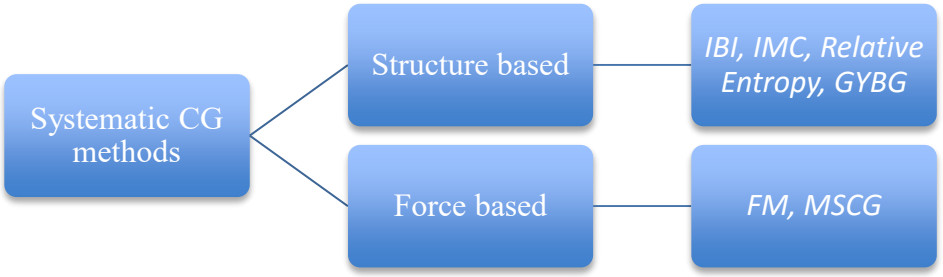
(Multi-thread, 32 Threads of BW, makes it really fast)

- Scalability of GROMACS



System	Type	Size	Cases	Time
C_4MIM	AA	24000	10	50 ns
C_6MIM	AA	25000	2	20 ns
C_8MIM	AA	26000	10	50 ns
$C_{10}MIM$	AA	28000	2	20 ns
C_4MIM	CG	4000	1000	5 ns
C_6MIM	CG	4000	4	20 ns
C_8MIM	CG	4000	500	5 ns
$C_{10}MIM$	CG	4000	4	20 ns
Weighted average		~ 4500		9 μs

Introduction and Background



- Relative Entropy

Use information theory to connect all-atom and coarse-grained systems

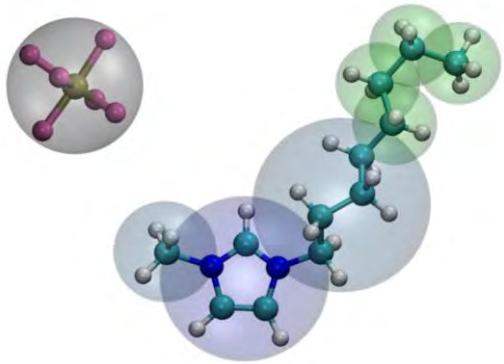
1. Systematic Charge Optimization
2. Thermodynamic Properties by adding constraint

$$S_{rel} = \beta\langle U_{CG} - U_{AA}\rangle_{AA} - \beta\langle A_{CG} - A_{AA}\rangle_{AA} + \langle S_{map}\rangle_{AA}$$

$$\nabla_\lambda S_{rel} = \beta\left\langle \frac{\partial U_{CG}}{\partial \lambda}\right\rangle_{AA} - \beta\left\langle \frac{\partial U_{CG}}{\partial \lambda}\right\rangle_{CG}$$

$$\lambda^{k+1} = \lambda^k - \chi H_{S_{rel}}^{-1} \cdot \nabla_\lambda S_{rel}$$

$$H_{ij,Srel} = \beta\left\langle \frac{\partial^2 U_{CG}}{\partial\lambda_i \partial\lambda_j}\right\rangle_{AA} - \beta\left\langle \frac{\partial^2 U_{CG}}{\partial\lambda_i \partial\lambda_j}\right\rangle_{CG} + \beta^2\left\langle \frac{\partial U_{CG}}{\partial\lambda_i}\frac{\partial U_{CG}}{\partial\lambda_j}\right\rangle_{CG} - \beta^2\left\langle \frac{\partial U_{CG}}{\partial\lambda_i}\right\rangle_{CG}\left\langle \frac{\partial U_{CG}}{\partial\lambda_j}\right\rangle_{CG}$$

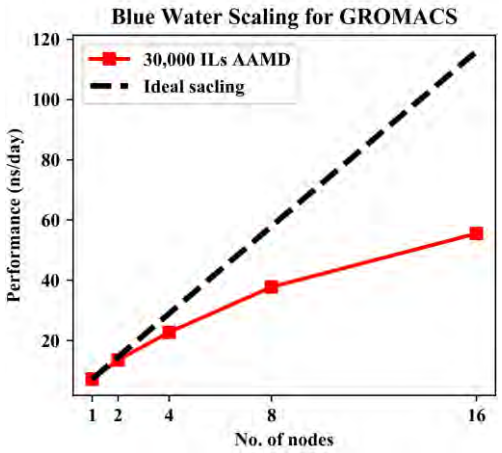


Why: Blue Waters for Coarse-graining

- BW nodes provide sufficiently high computational memory and power, at the request or with limited queue time

- BW provides rigorous platform for data processing

32 threads for VOTCA, data processing compared to 16 on common clusters
Electrostatic interaction are long-range, so computational study demands PME algorithms to be computed efficiently.



Node	Peak Memory GB/s
Blue Water Cray XE	102
NICS Kraken Cray XT	25.6
NERSC Hopper XE	85.3
ANL IBM BG/Q	42.6

Results: Mapping and Potential Parameters

For typical RTIL like BMIM PF6 with crude approximation for interaction between just one pair of Cation and Anion

Non-bonded: $\binom{32}{2} = 496$ # Bond: 32 # Angle: 45 # Dihedral: 59

Note: Consider number of atoms involved for angle (3) and dihedral (4) interaction

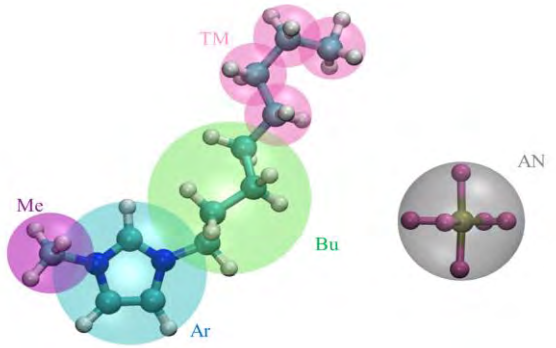
MD simulation details: (NPT ensemble) Annealing (5 ns, T = 600 K) , Equilibrium (15 ns, T = 400 K), Production (35 ns, T = 400 K)

$$u_{LJ}(r) = \frac{C_{12}}{r^{12}} - \frac{C_6}{r^6}$$

$$u_{Coul}(r_{ij}) = A_c \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}}$$

Obtaining optimal parameters need hundreds of iterations of MD simulation and relative entropy optimization

$$u_{sp}(r) = [1 \quad t \quad t^2 \quad t^3] \frac{1}{6} \begin{bmatrix} 1 & 4 & 1 & 0 \\ -3 & 0 & 3 & 0 \\ 3 & -6 & 3 & 0 \\ -1 & 3 & -3 & 1 \end{bmatrix} \begin{bmatrix} c_j \\ c_{j+1} \\ c_{j+2} \\ c_{j+3} \end{bmatrix}$$



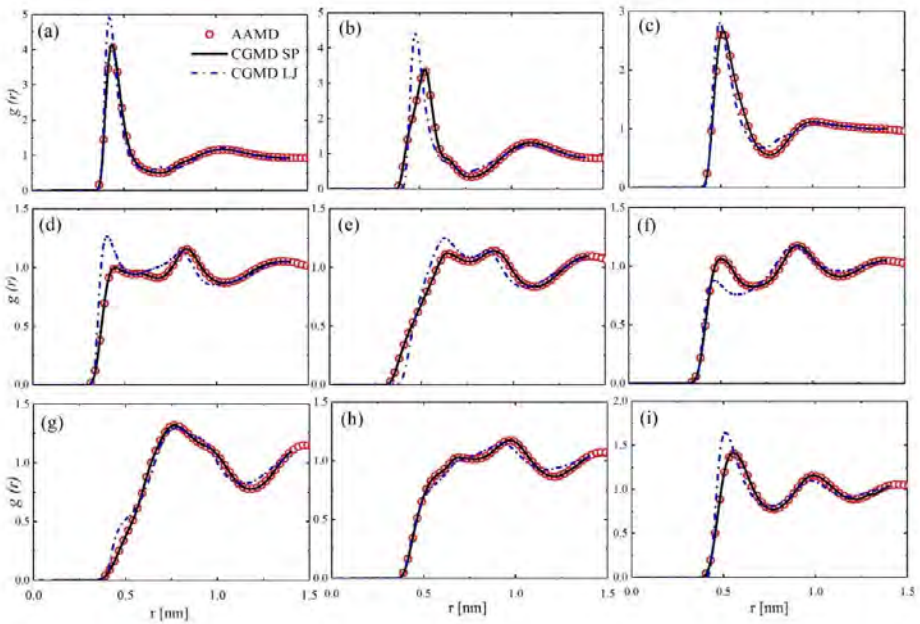
Results: Radial Distribution Function Bead-Bead

- Hierarchical Map: Moving from C_4C_1IM to C_8C_1IM

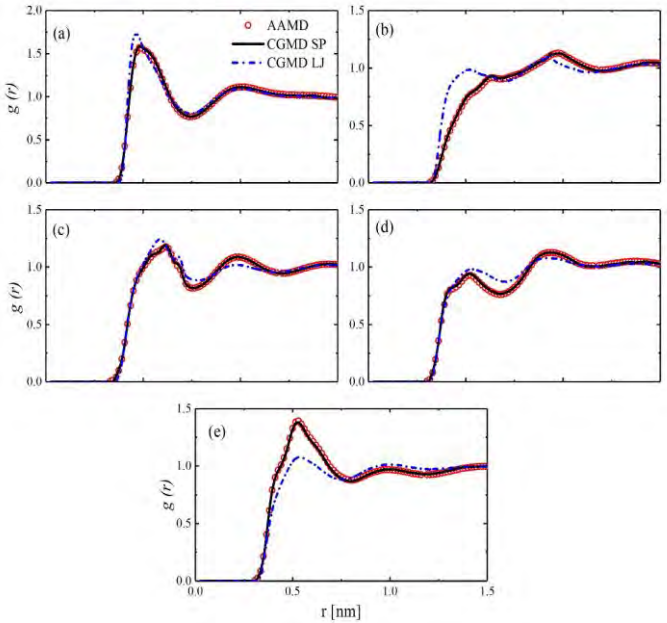
C4 has 10 interactions C8 has 15 interactions

10 Out of 15 interactions are present in C4 so optimization is done for 5 interaction

C_4MIM

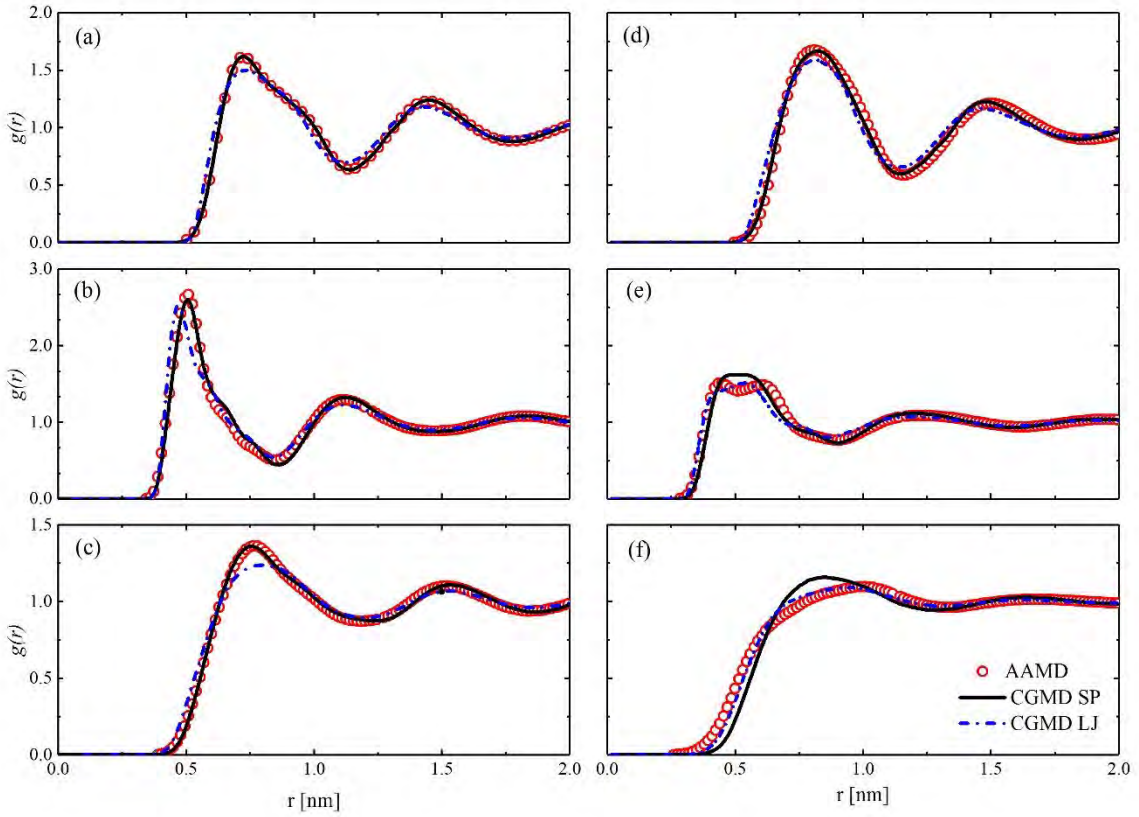


C_8MIM



Results: Radial Distribution Function Center of Mass

- Anion-Anion
- Anion-Cation
- Cation-Cation



Results: Charge-Ordering and Screening

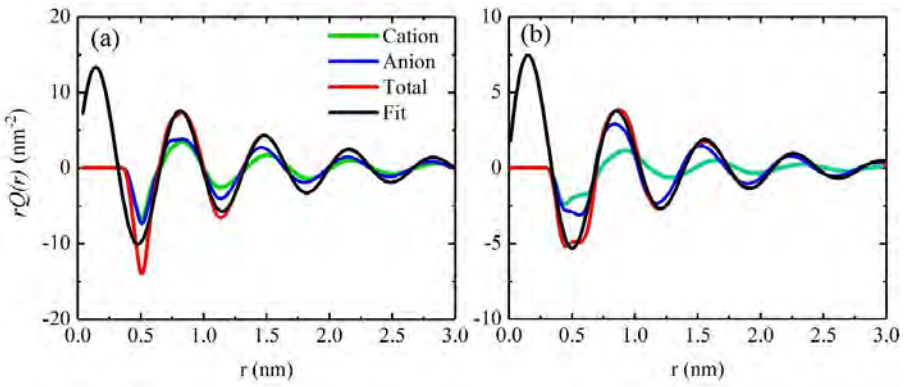
- Ionic liquids are mostly composed of charged species, how long charge-ordering goes is not well-understood. Application: touch screen, supercapacitor
- Charge-ordering and screening length depend on radial distribution function *i.e.* structure
- λ_{IL} is screening length

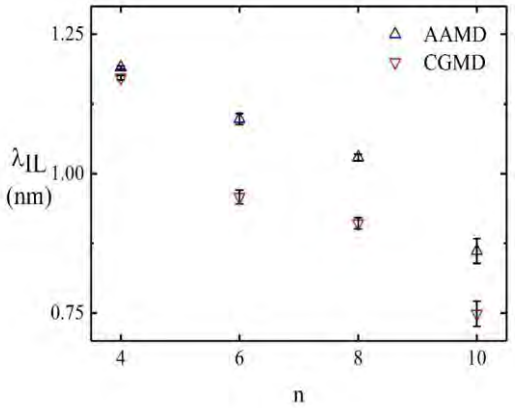
$$Q^{CA}(r) = \rho\big(g^{CA-CA}(r) - g^{CA-AN}(r)\big)$$

$$Q^{AN}(r) = \rho\big(g^{AN-AN}(r) - g^{CA-AN}(r)\big)$$

$$Q(r) = Q^{CA}(r) + Q^{AN}(r)$$

$$Q(r) = \frac{A}{r} e^{-r/\lambda_{IL}} \sin\left(\frac{2\pi r}{d} + \psi\right)$$





Results: Thermodynamic Properties

Transferability in temperature

$T\ (K)$	$C_4C_1IM\ PF_6\ , \rho\ (nm^{-3})$			$C_8C_1IM\ PF_6\ , \rho\ (nm^{-3})$		
	AAMD	CGMD SP	CGMD LJ	AAMD	CGMD SP	CGMD LJ
300	2.89	2.82 (2.31%)	2.93 (1.51%)	2.20	2.13 (3.18%)	2.22 (0.91%)
350	2.80	2.76 (1.21%)	2.81 (0.44%)	2.13	2.09 (1.88%)	2.14 (0.47%)
400	**2.71**	**2.71 (0.00%)**	**2.69 (0.6%)**	**2.05**	**2.05 (0.00%)**	**2.05 (0.00%)**
450	2.62	2.65 (1.14%)	2.58 (1.64%)	1.98	2.01 (1.52%)	1.97 (0.51%)

Transferability for different alkyl chain lengths

$C_nC_1IM\ PF_6$	n	4	6	8	10
AAMD	Density	**2.71**	2.33	**2.05**	1.75
CGMD SP	Density	**2.71**	2.27	**2.05**	1.77
	Relative error	**(0.00%)**	(2.64%)	**(0.00%)**	(1.14%)
CGMD LJ	Density	**2.69**	2.26	**2.05**	1.78
	Relative error	**(0.6%)**	(3.00%)	**(0.00%)**	(1.71%)

Results: Dynamical Properties

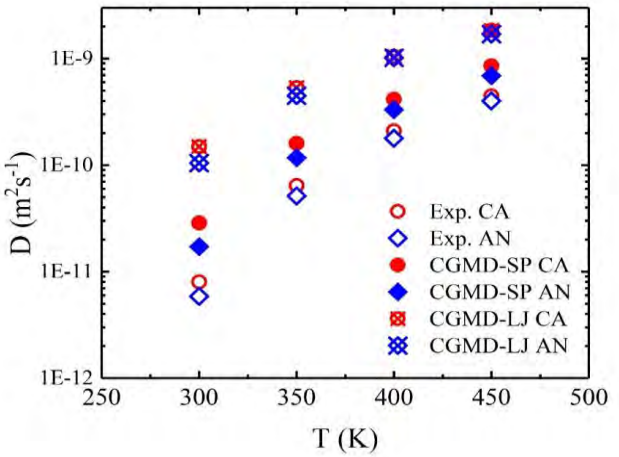
1. Due to high charge concentration RTILs have a very slow dynamics

2. Non-polarizable all-atom force fields fail to reproduce experimental results by an order of magnitude slower dynamics, polarizable force fields are computationally expensive

Testing Current Coarse-grained force fields:

1. Diffusion coefficient is two to five times higher than experiments
2. Qualitative behavior of dynamics is preserved during coarse-graining

Bulky cation moves faster than small anion



Conclusions and Acknowledgment

I. Development of a systematic method for coarse-grained force fields of ionic liquid with systemic accounting for charge optimization

II. Transferability of coarse-grained force field is analyzed for Imidazolium-based ionic liquids with different alkyl chain lengths at various thermodynamic states

III. Charge ordering and screening analyzed for all-atom and coarse-grained model, which shed lights on recent experimental discovery regarding screening and long-range interactions in ionic liquid

IV. Coarse-grained force field preserves the qualitative dynamical properties

Without Blue Waters, this was not possible, Special Thanks!

Any Questions?
Thank you for your attention