

Polarizable molecular dynamics simulations of ionic liquid based electrolytes for Na-ion batteries

Andrzej Eilmes, Piotr Kubisiak

Jagiellonian University, Faculty of Chemistry

Motivation

- Although rechargeable lithium-ion batteries have become very successful devices, prospect of growing demand and concerns about possible shortages in supply of lithium salts stimulate interest in alternative chemistries



- Significant effort is invested in research on sodium-ion batteries
- Experimental studies are supported by computational modeling

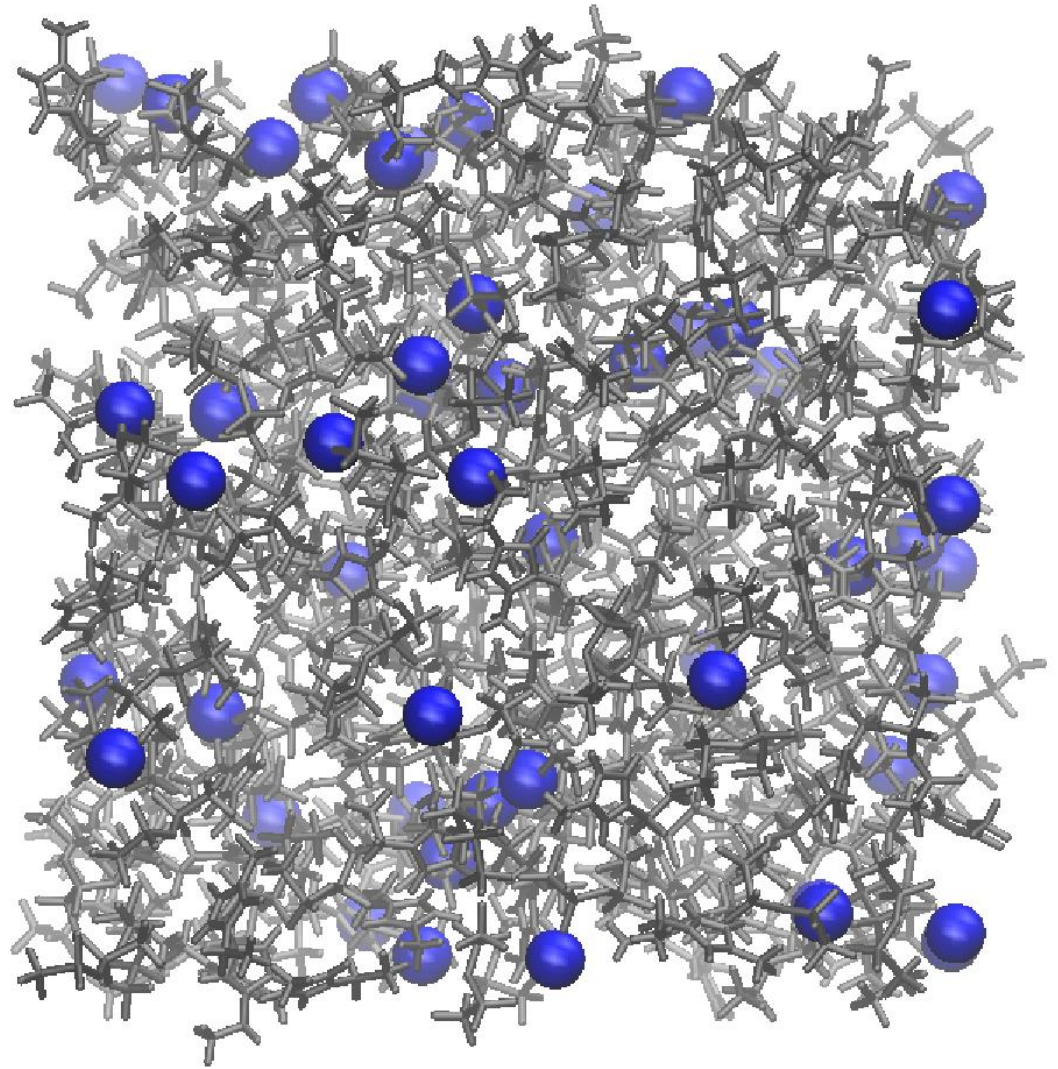
Motivation

- An important part of an ion battery is the electrolyte
- Several types of electrolytes for Na-ion devices have been proposed, based on molecular solvents, ionic liquids or polymers
- In this work we performed molecular dynamics simulations in order to check the performance of available force fields in reproduction of experimentally measured properties of ionic liquid based electrolyte
- Different parameterizations tested

Experimental data: D. Monti, E. Jónsson, M.R. Palacin, P. Johansson:
“Ionic Liquid Based Electrolytes for Sodium-Ion Batteries: Na⁺ Solvation and Ionic Conductivity”, J. Power Sources 2014, 245, 630–636

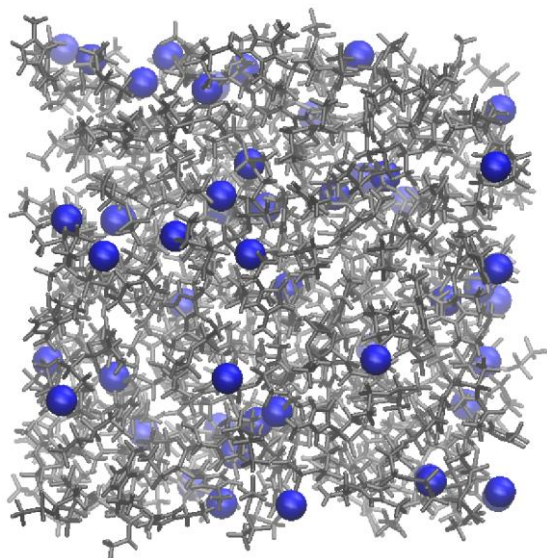
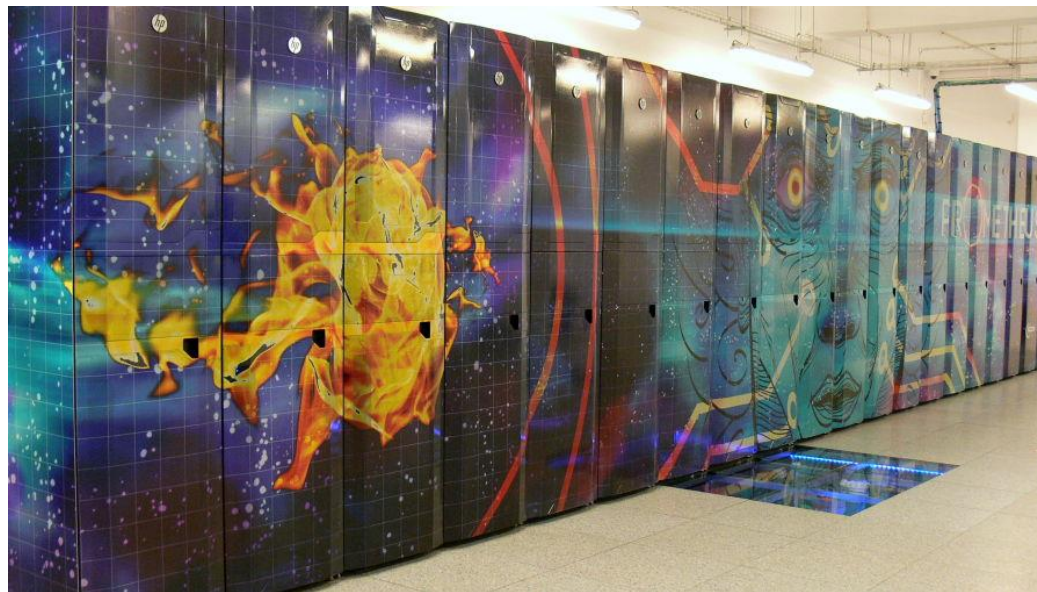
MD simulations

- simulation boxes of NaTFSI salt dissolved in EMIM-TFSI ionic liquid
- increasing content x of Na salt in $\text{Na}_x\text{EMIM}_{(1-x)}\text{TFSI}$ electrolytes
- several studies show the importance of polarization effects – but accounting for polarization is expensive
- three variants tested:
 - no polarizability NP1
 - Drude polarizability (charge-on-a-spring) Dr-P1
 - charge rescaling $\times 0.7$ approach sc-P1



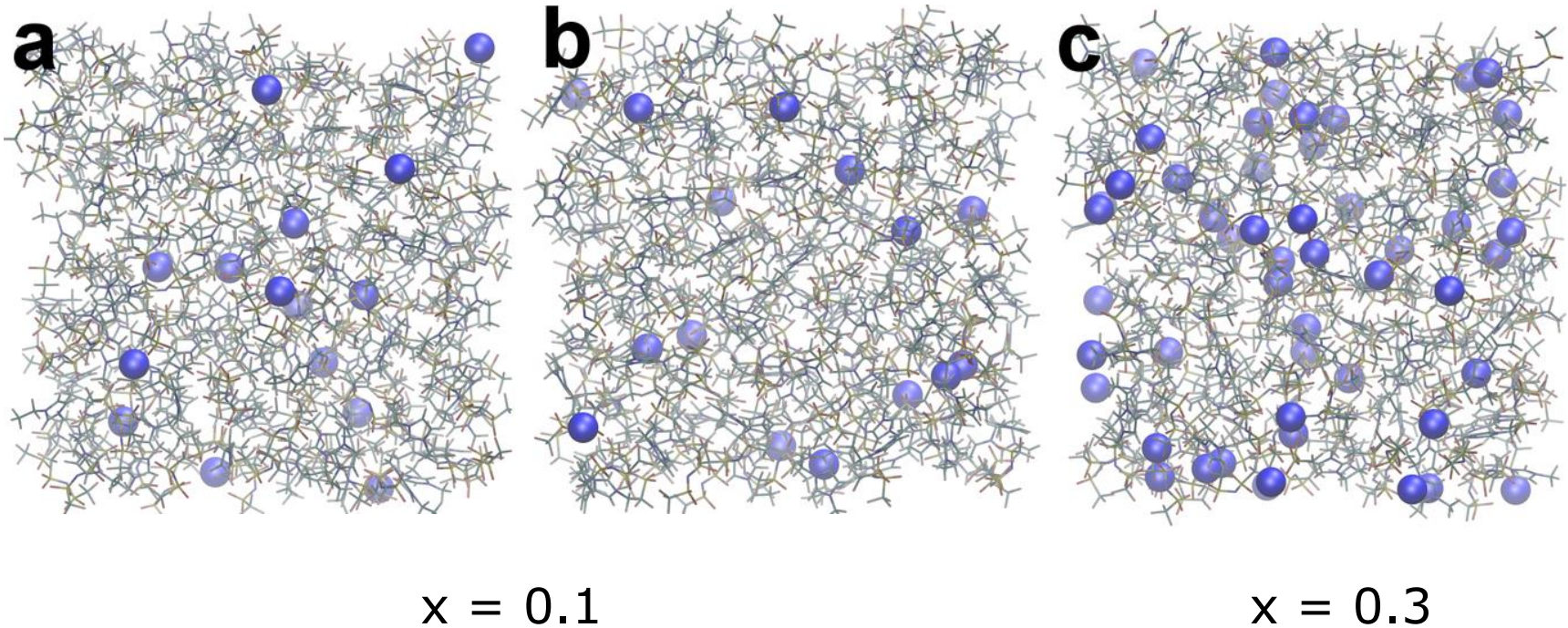
MD simulations

- NAMD v. 2.12 MD software
- NpT simulations with Nose-Hoover thermostat ($T=298$ or 333 K) for 140-170 ion pairs
- about $1.1 \mu\text{s}$ of the MD trajectory collected



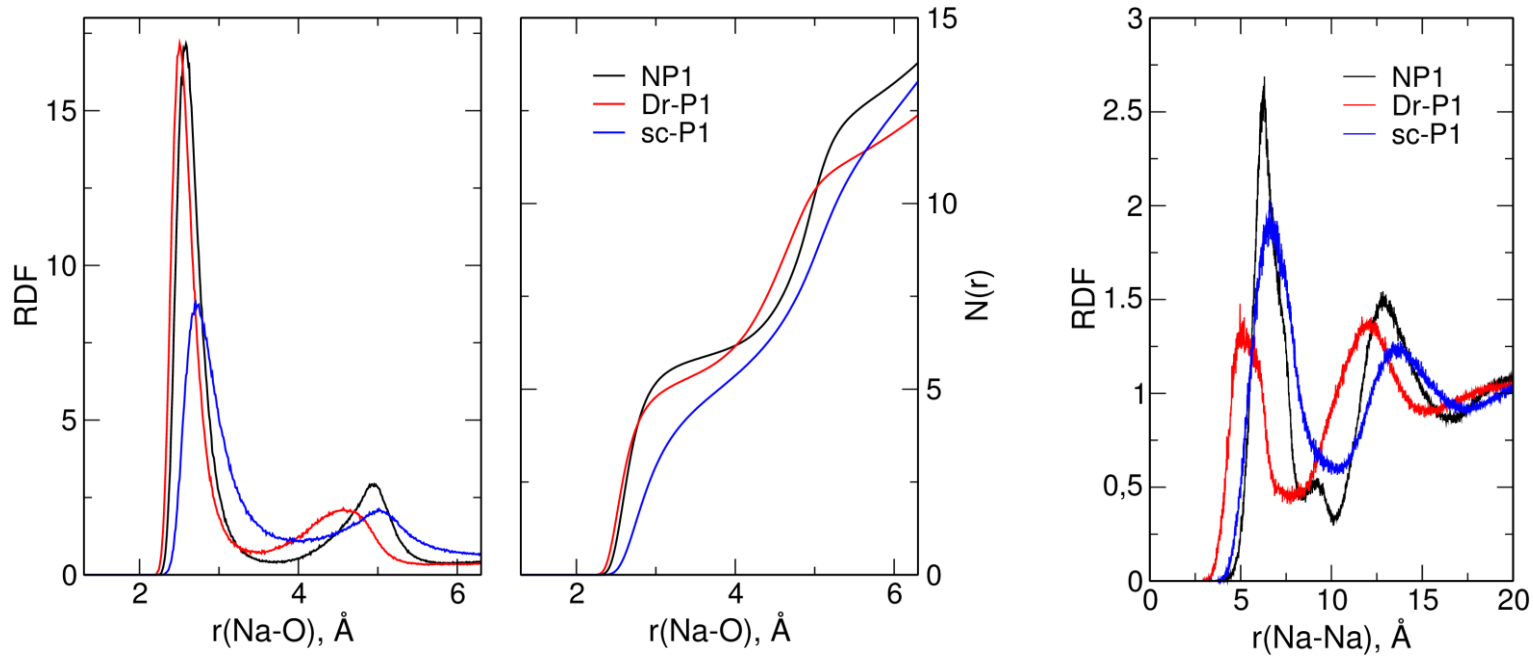
- two Prometheus nodes (2x24 CPU cores) were used for each simulation
- each run produced approx. 48 ns (NP1, sc-P1) or 27 ns (Dr-P1) trajectory per day
- about 100k or 180k walltime hours were spent per simulation

Structures of electrolytes



Although at short times there are differences in spatial distribution of Na^+ ions, electrolytes are homogenous at long timescales

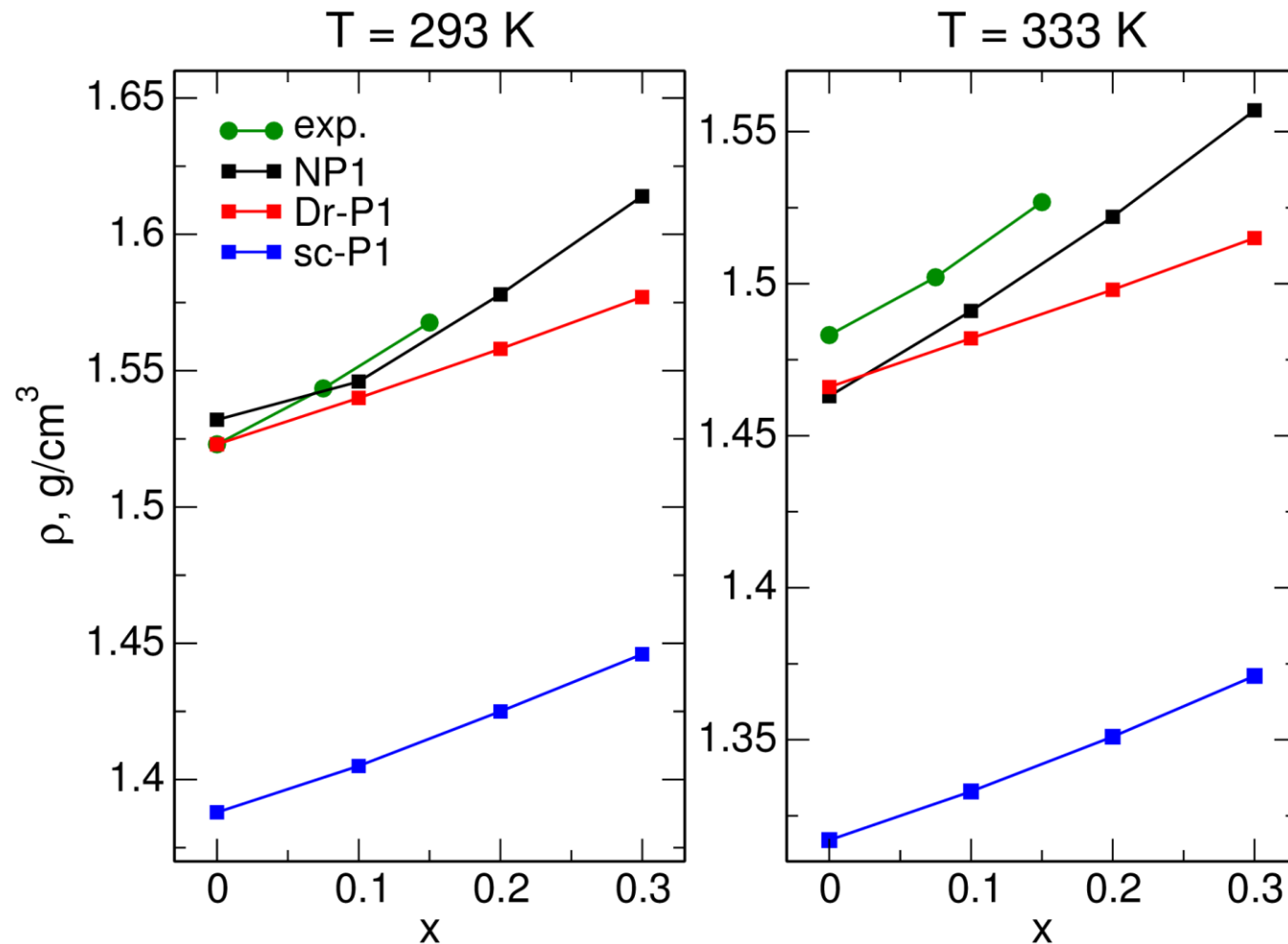
Structures of electrolytes



In polarizable force field (Dr-P1) maxima in distributions of Na-O and Na-Na distances move to smaller distances

Effect of charge rescaling is the opposite

Densities of electrolytes



The best agreement with experiment is obtained in non-polarizable simulations

Charge rescaling yields seriously underestimated values

Transport properties

- Transport properties estimated from recorded MD trajectories
- viscosity: integral over time of pressure autocorrelation tensor

$$\eta = \frac{V}{kT} \int_0^{\infty} \langle P_{\alpha\beta}(t) P_{\alpha\beta}(0) \rangle dt$$

- diffusion coefficients: from mean square displacements of ions

$$D_i = \lim_{t \rightarrow \infty} \frac{1}{6t} \langle |\mathbf{R}_i(t) - \mathbf{R}_i(0)|^2 \rangle$$

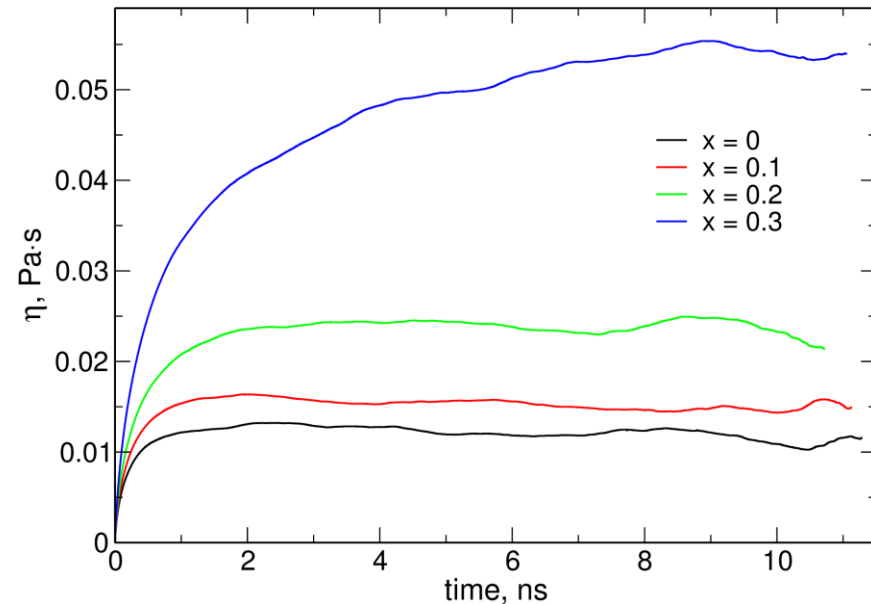
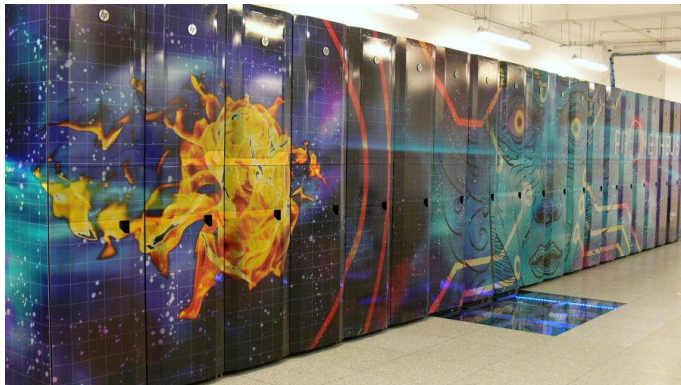
- conductivity: related to the collective ion diffusion coefficient

$$D_{coll} = \lim_{t \rightarrow \infty} \frac{1}{6tN} \sum_{i,j} z_i z_j \langle [\mathbf{R}_i(t) - \mathbf{R}_i(0)][\mathbf{R}_j(t) - \mathbf{R}_j(0)] \rangle$$

Why do we need computational power?

- viscosity:

$$\eta = \frac{V}{kT} \int_0^{\infty} \langle P_{\alpha\beta}(t) P_{\alpha\beta}(0) \rangle dt$$



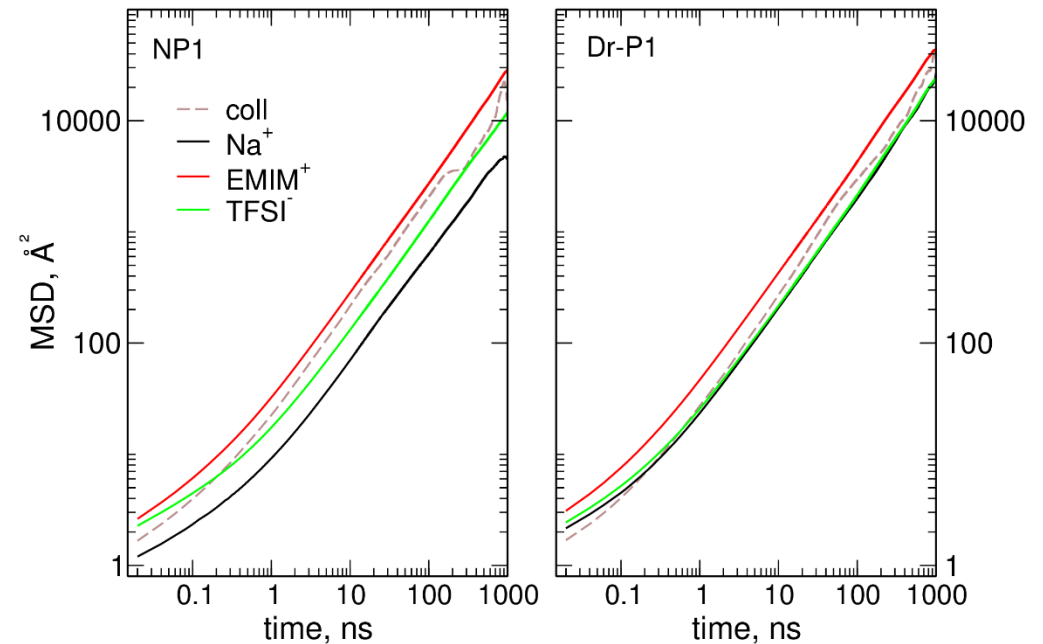
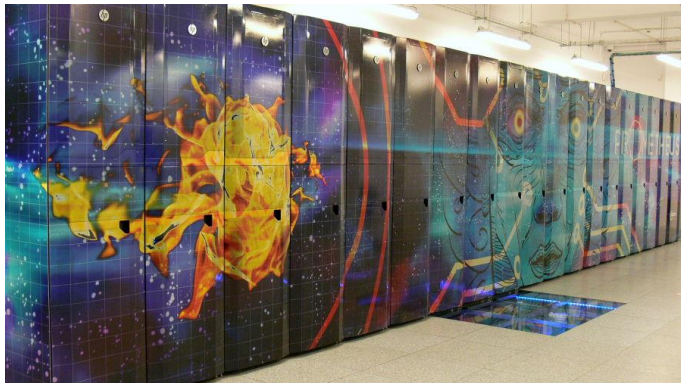
- time long enough is needed to get the integral constant
- but there is inevitable noise
- data averaged over 1000 ns to get reasonable accuracy for 10 ns

Why do we need computational power?

- diffusion and conductivity:

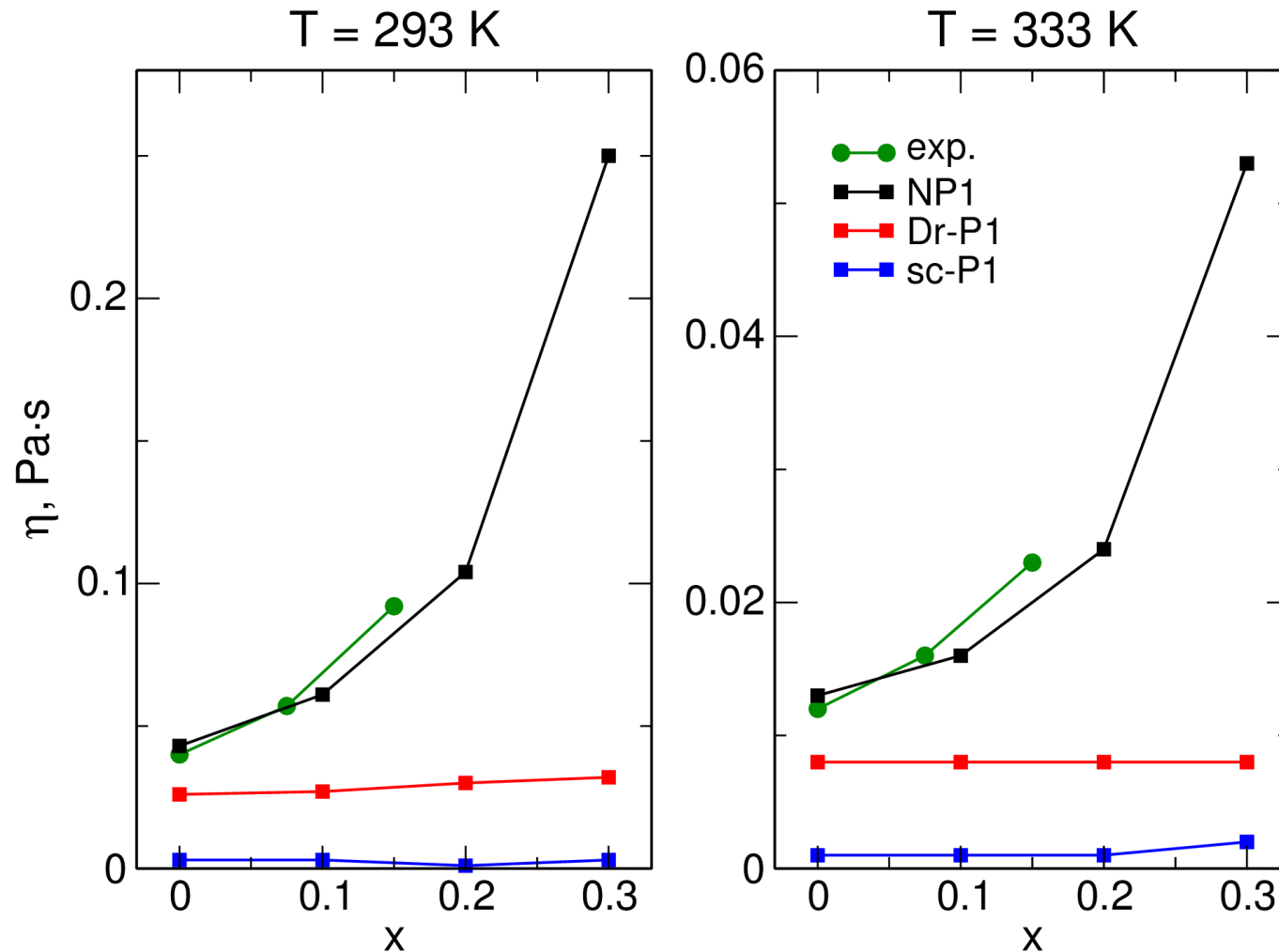
$$D_i = \lim_{t \rightarrow \infty} \frac{1}{6t} \langle |\mathbf{R}_i(t) - \mathbf{R}_i(0)|^2 \rangle$$

$$D_{coll} = \lim_{t \rightarrow \infty} \frac{1}{6tN} \times \sum_{i,j} z_i z_j \langle [\mathbf{R}_i(t) - \mathbf{R}_i(0)][\mathbf{R}_j(t) - \mathbf{R}_j(0)] \rangle$$



- we have to achieve timescale beyond subdiffusive regime (> 10 ns)
- to get reasonable data for 100 ns we average over whole 1000 ns

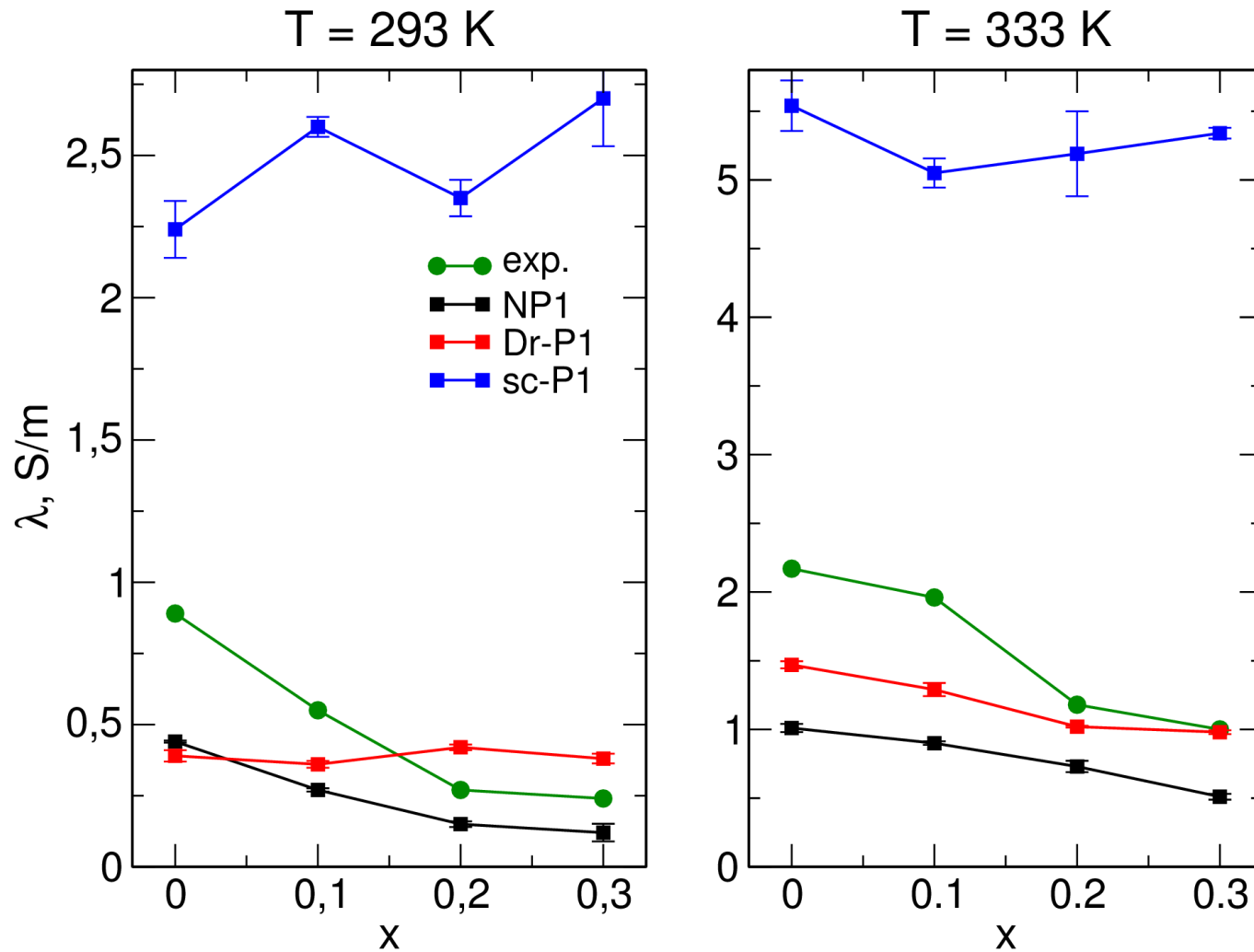
Viscosity



The best agreement with experiment again is obtained in non-polarizable simulations

Polarizable FF yields seriously underestimated values and no dependence on x and charge rescaling gives wrong order of magnitude

Conductivity

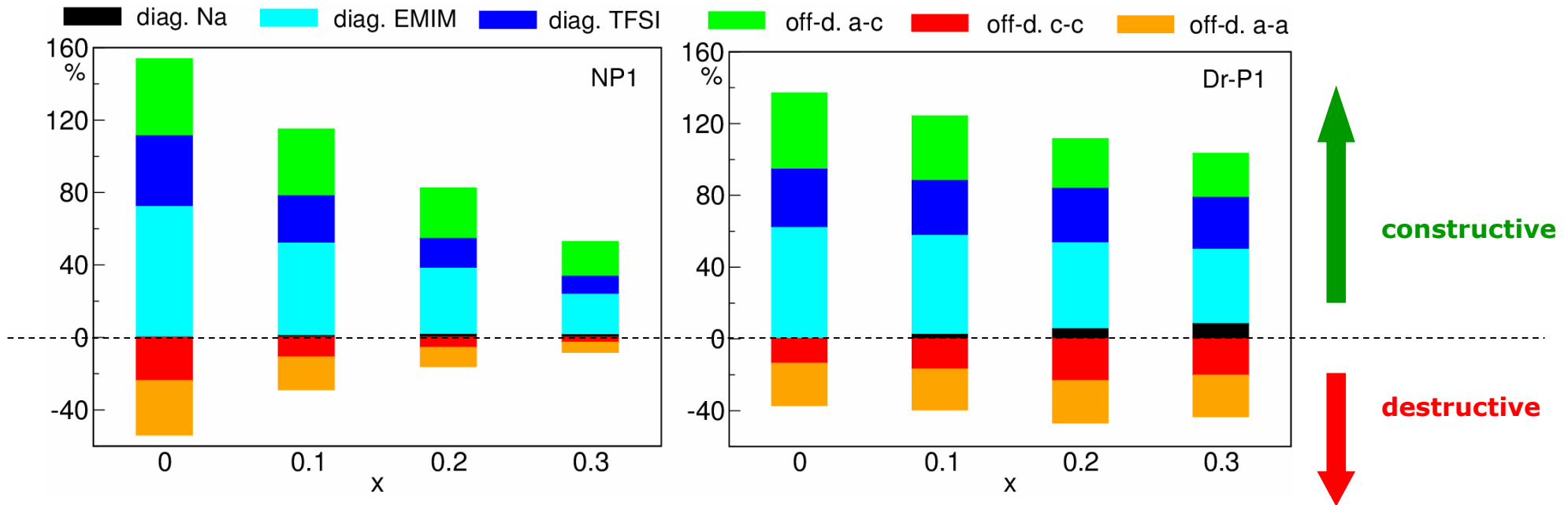


Values increase in polarizable Dr-P1 field and are closer to experiment
Charge rescaling wrong again (too large values)

Conductivity

Collective diffusion may be decomposed into different components

$$D_{coll} = \lim_{t \rightarrow \infty} \frac{1}{6tN} \sum_{i,j} z_i z_j \langle [\mathbf{R}_i(t) - \mathbf{R}_i(0)][\mathbf{R}_j(t) - \mathbf{R}_j(0)] \rangle$$



- Unlike molecular liquids, in ionic liquids anion-cation motions are anticorrelated and contribute positively to conductivity
- In nonpolarizable FFs, conductivity decreases with x , because all terms, including diagonal decrease
- In polarizable FFs, diagonal terms decrease slowly, and the reduction of conductivity is due to anion-anion and cation-cation anticorrelations

Summary

- Some properties (density, viscosity) of $\text{Na}_x\text{EMIM}_{(1-x)}\text{TFSI}$ electrolytes are better described by non-polarizable parameterization
- Polarizable FF gives better values of conductivity and IL diffusion coefficients
- Cheap method of charge rescaling fails completely, yielding too low densities, and accordingly too low viscosities and too high conductivities
- Details of some processes (contributions to conductivity) depend on the polarizable vs. nonpolarizable parameterization – need for further studies

P. Kubisiak, A. Eilmes: "Molecular Dynamics Simulations of Ionic Liquid Based Electrolytes for Na-Ion Batteries: Effects of Force Field", J. Phys. Chem. B 2017, 121, 9957-9968.

Acknowledgments

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