Solvent activity in electrolyte solutions by molecular simulation of the osmotic pressure

Martin Thomas Horsch, Maximilian Kohns, Steffen Reiser and Hans Hasse

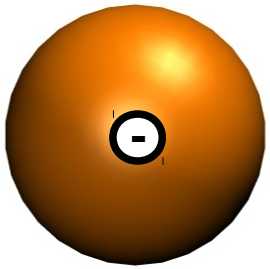
Laboratory of Engineering Thermodynamics
University of Kaiserslautern, Germany

Computational Molecular Engineering

Physics of Liquid Matter: Modern Problems
Kyiv, 29th May 2016

Molecular simulation of salt solutions

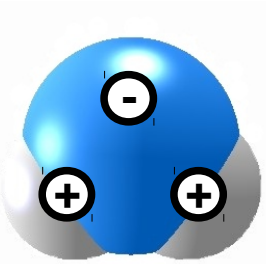
Molecular models:



Ions

1 Lennard-Jones

1 point charge



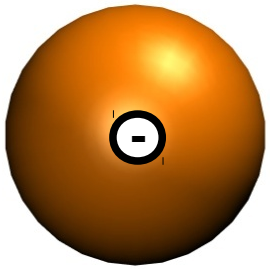
Water (here: SPC/E)

1 Lennard-Jones

3 partial charges

Molecular simulation of salt solutions

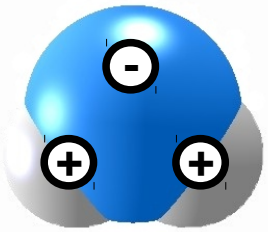
Molecular models:



Ions

1 Lennard-Jones

1 point charge



Water (here: SPC/E)

1 Lennard-Jones

3 partial charges

Literature models:

- Scattering of model parameters

Parameters for Na^+:

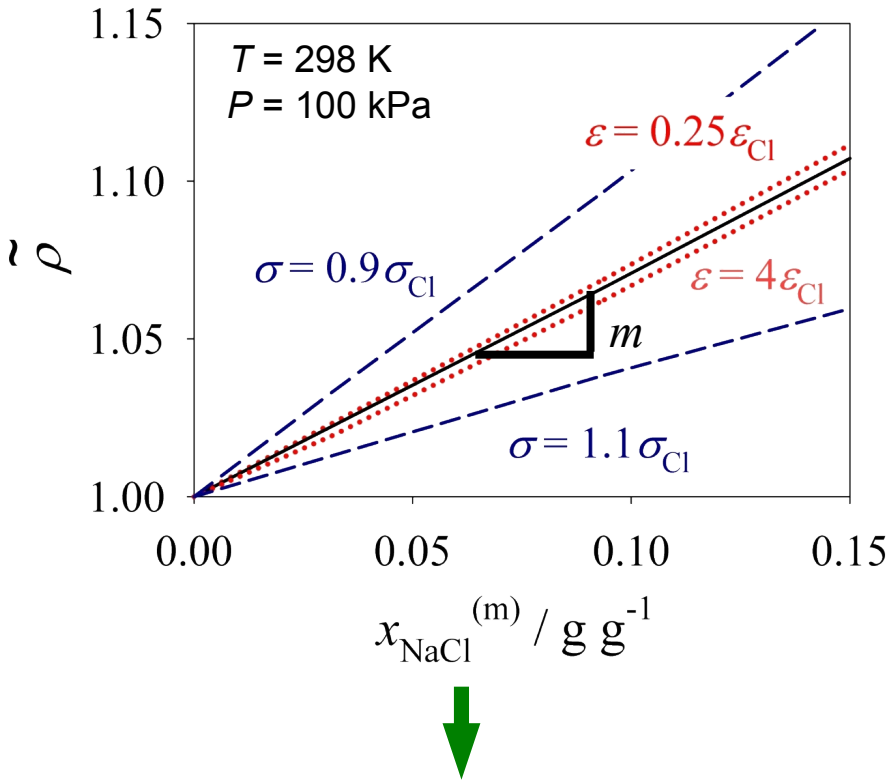
$1.9 < \sigma_{Na+} / Å < 4.1$

$0.06 < \varepsilon_{Na+} / K < 1068.8$

⇨ Large deviation from experimental data!

Adjusting the model to experimental data

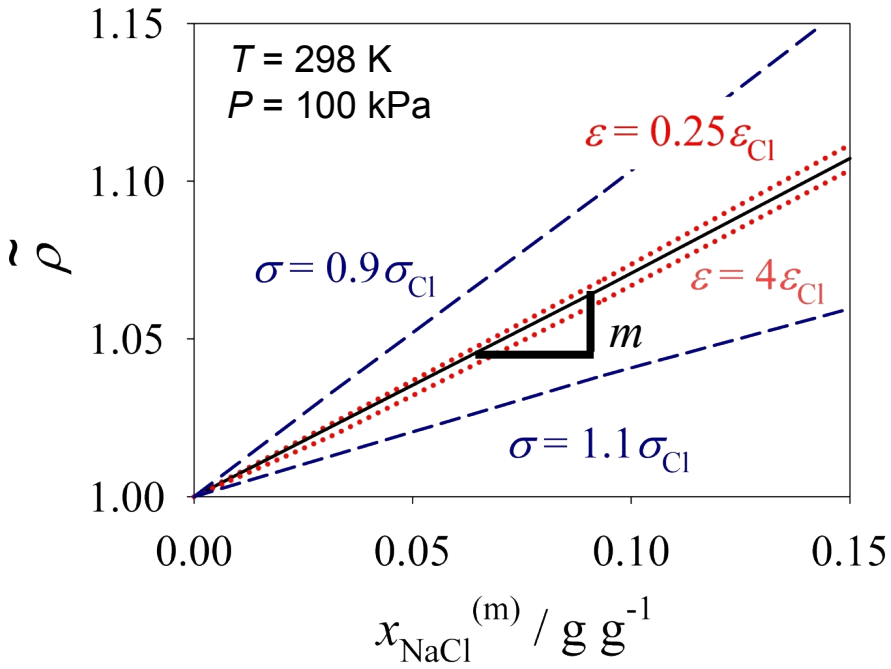
Density ratio “solution : pure”



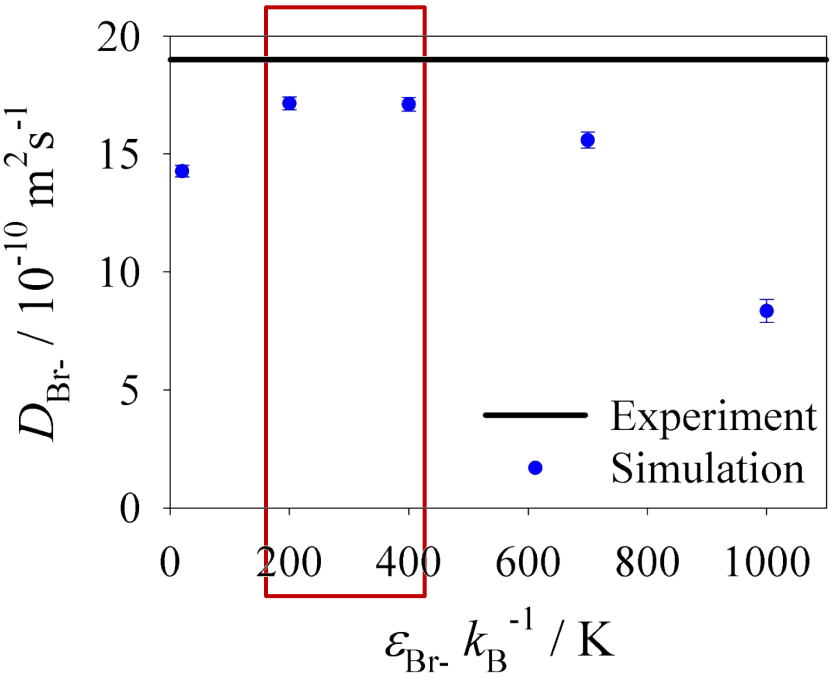
Lennard-Jones size parameter σ

Adjusting the model to experimental data

Density ratio “solution : pure”



Self-diffusion coefficients

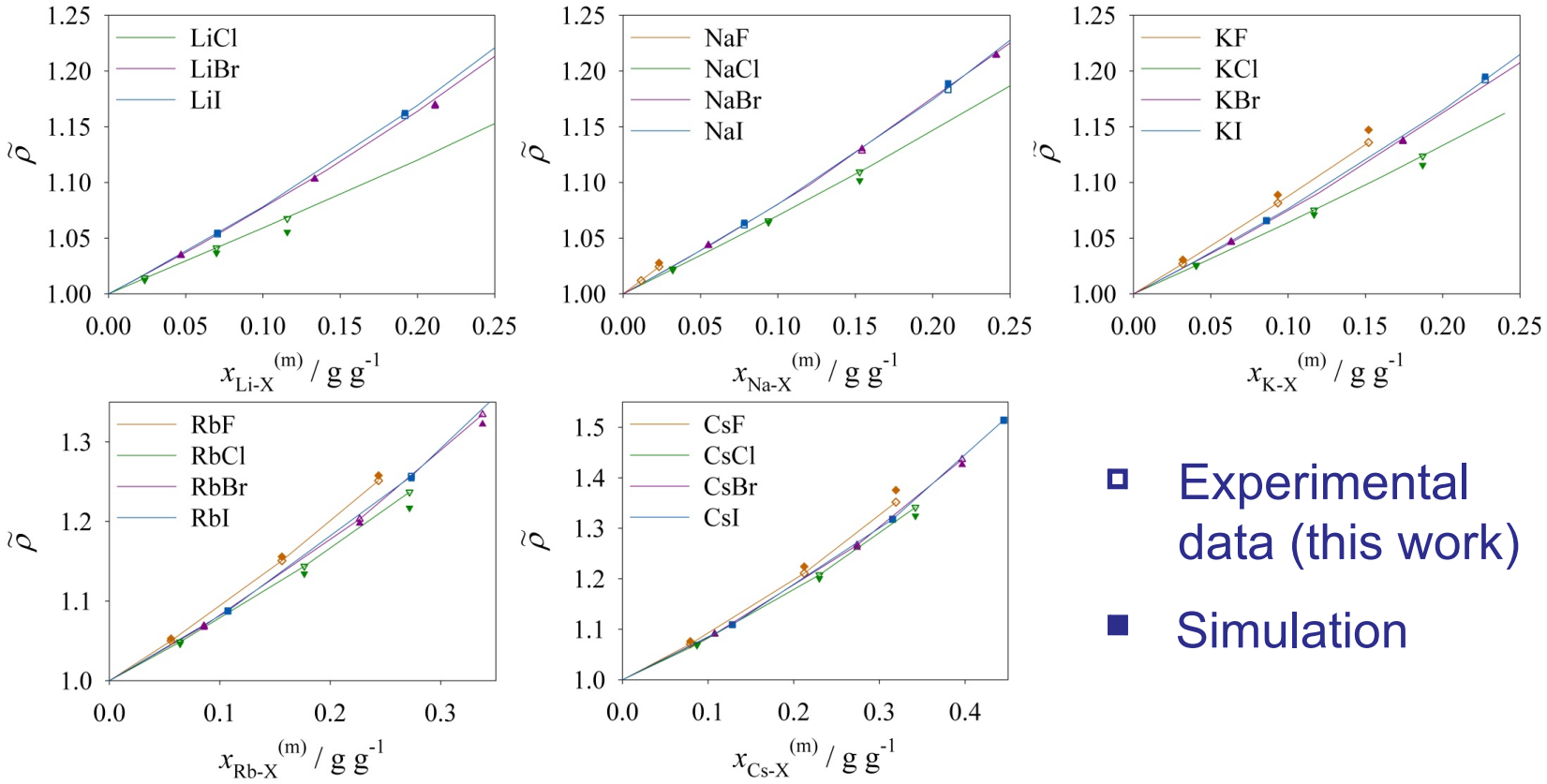


Lennard-Jones size parameter σ

Lennard-Jones energy parameter ε

Validation: Density at higher temperature

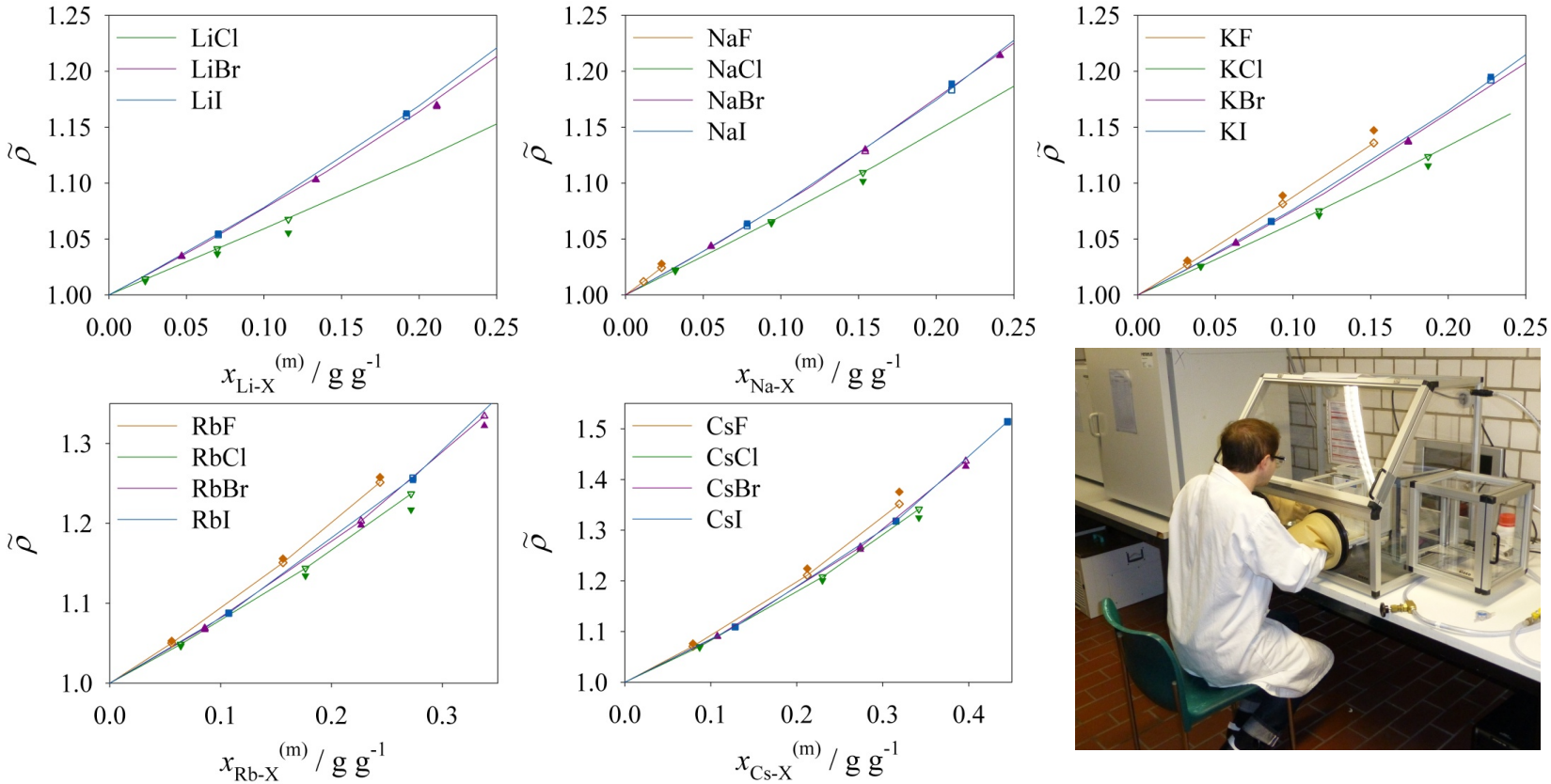
Prediction of the density for aqueous solutions at T = 333 K and P = 1 bar:



- Experimental data (this work)
- Simulation

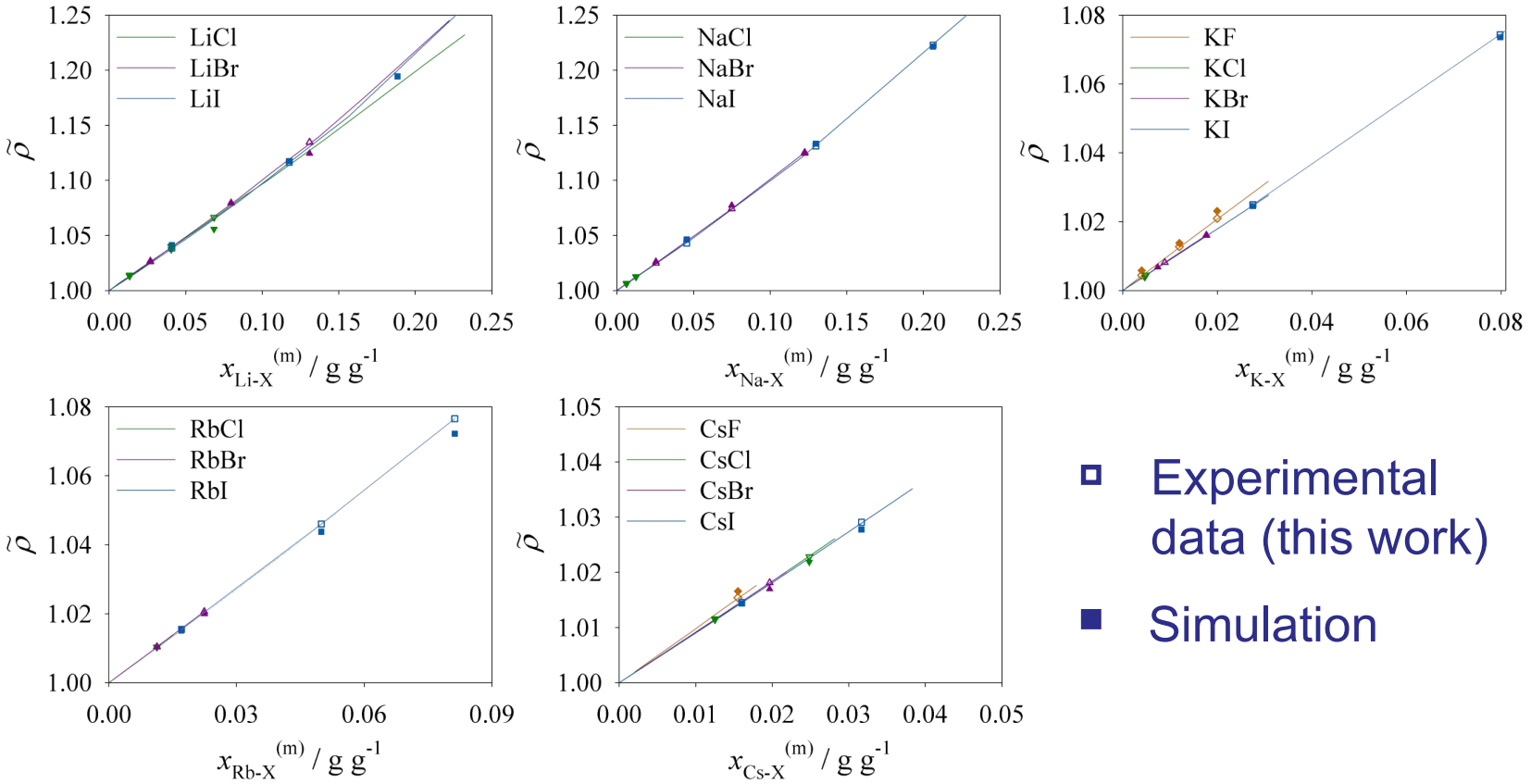
Validation: Density at higher temperature

Prediction of the density for aqueous solutions at T = 333 K and P = 1 bar:



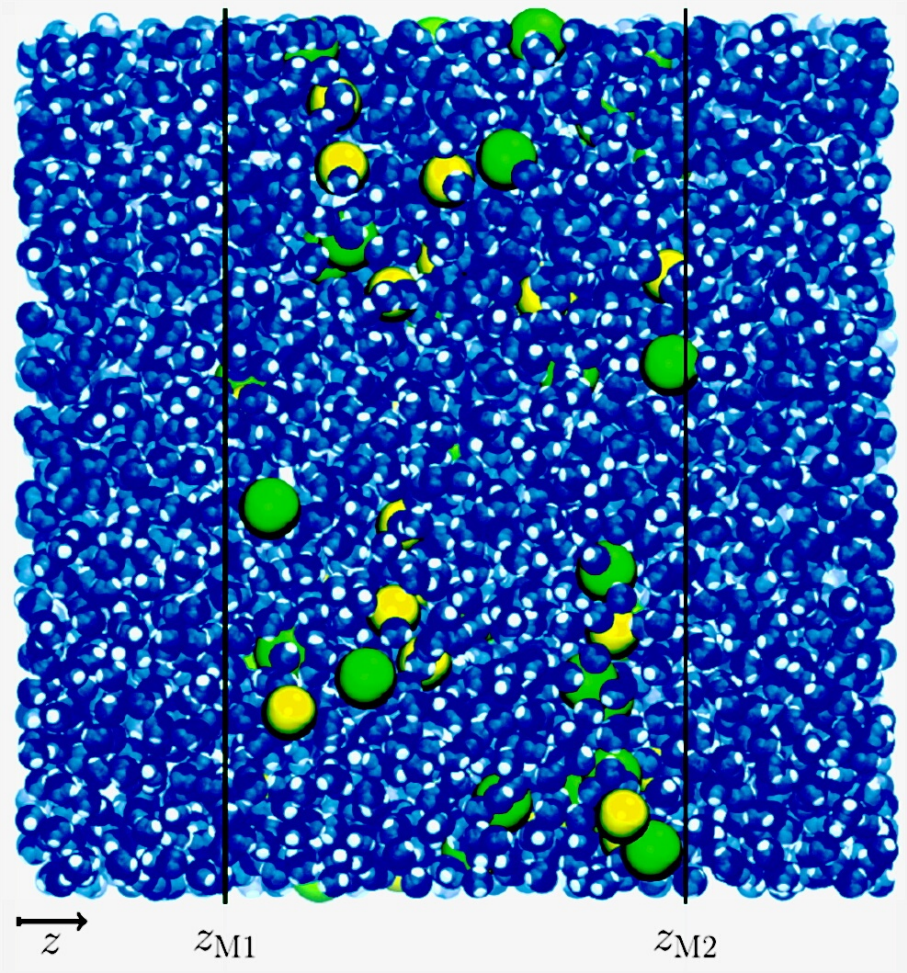
Validation: Non-aqueous solutions

Density of methanolic electrolyte solutions at T = 298 K and P = 1 bar:



- Experimental data (this work)
- Simulation

Osmotic pressure for activity of solvents



In a dense liquid, it is hard to compute the chemical potential (or activity) by inserting test particles.

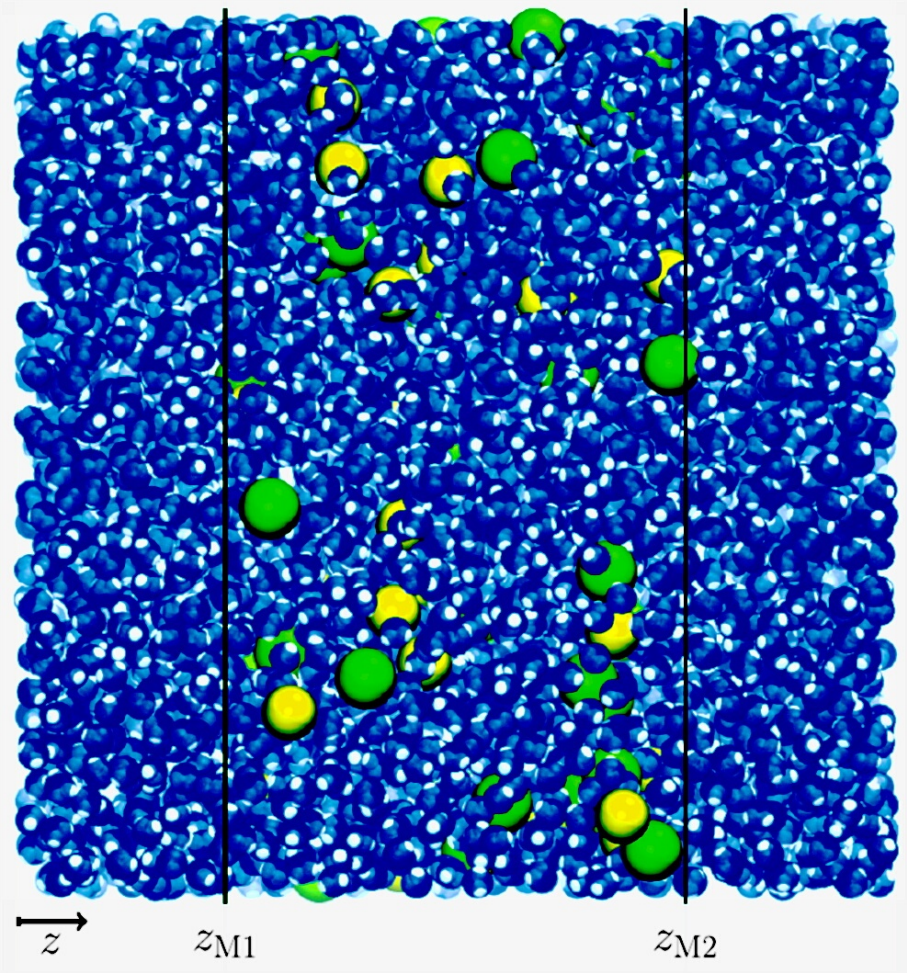
OPAS method: Compute the osmotic pressure from the force acting on a virtual semipermeable membrane.

External harmonic potential constraining the solute inside.

No external potential for the solvent.

$$\Pi = P^{in} - P^{out}$$

Osmotic pressure for activity of solvents



Step 1: Pseudo-*NPT* run, where the barostat is adjusted to regulate P^{out}.
Step 2: *NVT* simulation.

OPAS method: Compute the osmotic pressure from the force acting on a virtual semipermeable membrane.

Solvent activity (Raoult normalization) from osmotic pressure:

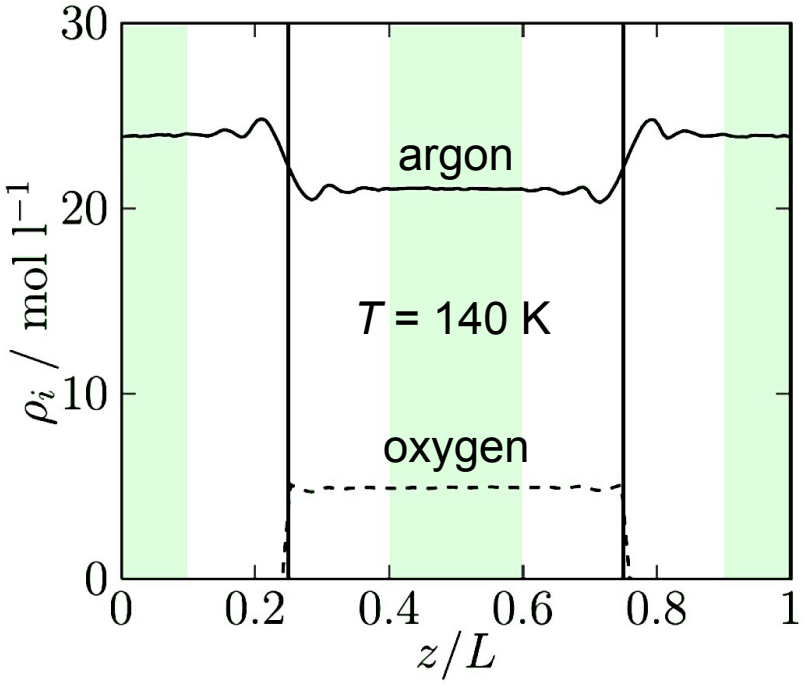
$$T \ln a_{solv}^{in} = -\int_{P^{out}}^{P^{in}} dP\, v_{solv}^{pure} \approx -\Pi\, v_{solv}^{pure}$$

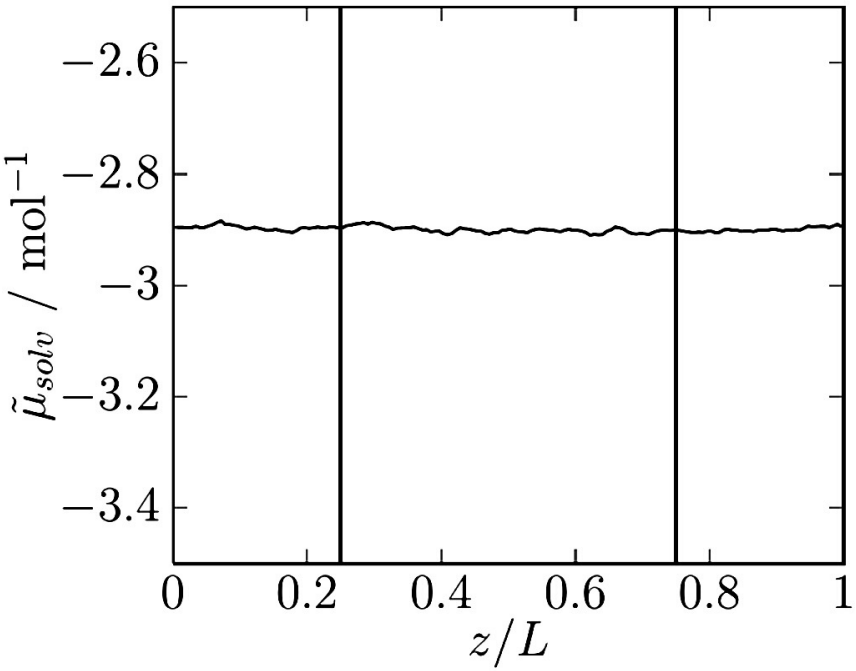
Density and compressibility of the pure solvent are easy to compute.

Validation of the OPAS method

Test case: Mixture of argon (LJ) and oxygen (2CLJQ).

Ar is treated as solvent and moves freely through the simulation volume.
The solute O_2 is confined by the membranes to the inner compartment.

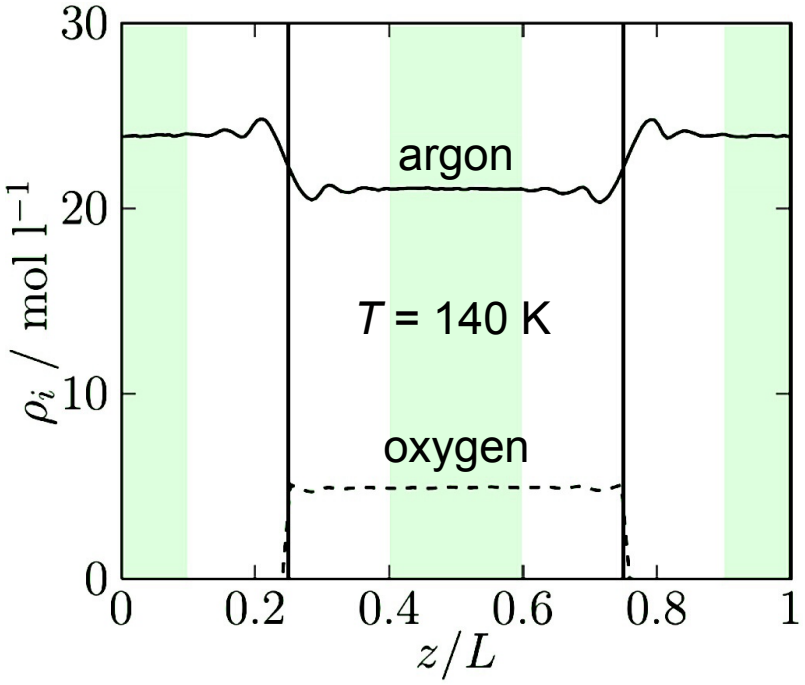


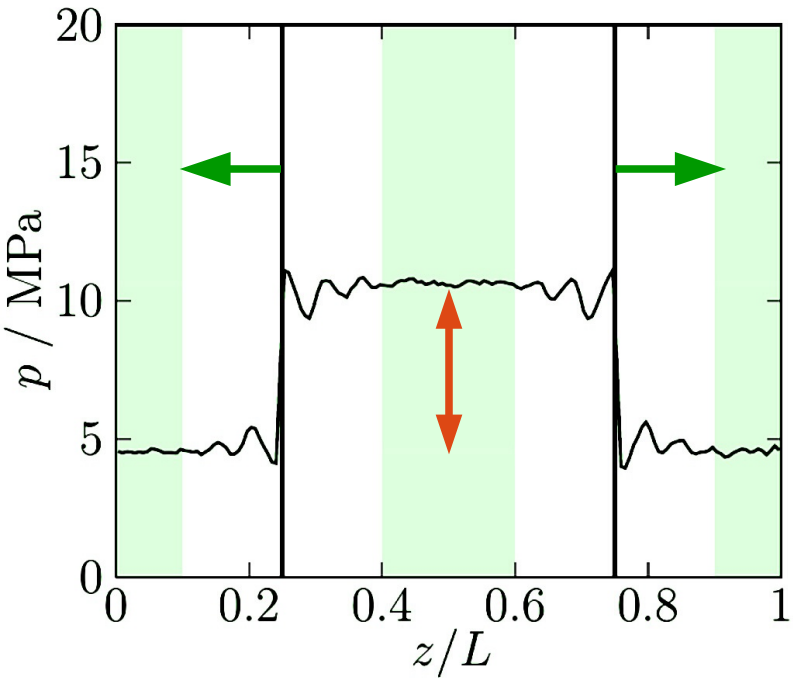


Validation of the OPAS method

Test case: Mixture of argon (LJ) and oxygen (2CLJQ).

Osmotic pressure from force acting on the membranes: 6.33 ± 0.06 MPa.
Osmotic pressure from difference between compartments: 6.1 ± 0.2 MPa.

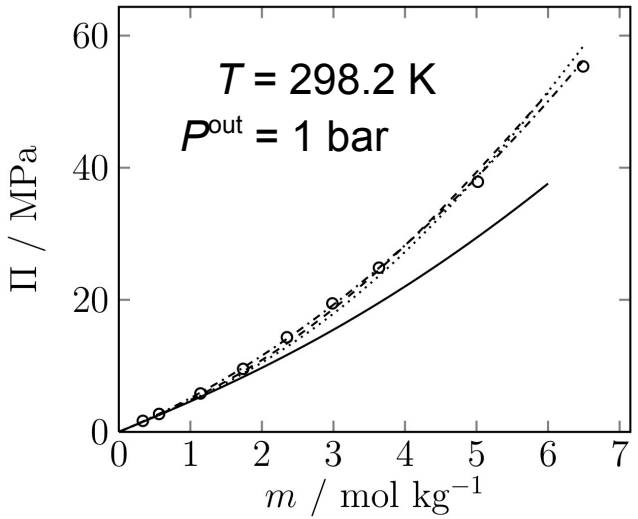


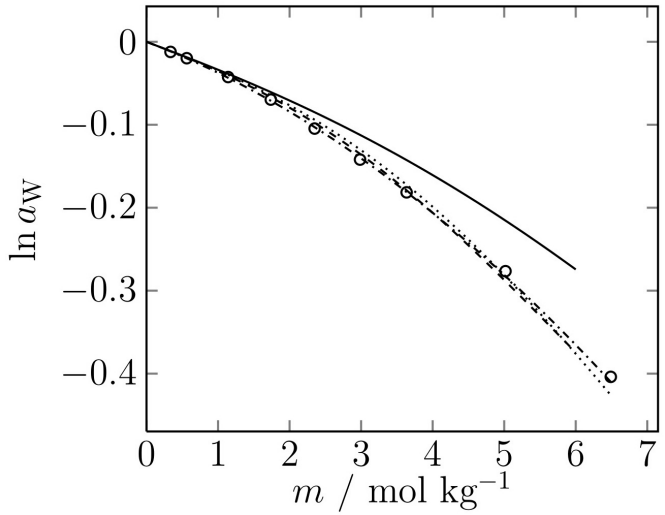


Water activity in electrolyte solutions

Validation of OPAS simulation results against literature data for aqueous NaCl solution using

- the SPC/E water model,
- the Joung-Cheatham NaCl model.





OPAS simulation results (this work)

Correlation to present OPAS results

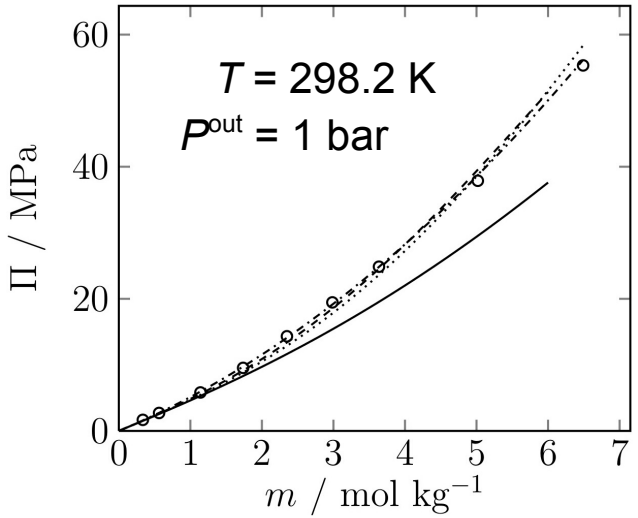
Moucka *et al.* (sim.), SPC/E + JC

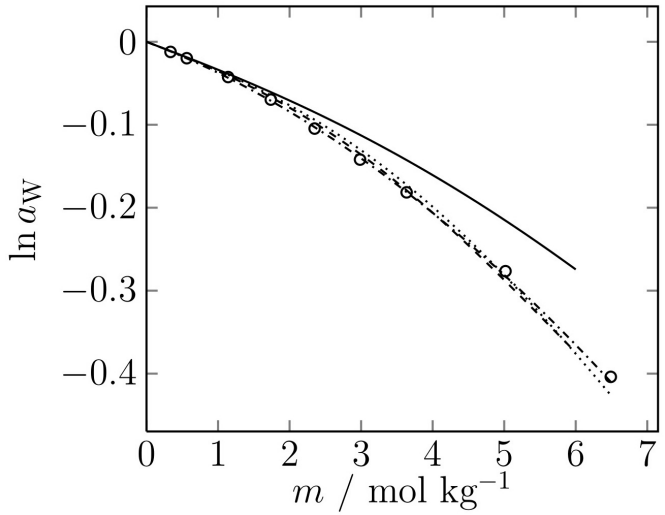
Hamer and Wu (exp.)

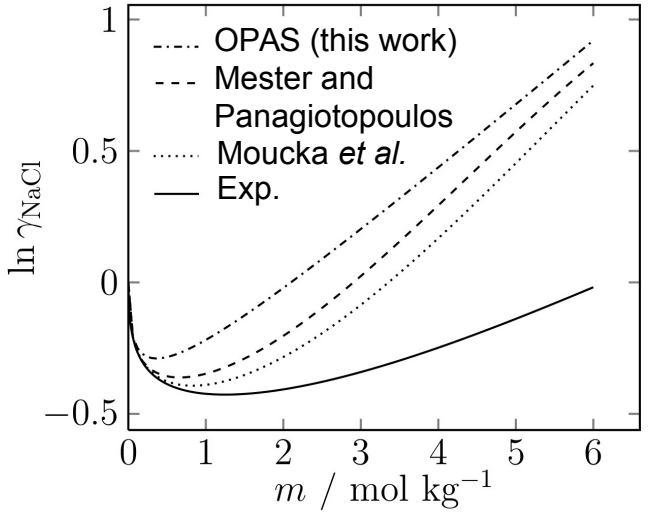
Salt activity in aqueous solution

Chemical potentials of the solute and the solvent are related by the Gibbs-Duhem equation.

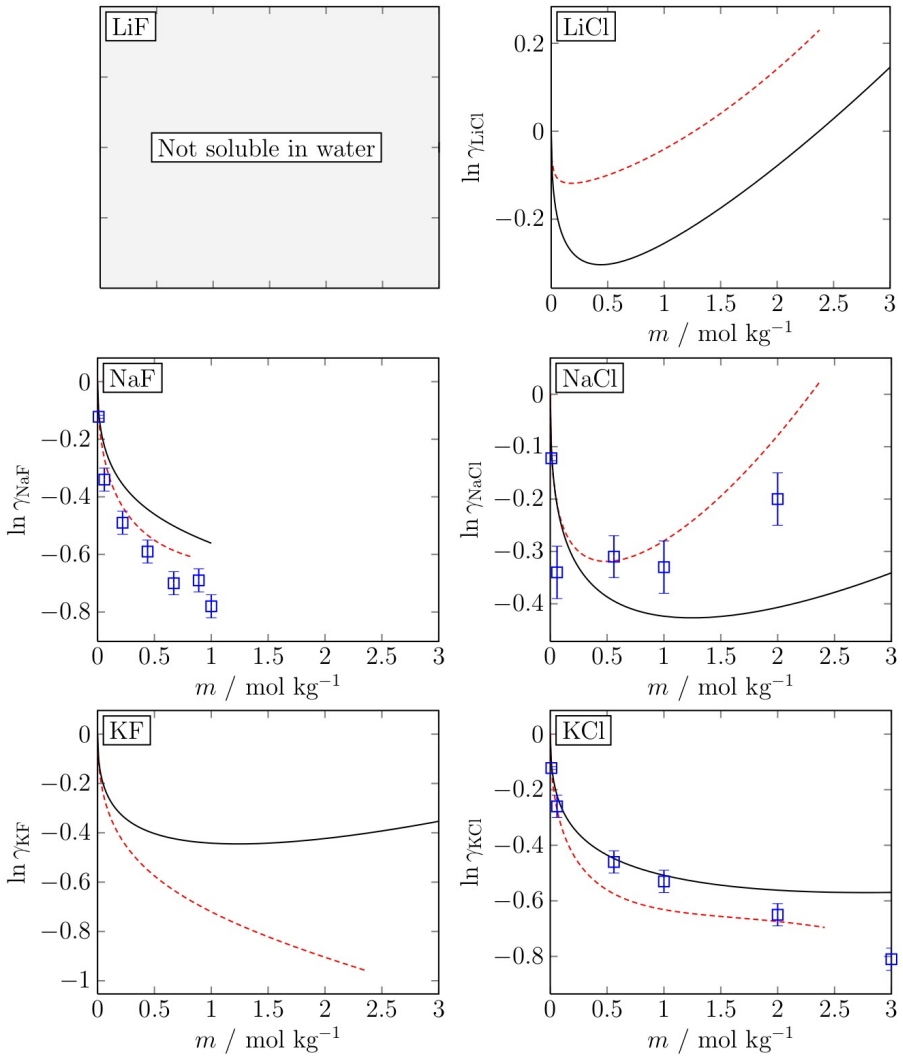
Chemical potential of the salt expressed as activity coefficient (Henry normalization).







Salt activity in aqueous solution



Series of models for

- alkali cations
- and halide anions,

collectively adjusted to

- reduced solution densities
- and self-diffusion coefficients.

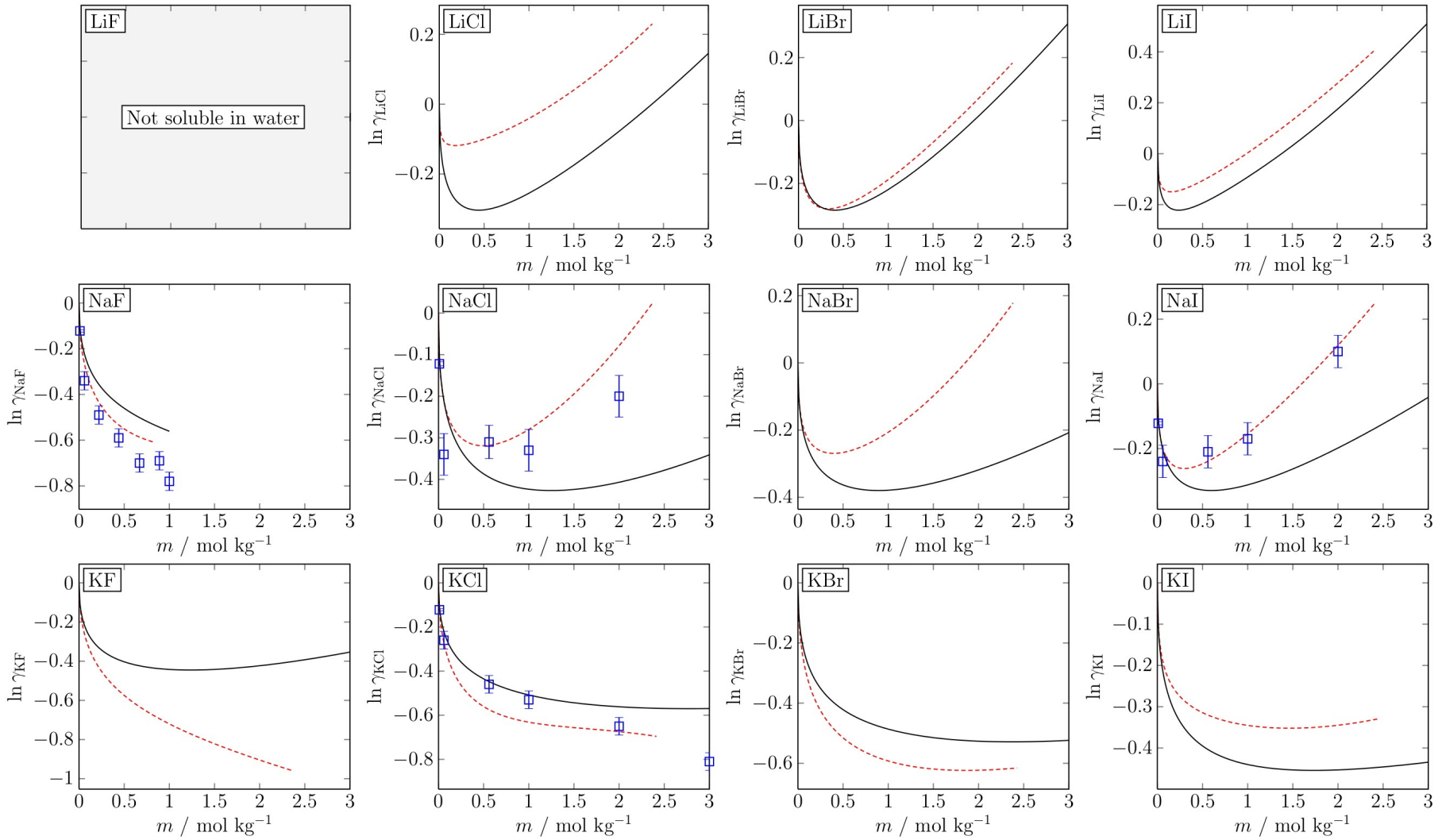
Present simulation results

Mester and Panagiotopoulos

Validation against:

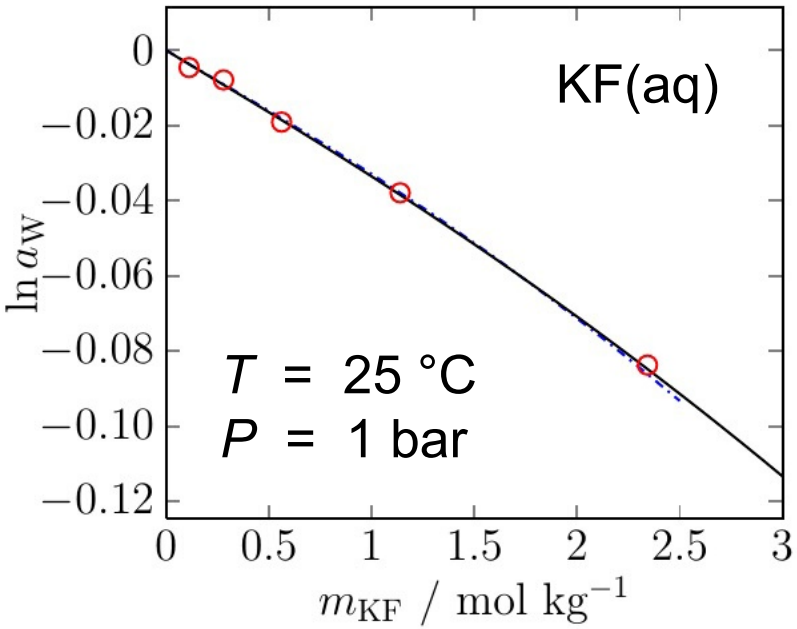
Correlation to experimental data by Hamer and Wu

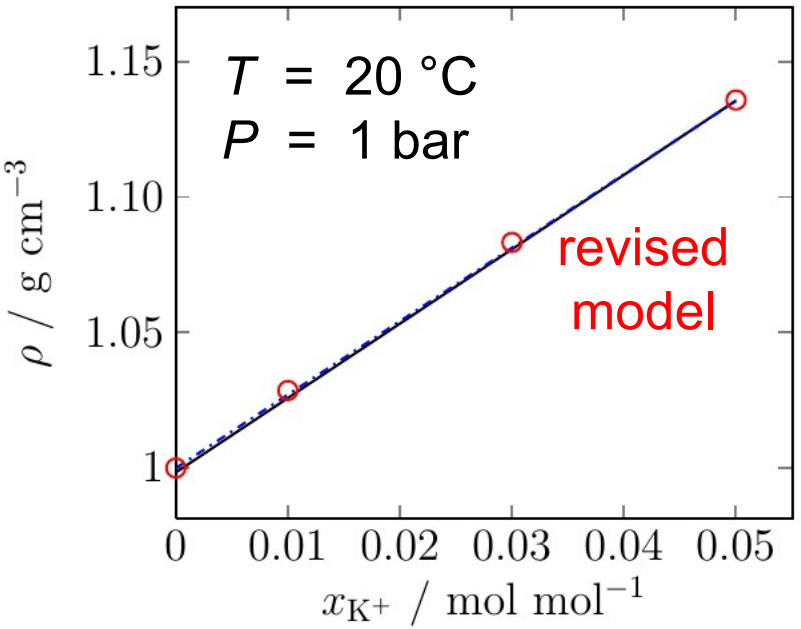
Salt activity in aqueous solution



Reparameterization to solvent activity

New $\sigma(K^+)$ = 2.06 Å (old: 2.77 Å), $\sigma(F^-)$ = 3.94 Å (old: 3.66 Å).





For a specific combination of ions, the accuracy for the chemical potential can be improved without a loss in accuracy for the density.

Conclusion

In previous work of our group, LJ + point charge models of the alkali and halide ions were developed. The σ parameters were collectively parameterized to the reduced **density of aqueous salt solutions**.

The models were validated against **new experimental data** for non-aqueous solutions, and for aqueous solutions at a different temperature.

By **OPAS simulation** with virtual semipermeable membranes, the influence of salts on the chemical potential or **activity of water** can be determined at a higher precision than e.g. by test particle insertion.

The **activity of the solute** can be obtained by Gibbs-Duhem integration.

In many cases, the models from previous work agree well with experimental activity data. In other cases, the agreement can still be improved.