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Aqueous solutions of alkali halide salts under a thermal gradient: A non equilibrium molecular dynamic study.

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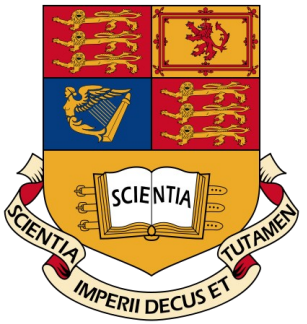

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outline

- motivation
- simulation method & potential models
- **NEMD of pure water**
  - **check EOS of model & implementation**
  - **thermal conductivity**
- NEMD of aqueous solutions
  - EOS
  - thermal conductivity
  - Soret coefficient
- conclusion

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motivation

- ***Soret* effect**: known since over 150 years but mechanism(s) still under debate
- **applications**: CVD, fractionation of suspensions, isotope separation, ...
- **involved in**:
  - degradation of functional materials[1]
  - thermodynamics of seawater[2]
  - DNA replication[3]
  - pattern formation in polymer blends[4]

1 J. Janek *et al.*, J. Korean Ceramic Soc. 49, 56 (2012)
2 D.R. Cadwell, S.A. Eide, Deep-Sea Res. 28A, 1605 (1981)
3 D. Braun, A. Libchaber, Phys. Biol. 1, 1 (2004)
4 T. Nambu et al., Faraday Discuss. 128, 285 (2005)

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motivation

- compared to polymer/colloid suspensions and molecular mixtures, aqueous solutions of ions are poorly investigated
- understanding the mechanism(s) of heat transport and thermodiffusion.
- non-equilibrium molecular dynamics (NEMD)
  - avoid practical problems (like e.g. convection)
  - allow to study structure, dynamic and other properties on a molecular level

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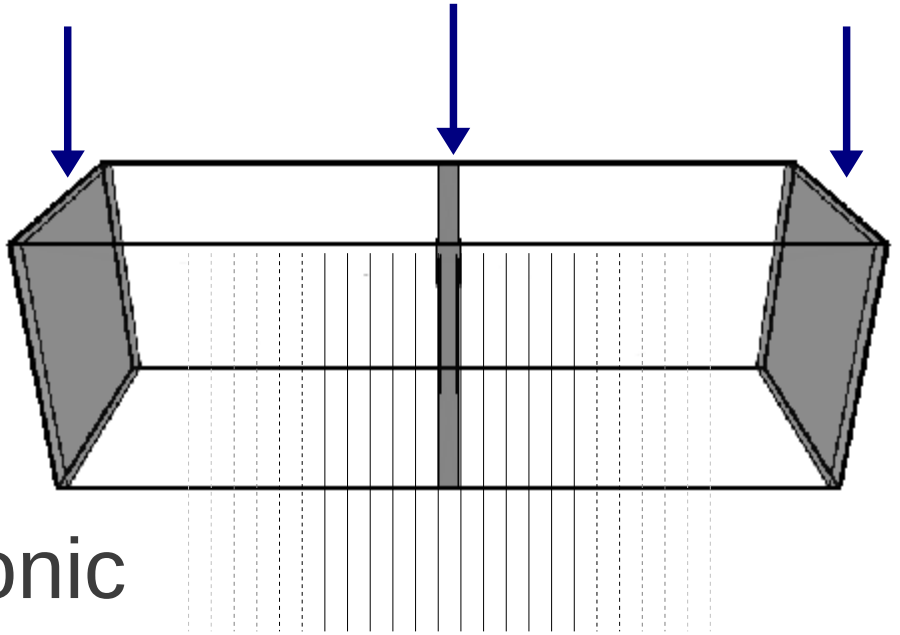
NEMD method

- new approach[1]
- divide the oblong simulation box in 120 layers
- some molecules in the outer and central layers are restrained by a harmonic bond: $k_h = 10^3$ kJ mol^{-1} nm^{-2}



- ensuring *equal numbers* in each region
- restrained molecules *still* fluctuate in kinetic energy

1 F. Römer, A. Lervik, F. Bresme, "Non equilibrium molecular dynamics simulations of the thermal conductivity of water: a systematic investigation of the SPC/E and TIP4P/2005 models.", submitted to J. Chem. Phys.

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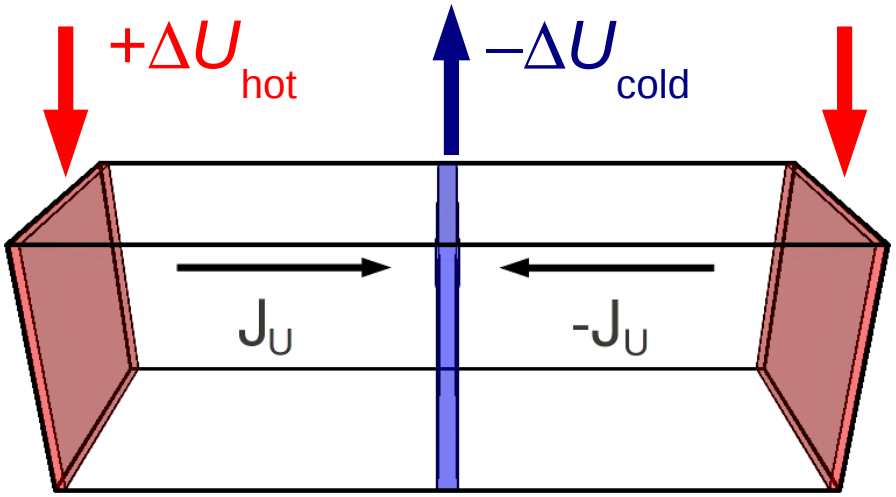
NEMD method

- thermalize restrained molecules by using the *v-rescale*[1] algorithm
- calc. energy flux from thermostat activity:

$$J_U = \left\{ \pm \frac{\Delta U}{2 \delta t A}, 0, 0 \right\}$$

- easy to implement in most (parallel) MD codes
- implemented in Gromacs[2]



- In absence of mass flux:

$$J_q = J_U$$

1 G. Bussi, D. Donadio, M. Parrinello. J. Chem. Phys. 126, 014101 (2007)
2 B. Hess *et al.*, J. Chem. Theory and Computation 4, 435 (2008)

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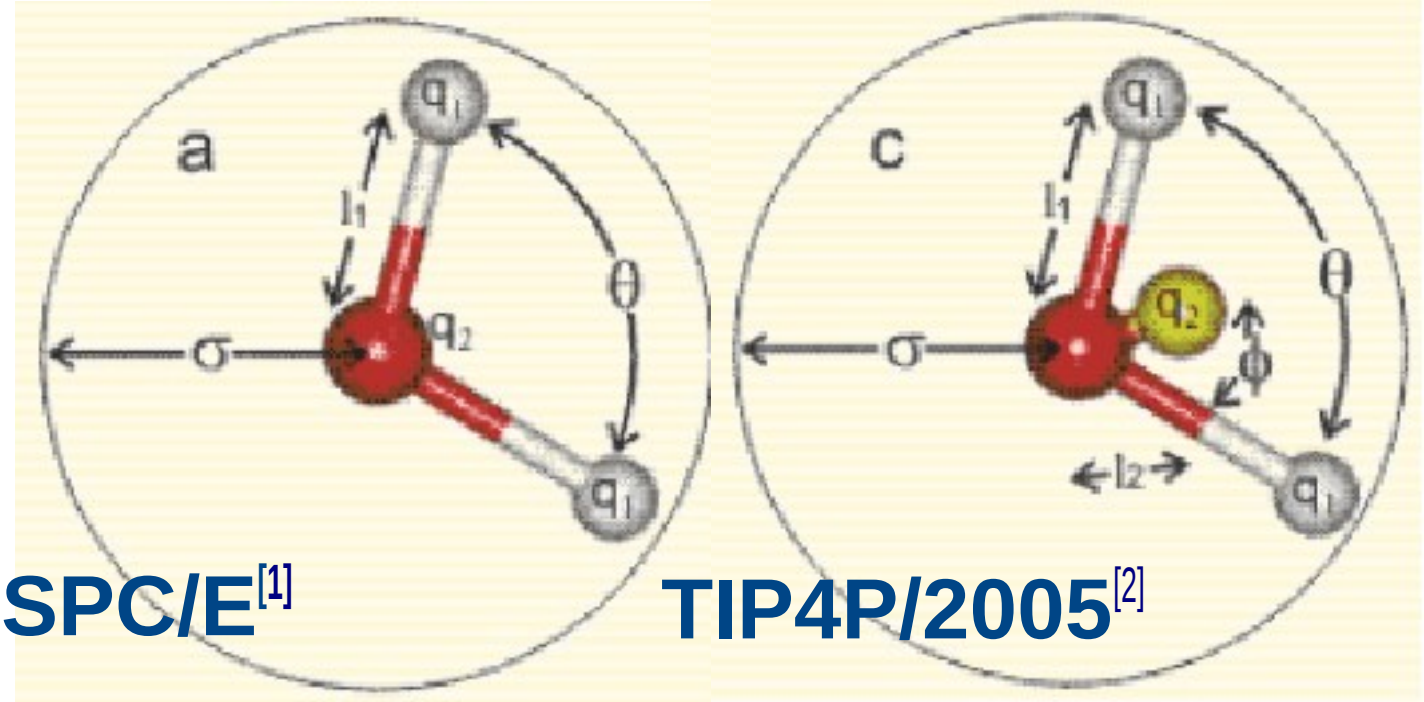
water models

- cover two prototypes: 3- and 4-site models
- the most successful and widely used models
- rigid, non-polarizable, effective dipole moment



[1] H. Berendsen, J. Grigera, T. Straatsma, JPC 91, 6269 (1987)
[2] J.L.F. Abascal, C. Vega, JCP 123, 234505 (2005)
Image: M. Chaplin, London South Bank University, http://www.lsbu.ac.uk/water/

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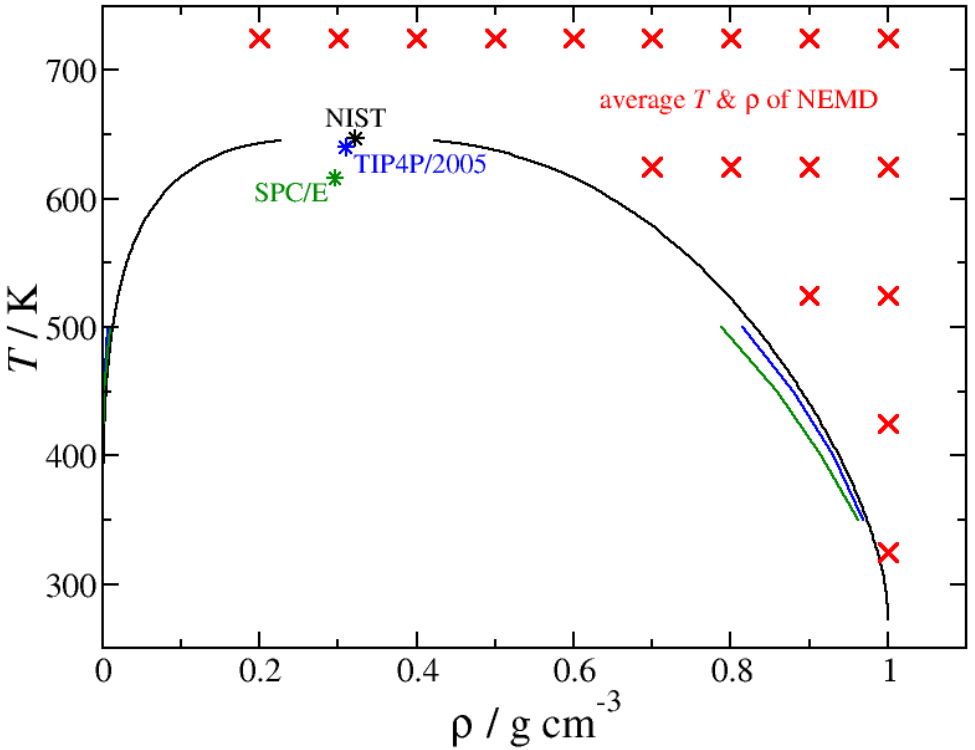
simulation conditions

- 2 water models
- 17 state points
- System:
  - δt = 2 fs
  - N_{water} = 5410
  - dT/dz = 20 K/nm
  - $1/3L_z = L_{y,x}$ = {3.8 – 6.5} nm
  - $r_{cut\text{-}off}$ = 1.9 nm
  - PME method



NIST Chemistry WebBook, http://webbook.nist.gov/chemistry/

C. Vega, E. de Miguel, J. Chem. Phys. 126, 154707 (2007)

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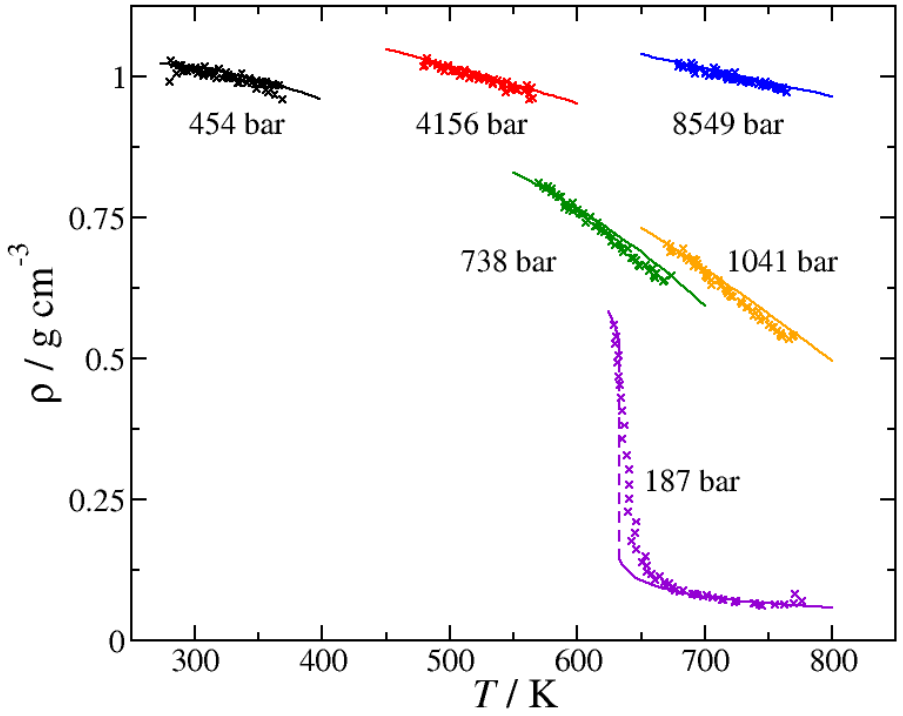
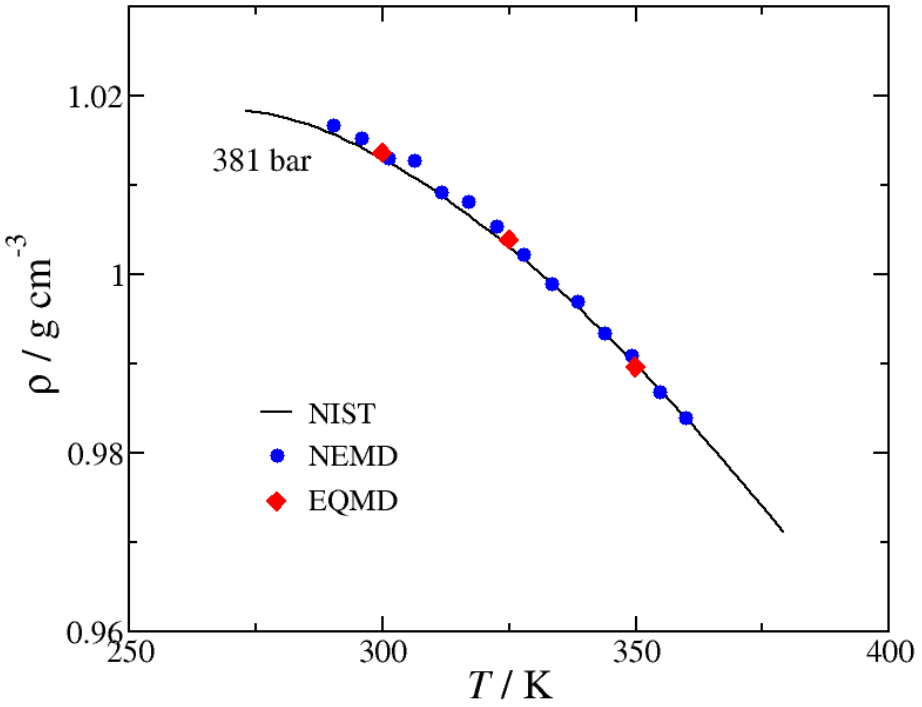
EOS of NEMD (TIP4P/2005)

- validate EOS of models (points) from NEMD and EQMD simulations with NIST reference (lines):





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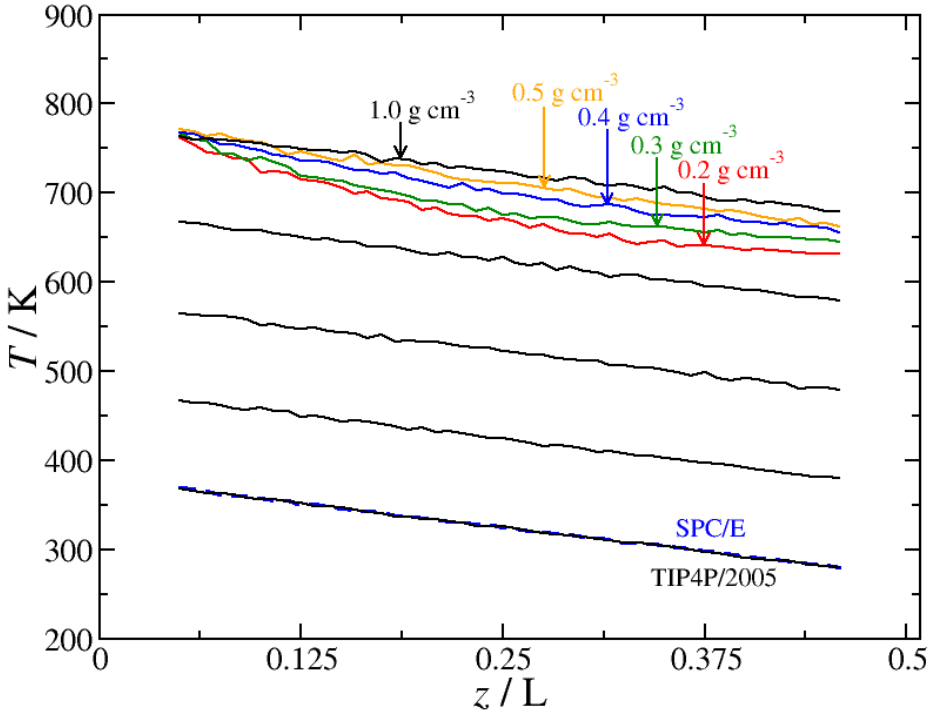
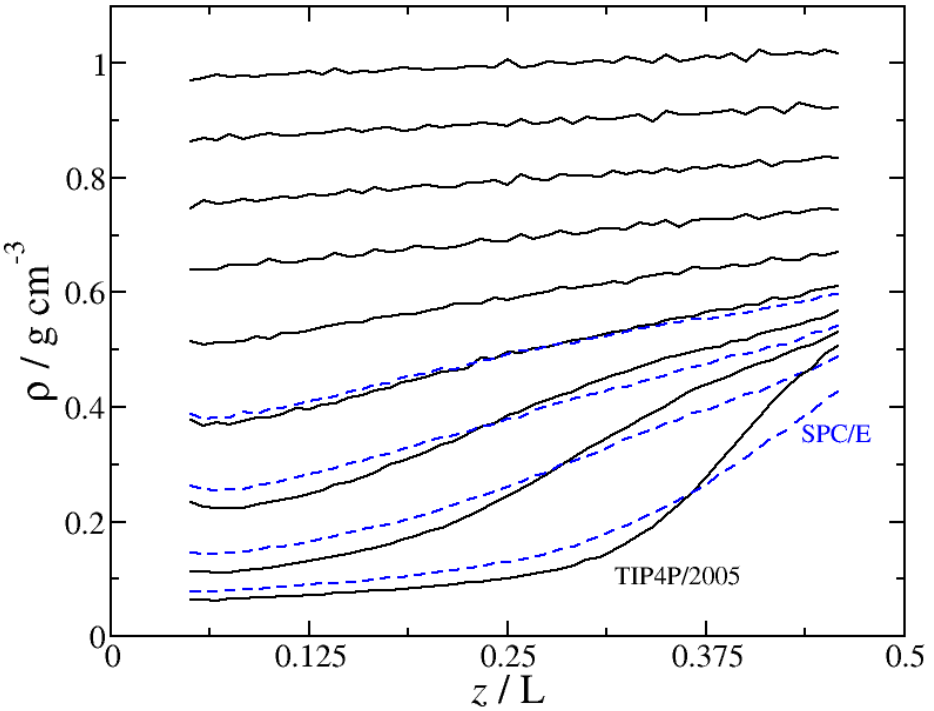
T- & ρ -profiles

- temperature and density (of water) profiles along the temperature gradient:





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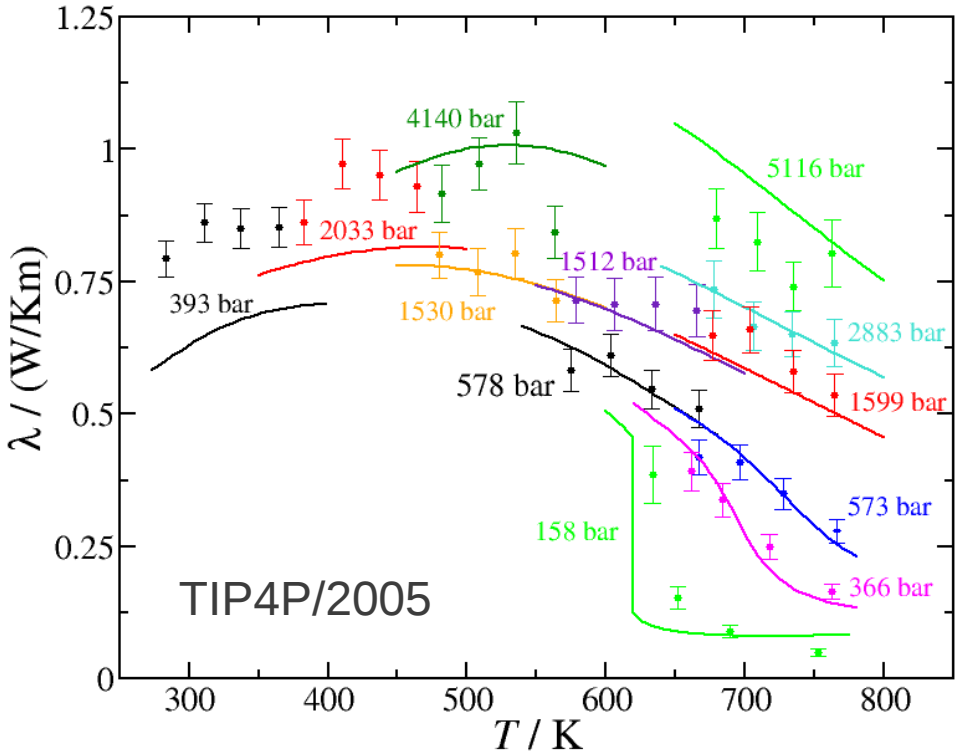
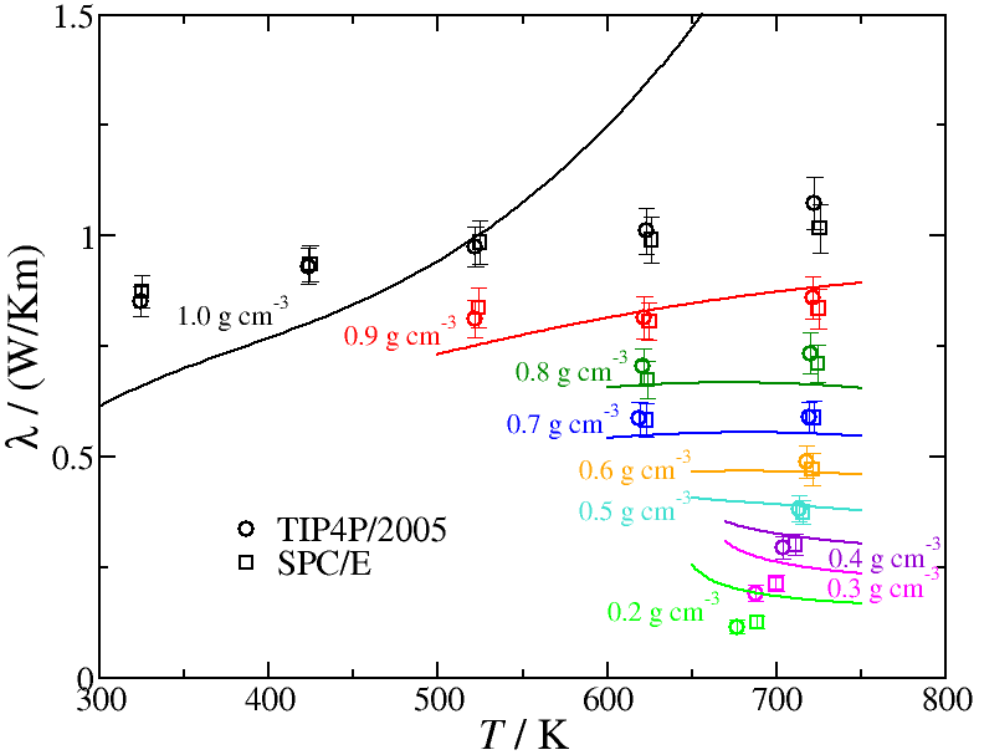
heat conductivity

- calculated segment-wise over 12 layers and over the whole system:





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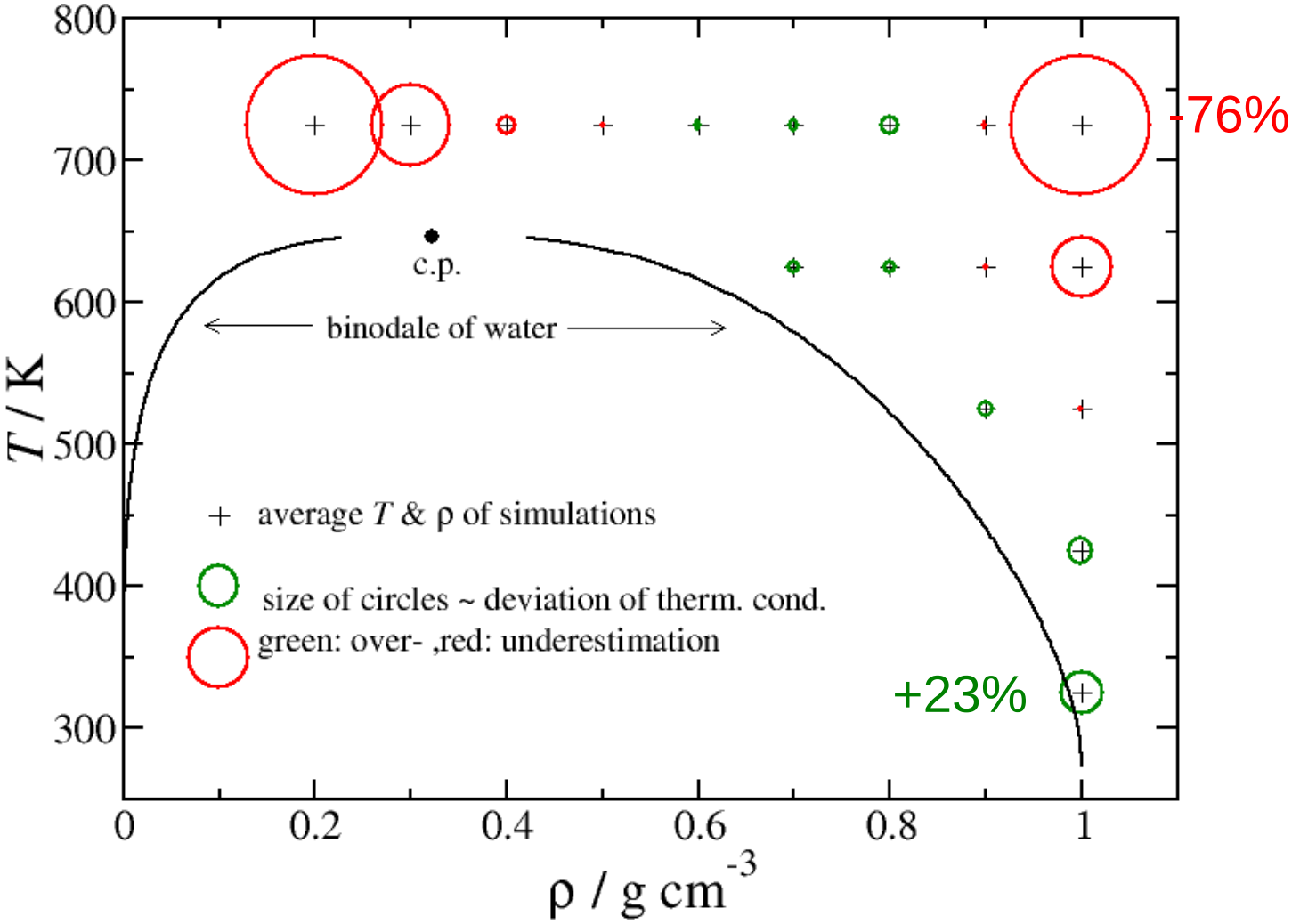
heat conduction (TIP4P/2005)

- relative deviation between NIST reference and the NEMD results:



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  - **Soret coefficient**
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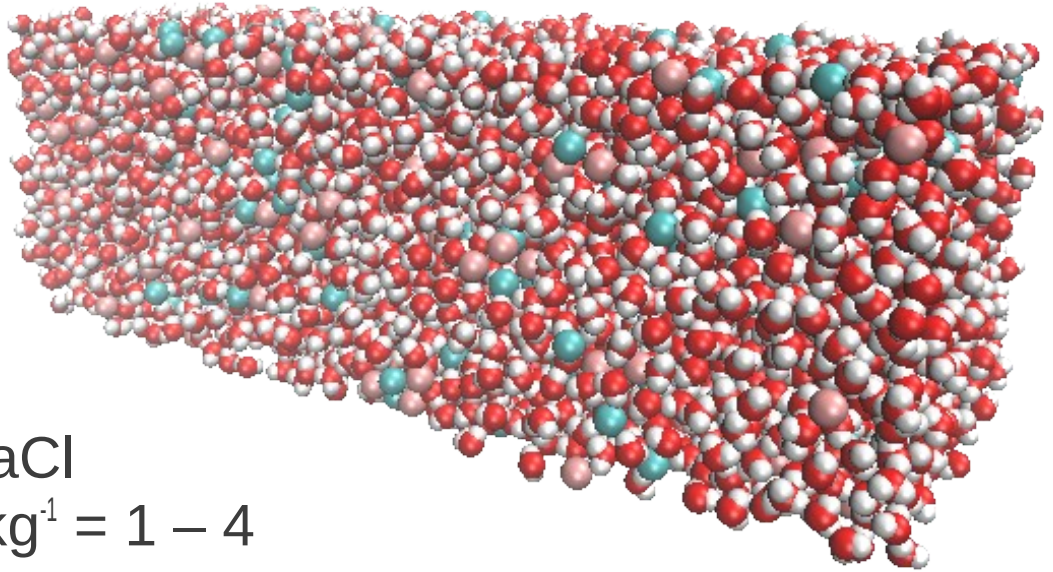
alkali halide solutions



- KCl & NaCl
- c_0 / mol kg^{-1} = 1 – 4
- N_{water} = 5000
- N_{salt} = 90 – 540
- $\partial T/\partial z$ / K nm^{-1} ≈ 36
- $\langle T \rangle$ / K = 350
- $\langle \rho_{water} \rangle$ / g cm^{-3} ≈ 0.9

	SPC/E		TIP4P/2005	
	σ / nm	ε / kJ mol^{-1}	σ / nm	ε / kJ mol^{-1}
Na$^+$	0.2350	0.54392	0.2583	0.41844
K$^+$	0.3332	0.41840	0.3332	0.41840
Cl$^-$	0.4401	0.41840	0.4046	0.41844

L.X. Dang, B.C. Garrett, JCP 99, 2972 (1993)
D.E. Smith, L.X. Dang, JCP 100, 3757 (1994)

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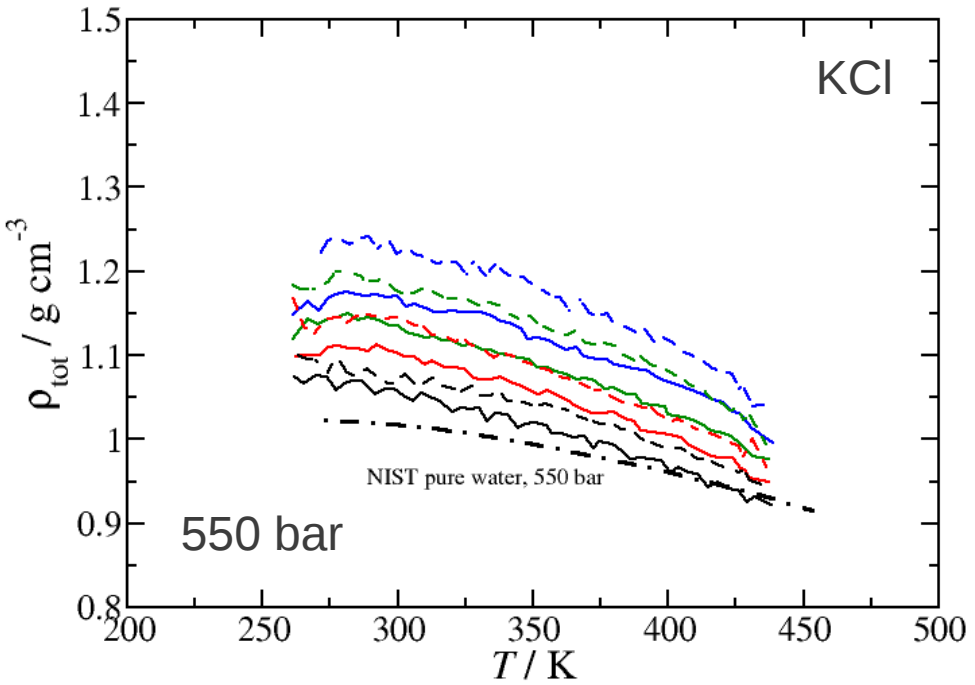
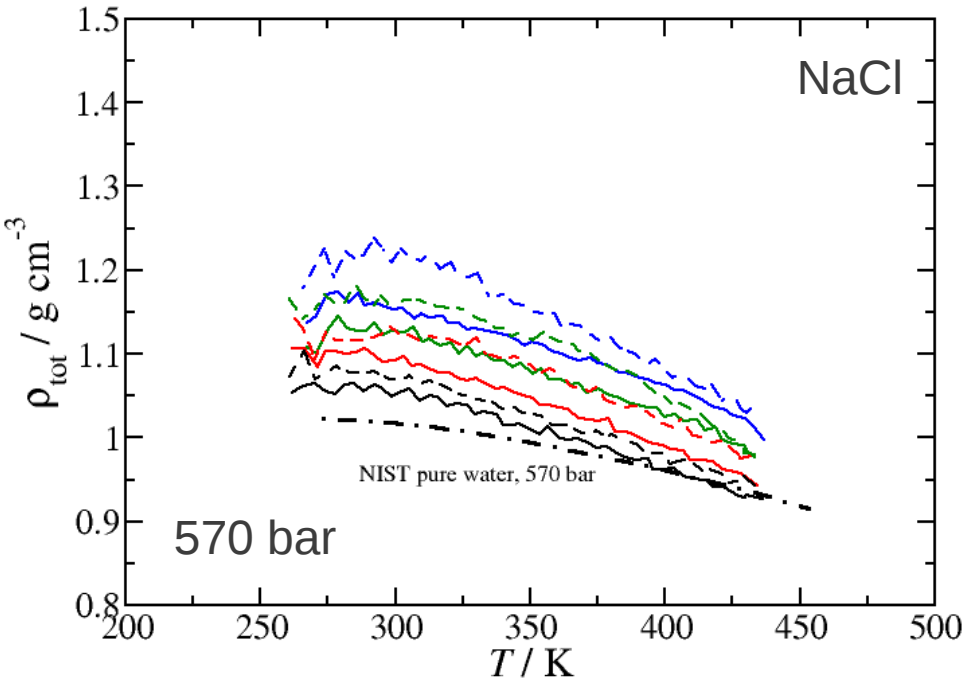
EOS of aqueous solutions

- EOS from SPC/E (—) and TIP4P/2005 (- -) compared with NIST (-··-) reference for **poor** water:





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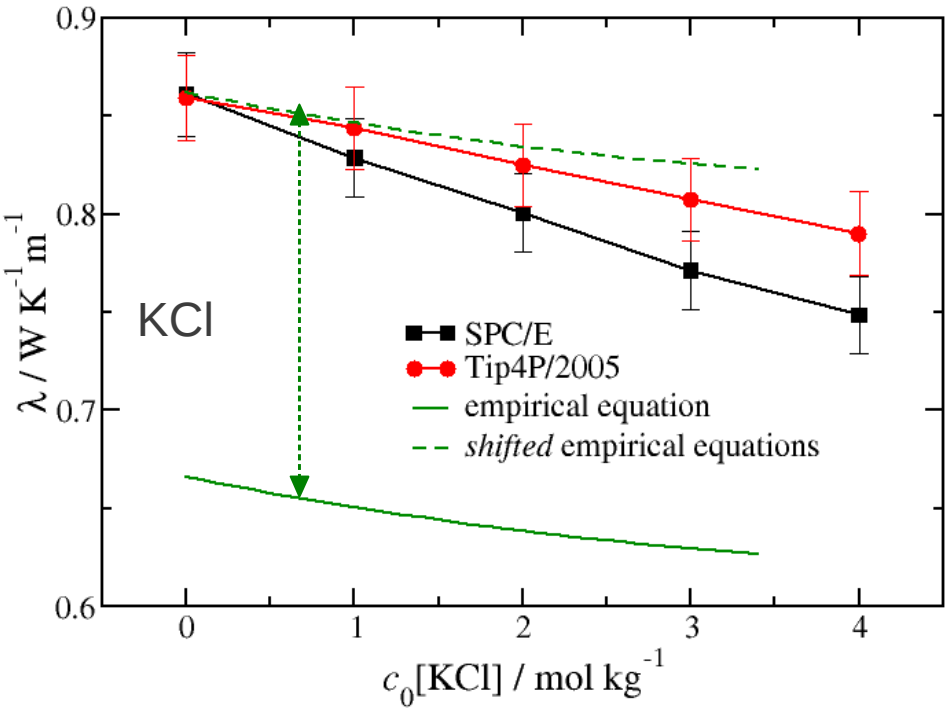
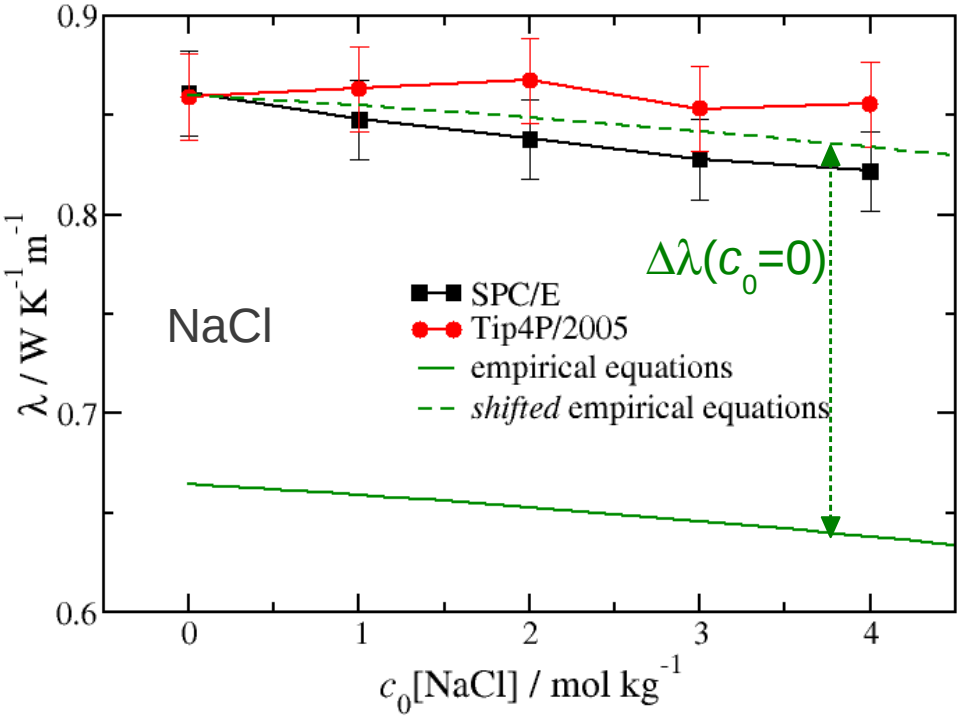
thermal conductivity

- comparison of results with empirical equations based on experimental data from Ramires *et al.*:





KCL: M.L.V. Ramires, C.A. Nieto de Castro, Int. J. Thermophys. 21, 671 (2000)
NaCl: M.L.V. Ramires *et al.*, J. Chem. Eng. Data 39, 186 (1994)

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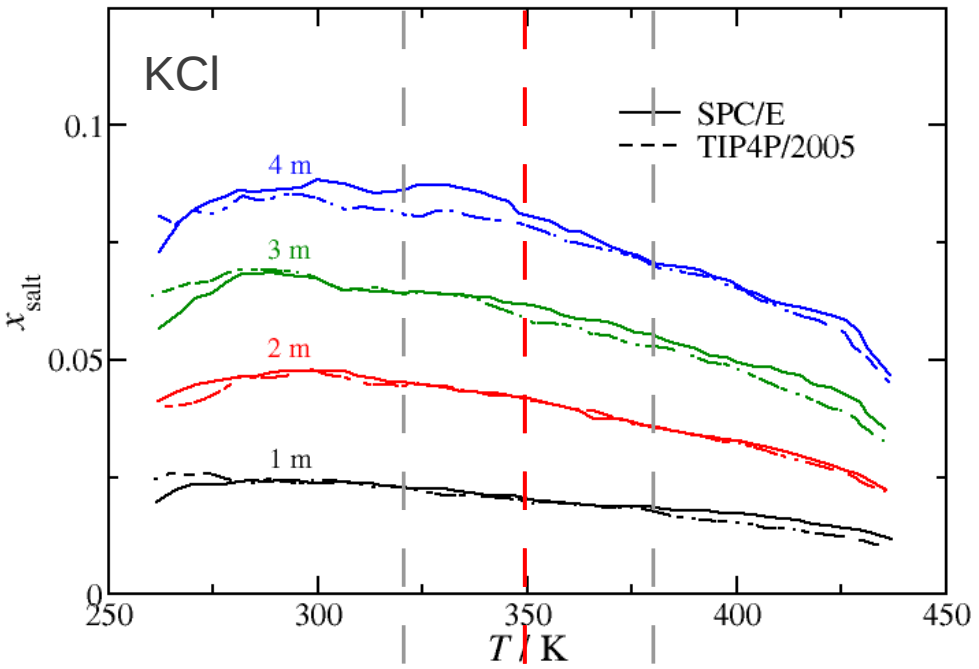
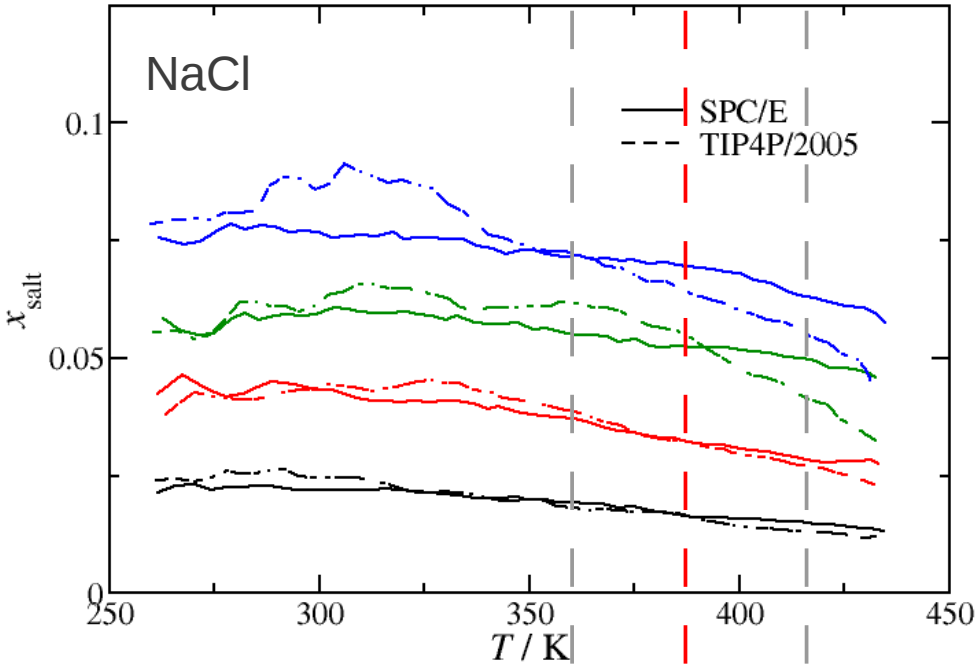
mole fraction vs temperature

- Determination of Soret coefficients from mole fraction of temperature gradient:





350 K

$$s_T = -\frac{1}{x_{\mathrm{salt}}(1-x_{\mathrm{salt}})}\frac{\nabla x_{\mathrm{salt}}}{\nabla T}$$

386 K

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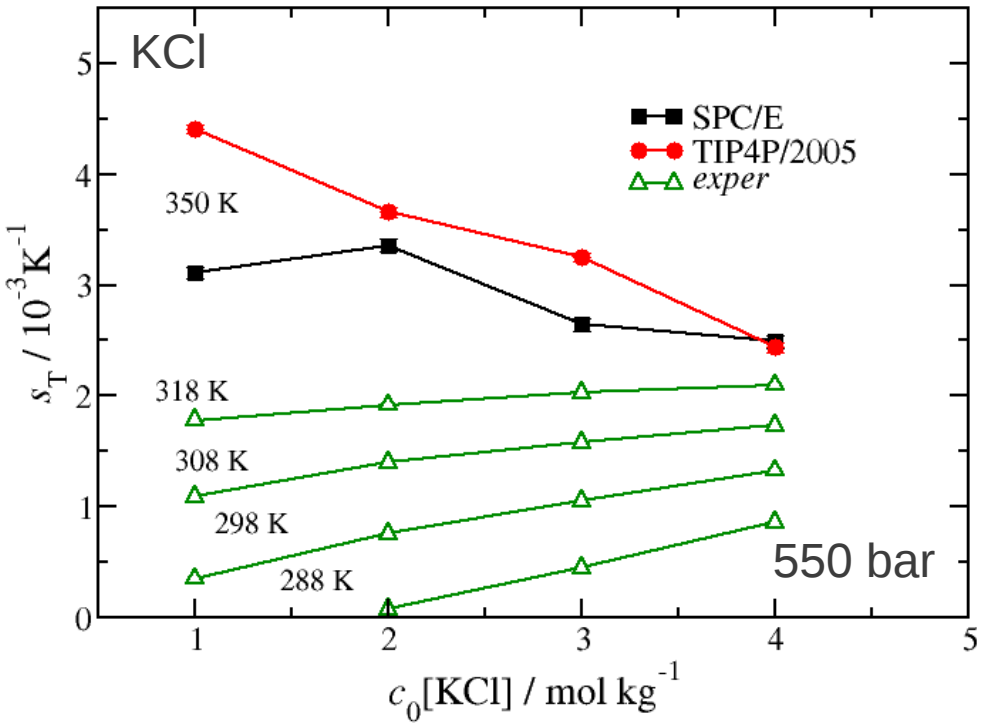
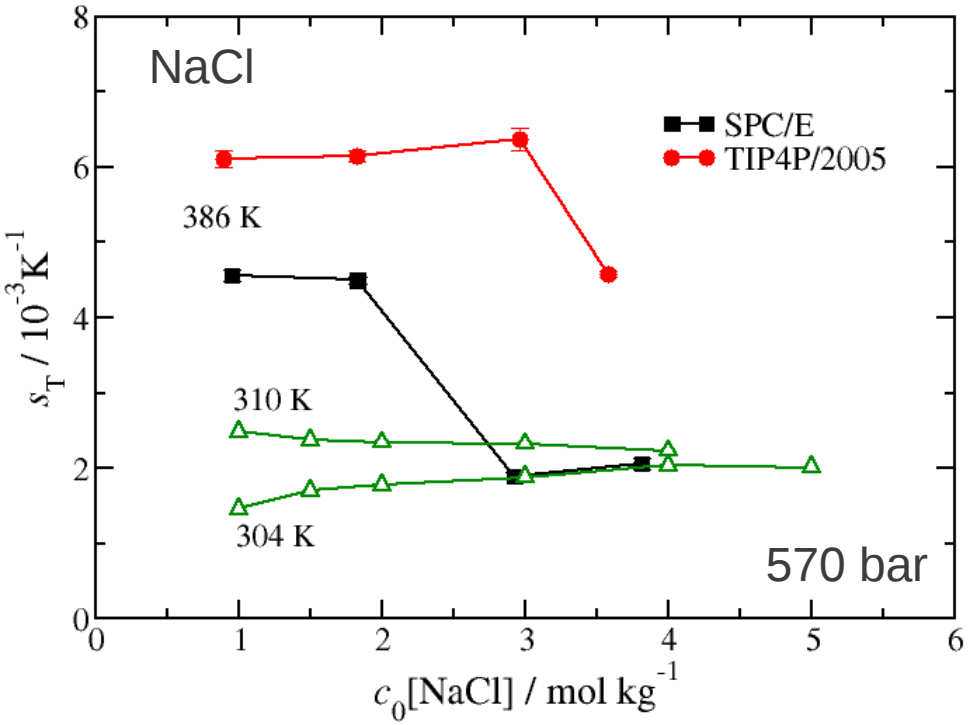
Soret coefficient

- Soret coefficient as a function of salt concentration compared with experimental data:





Exp. KCl: L.G. Longsworth, J. Phys. Chem. 61, 1557 (1957)
Exp. NaCl: C.C. Tanner, Trans. Faraday Soc. 23, 75 (1927)

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Conclusion

- We show a successful new approach to realize NEMD simulations with thermal gradients which is easy to implement.
- SPC/E and TIP4P/2005 reproduce the thermal conductivity of water at moderate temperatures and pressure surprisingly good.
- Thermal conductivity maximum of water (anomaly) is reproduced too.
- We present, as far as we know, the first NEMD studies of aqueous solutions of ions!
- Thermal conductivity of the solutions are in the right order of magnitude.
- Concentration dependency shows the right trend.
- The Soret coefficients have the right sign and order of magnitude.
- Concentration dependency of the Soret coefficient seems to be better modelled by the SPC/E, but further studies are needed here.

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Thank you for your attention!

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