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Lehrstuhl für Thermodynamik
Prof. Dr.-Ing. H. Hasse

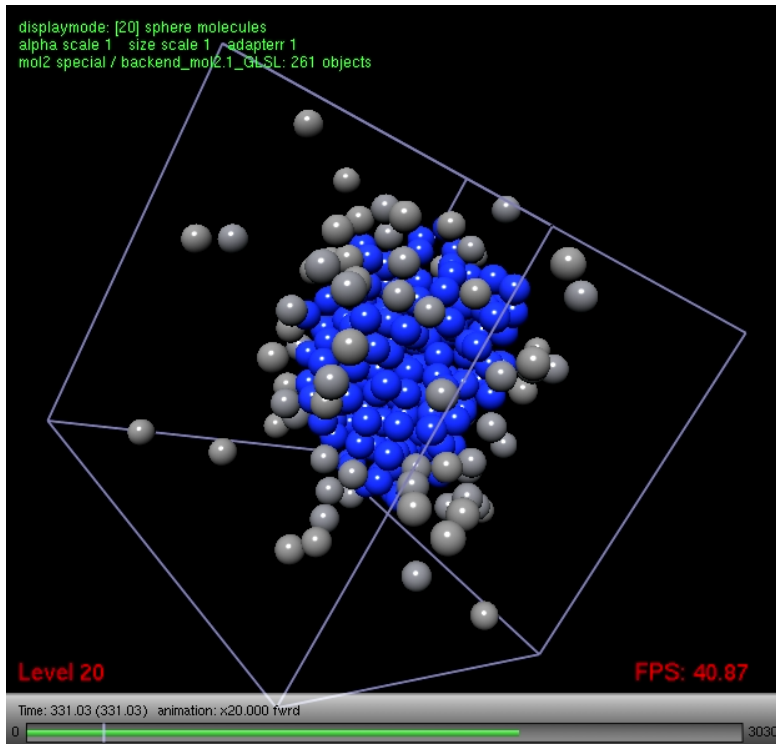# Interpretation of density profiles and pair correlation functions

Martin Horsch and Cemal Engin

Paderborn, 22nd June 12
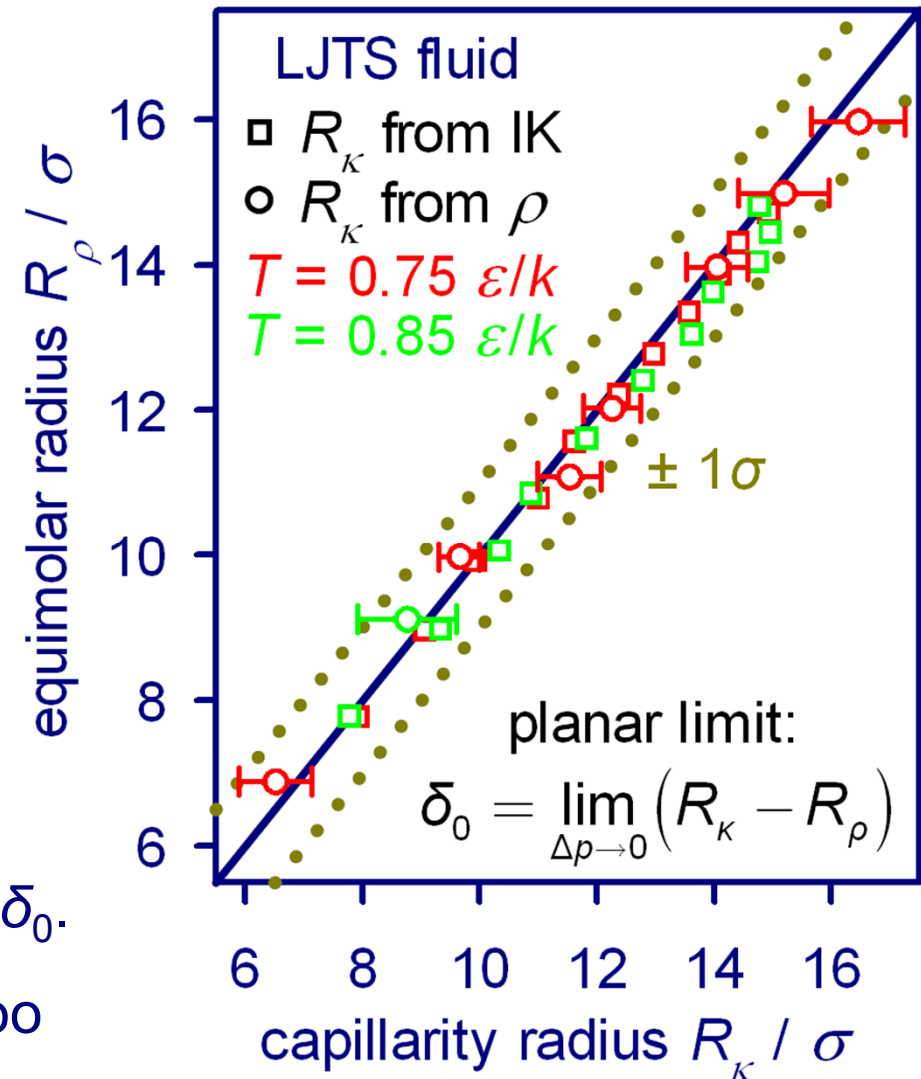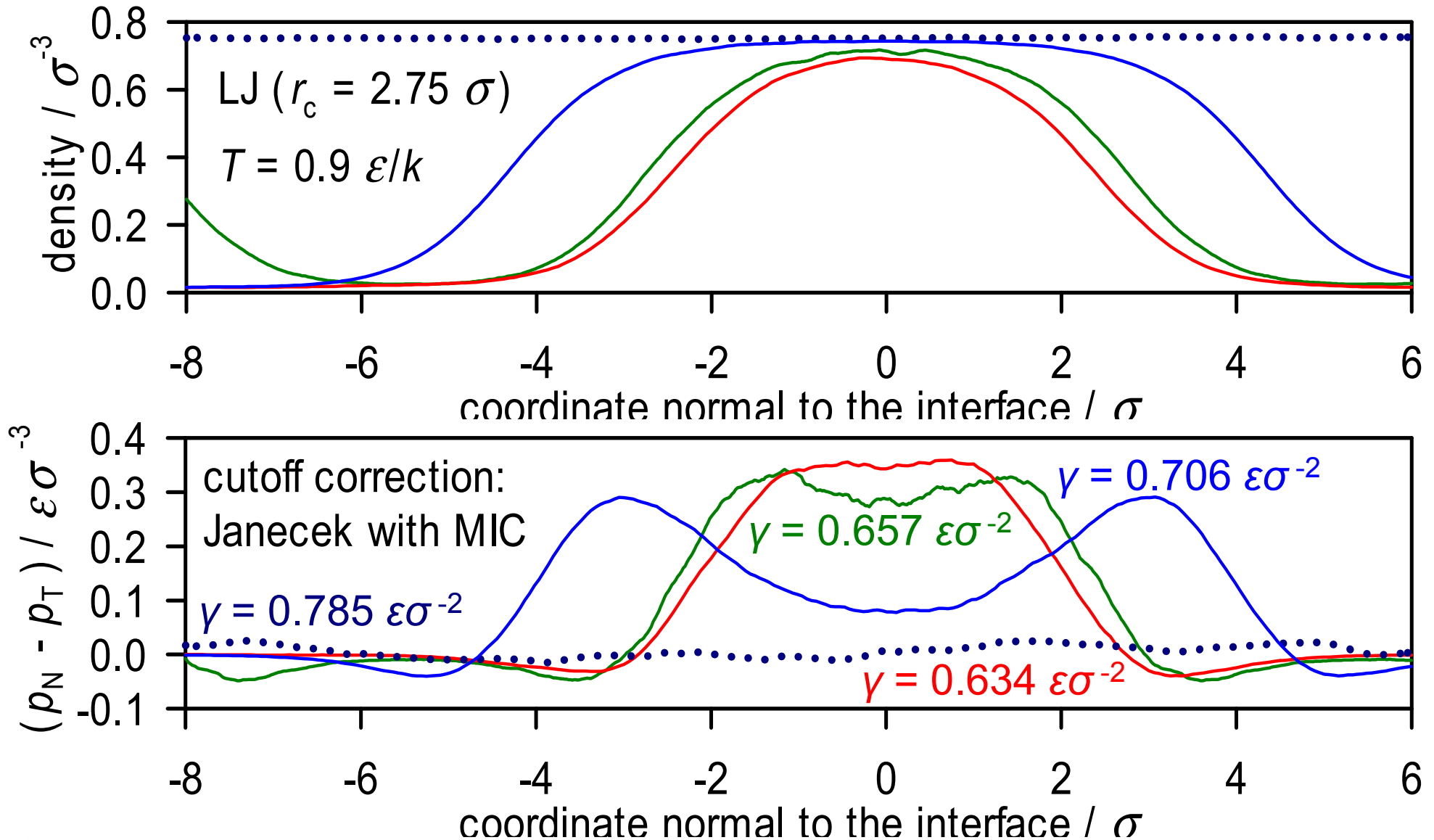
IV. Annual Meeting of the Boltzmann Zuse Society

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Surface tension of nanodroplets

Tolman (1949): Size dependence of γ is due to curvature, coupled by the length δ_0.

New consensus emerging today: δ_0 is too small to describe the dominating effect …

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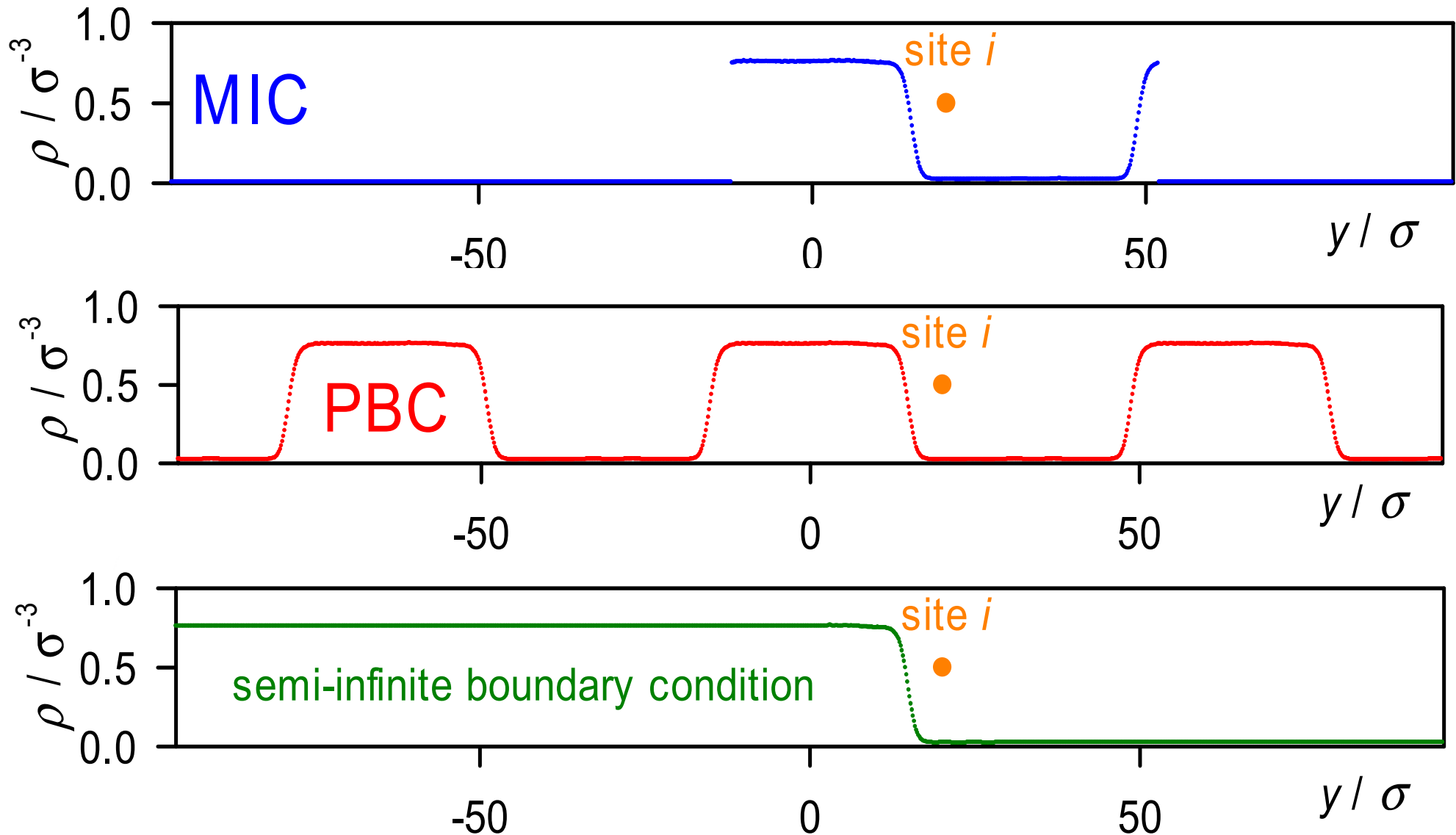
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Liquid slab size effect on interfacial profiles
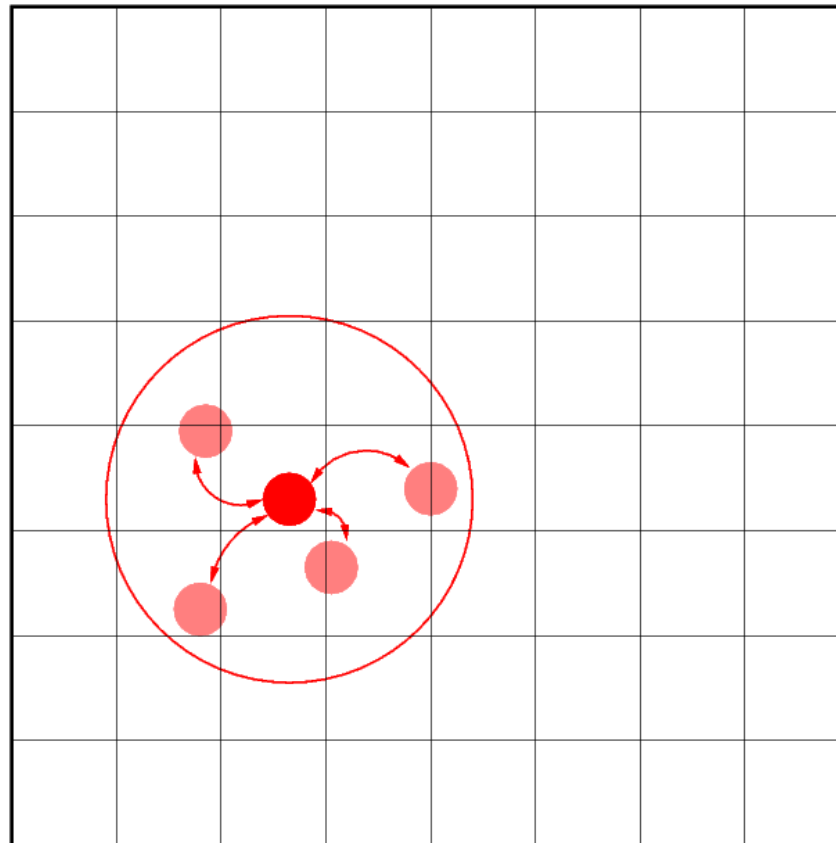
Mode of the long-range cutoff correction

Heterogeneous or fluctuating systems
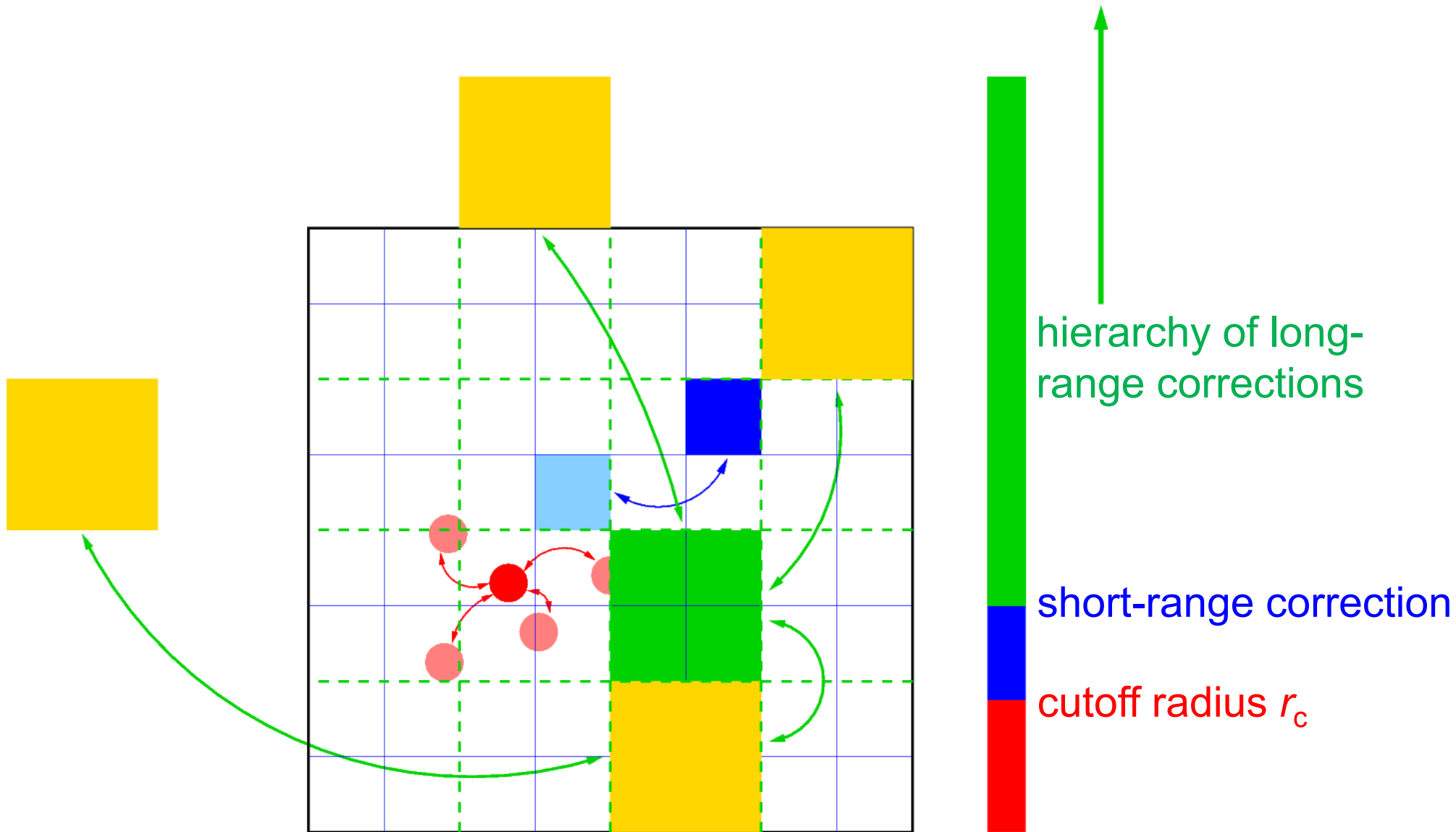
Objective: Simulation of systems with …

- an arbitrary heterogeneous structure
- significant long-range fluctuations (e.g., near T_c)

cutoff radius r_c

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Heterogeneous or fluctuating systems

hierarchy of long-range corrections

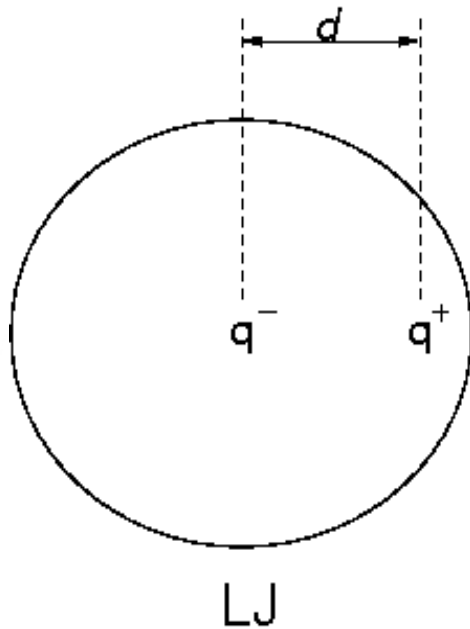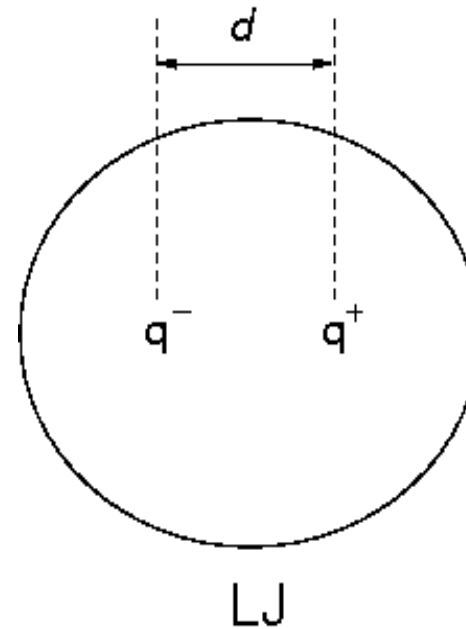short-range correction
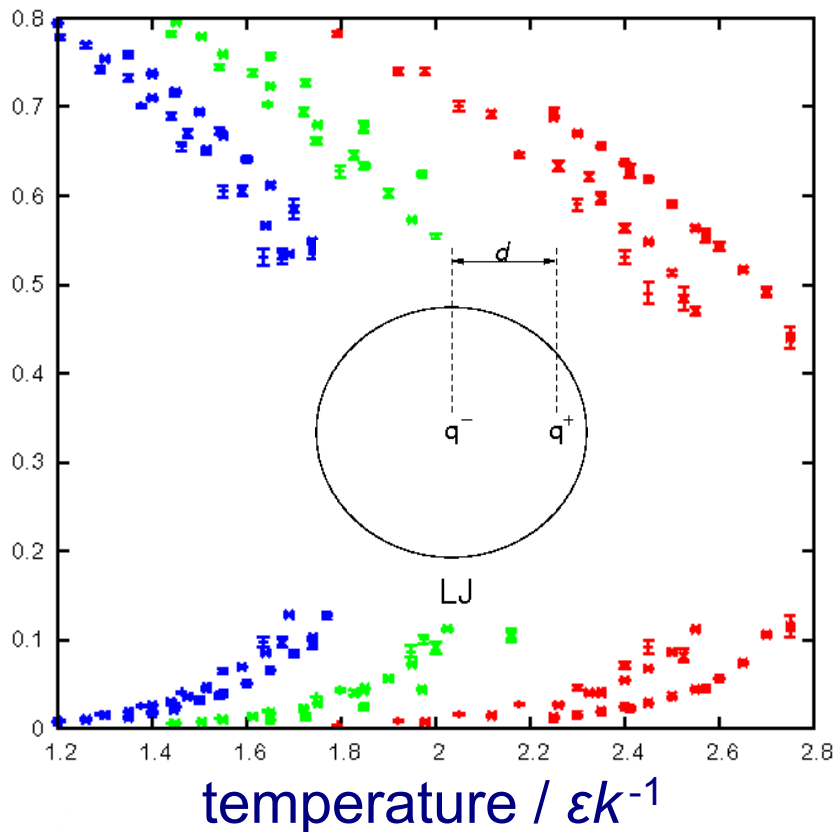
cutoff radius r_c

Modelling polarity and hydrogen bonding

Stockmayer model extended by an elongation parameter *d*

LJ concentric with point charge

LJ concentric with dipole

Modelling polarity and hydrogen bonding

Stockmayer model extended by an elongation parameter *d*
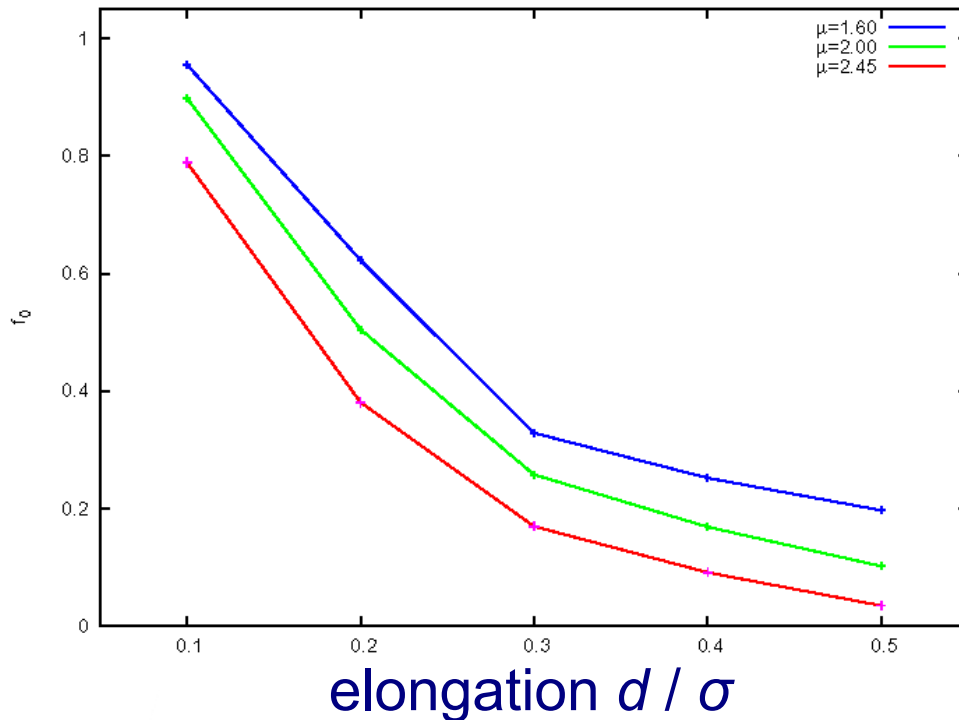
LJ concentric with point charge

LJ concentric with dipole

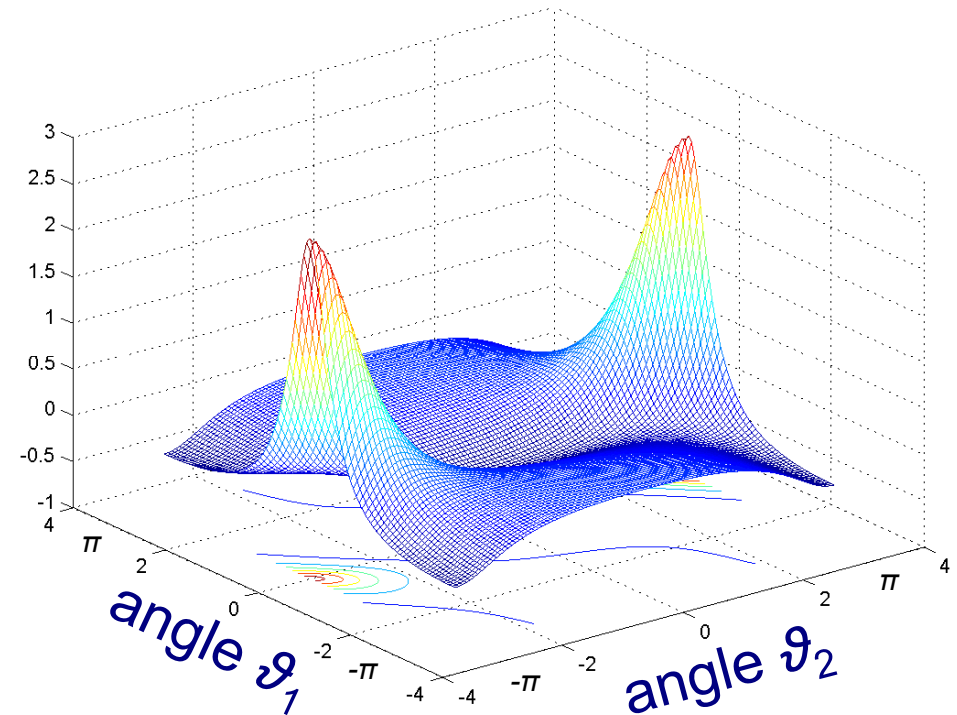Fluid properties de-termined by the dipole moment (undesired!)
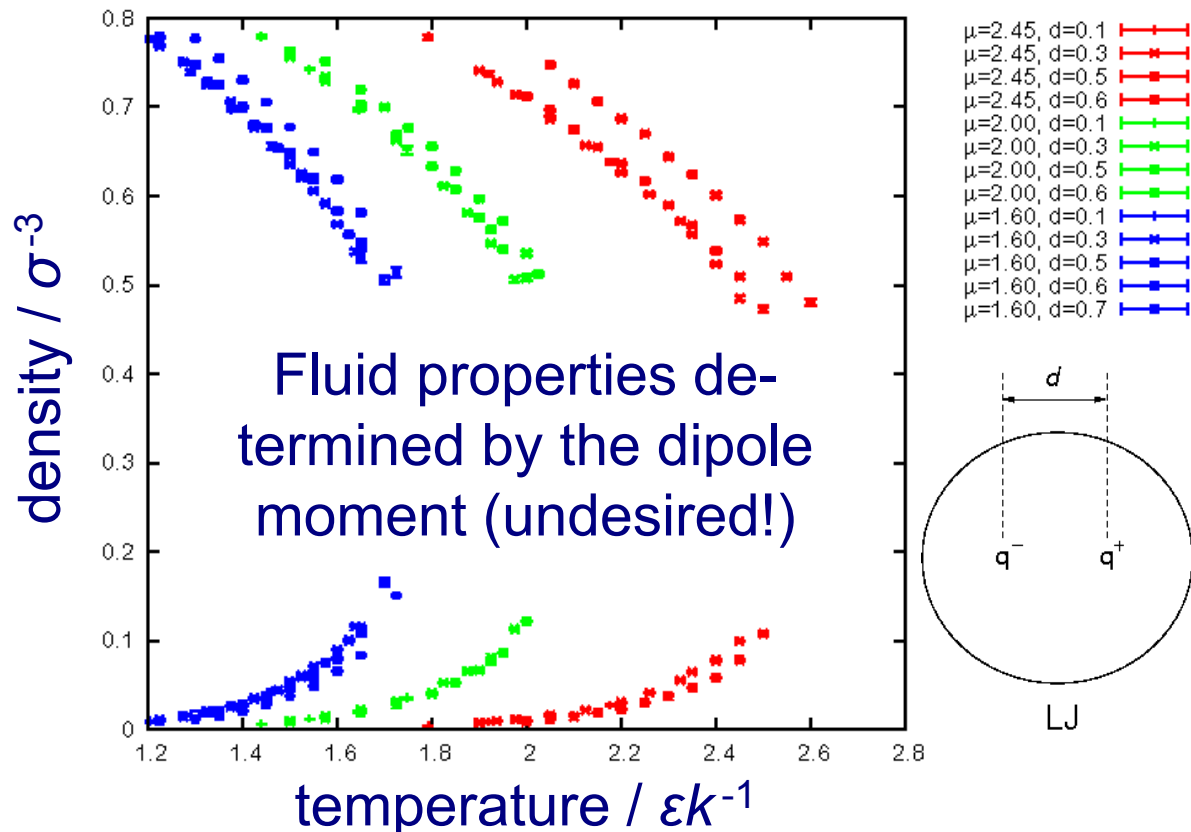
Modelling polarity and hydrogen bonding

monomer fraction

electrostatic pair potential

Further objectives on the basis of the present parameter study:

- SAFT-like equation of state for the elongated Stockmayer model
- Prediction of VLE for multi-site models of hydrogen bonding fluids
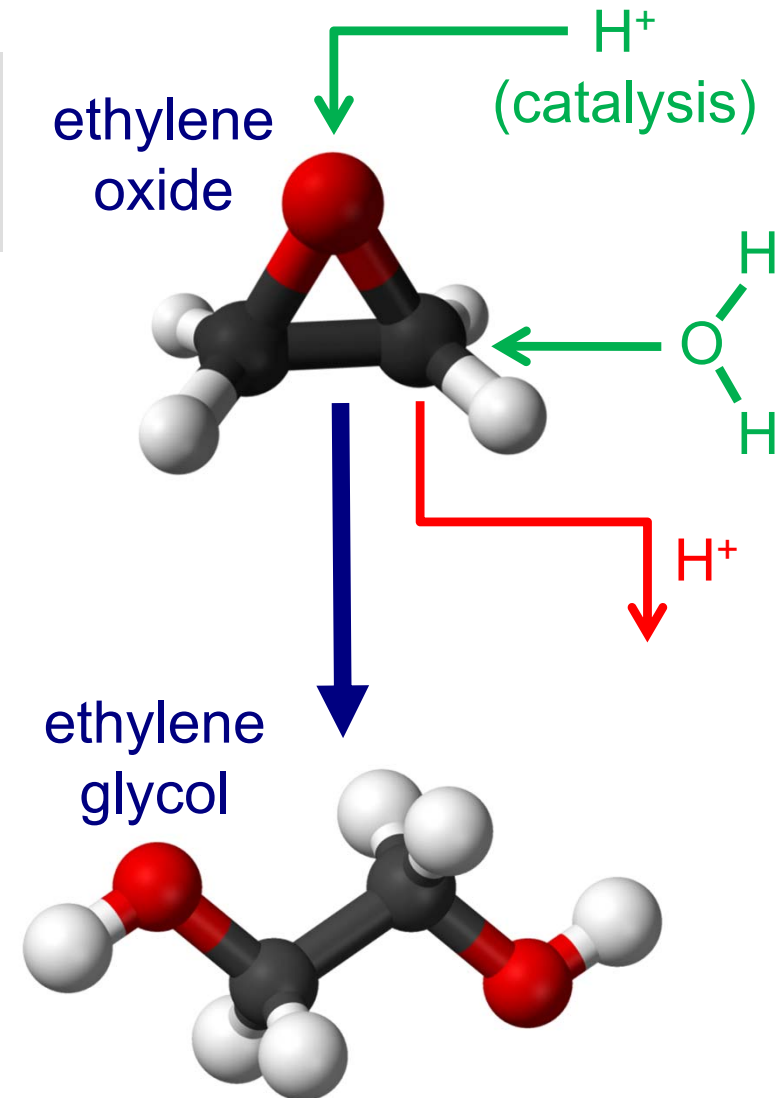
Industrially important reactive systems

Objective: Simulation of transition states

Here: EOX+ (based on reliable EOX model)

Correlation function controlling the S_N2 reaction of protonated EOX with water:
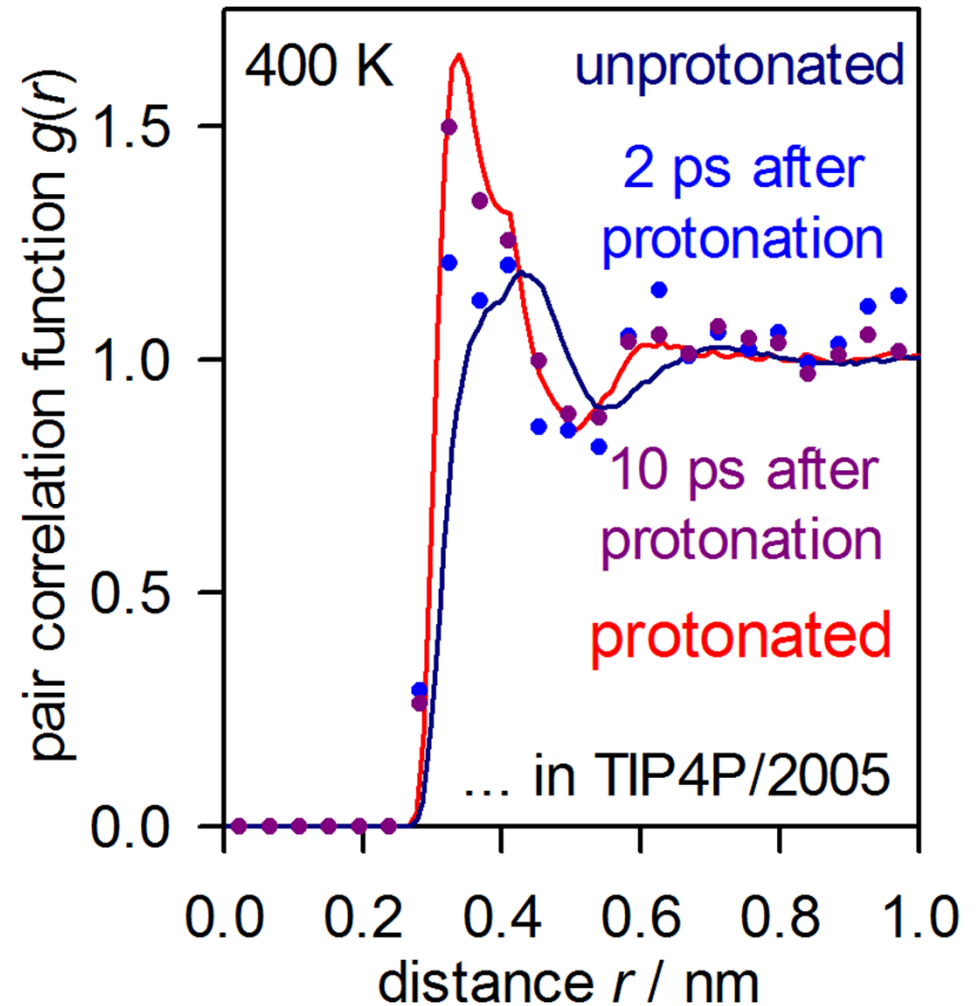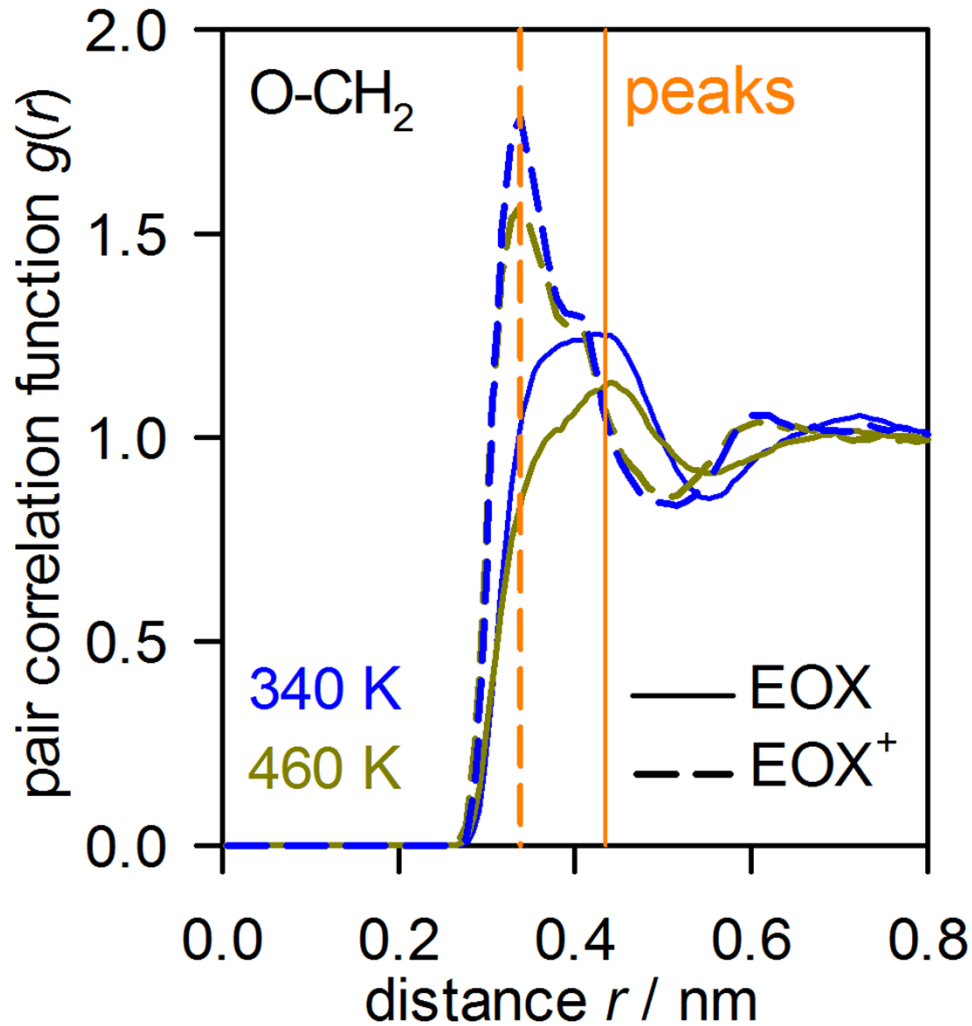
methylene (EOX$^+$) $\leftrightarrow$ oxygen (H_2O)

- High economic interest

- Difficult experiments

- Few reliable data

- Need for predictive modelling and simulation

ethylene oxide

H$^+$
(catalysis)

H
O
H

H$^+$

ethylene glycol

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Transient radial distribution function

Discussion

- Could it be that the diameter effect (rather than the curvature effect) determines the influence of droplet size on the surface tension?

- How should we implement the cutoff correction for anisotropic or fluctuating systems in (long-term!) future releases of *ls1 mardyn*?

- For modelling a chemical reaction: How does the relaxation time of the fluid phase, during which the correlation function for the transition state are established, relate to its average life time?

- Does it make sense – as a perspective – to work on methods for reactive ensembles with classical force fields? (E.g., with reaction probabilities speficied as a function of kinetic energy and orientation.)