



Molecular simulation of dispersed fluid phases and H bonding fluids

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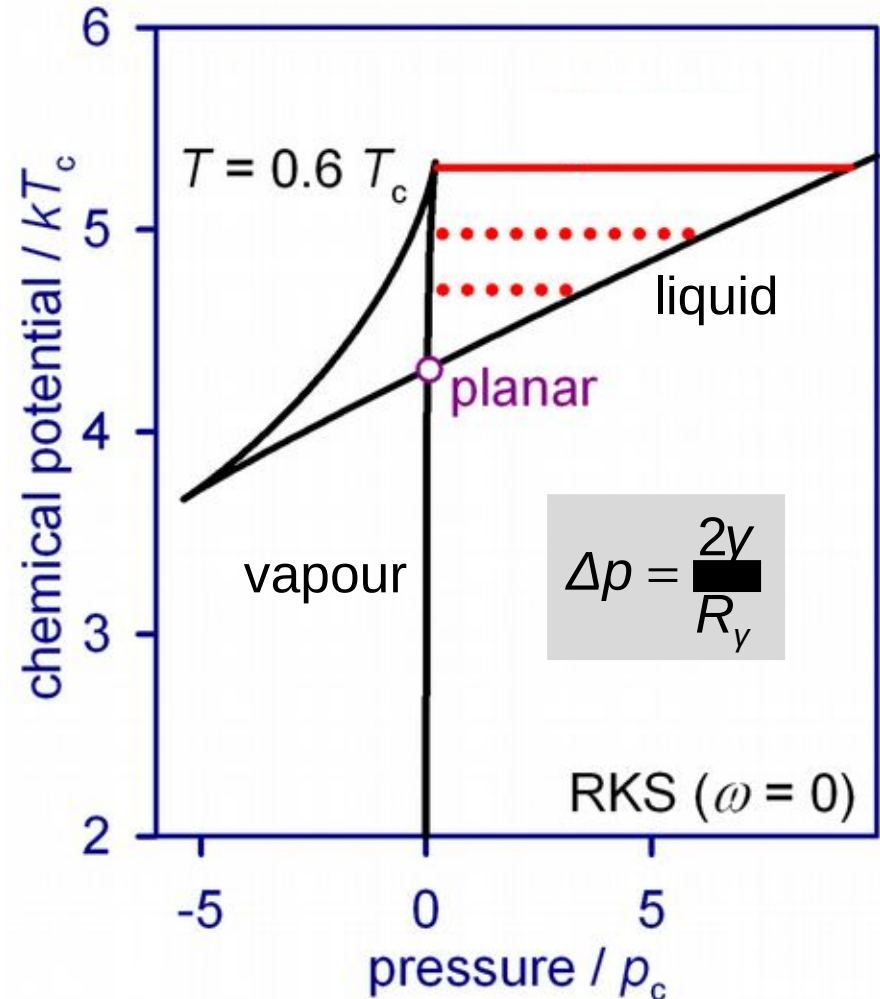
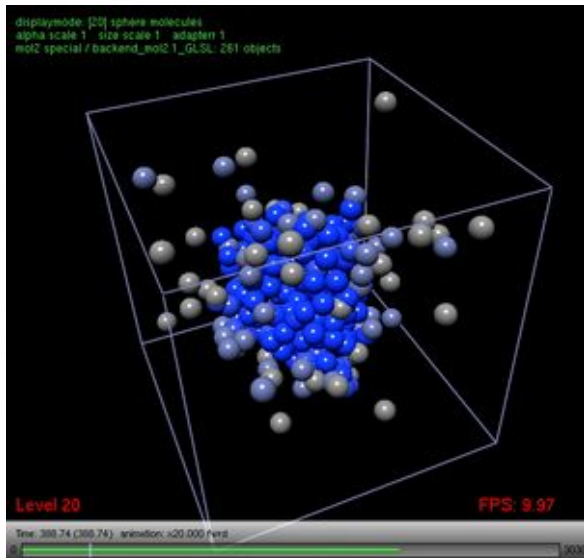
Microporous and Soft Matter Group Seminar



**Computational
Molecular Engineering**

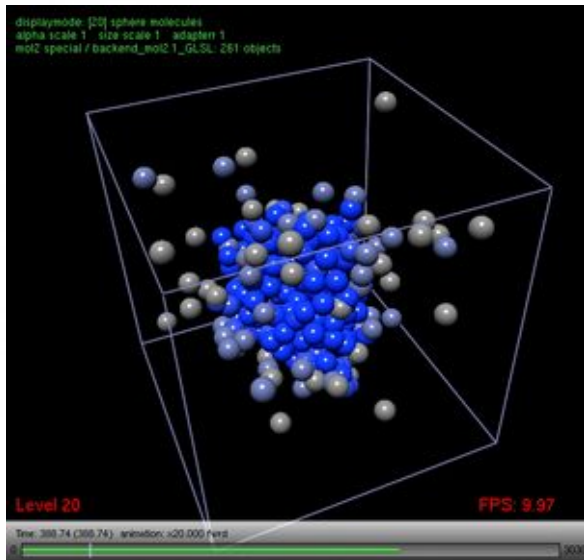
Dispersed fluid phases in equilibrium

- Droplet + metastable vapour

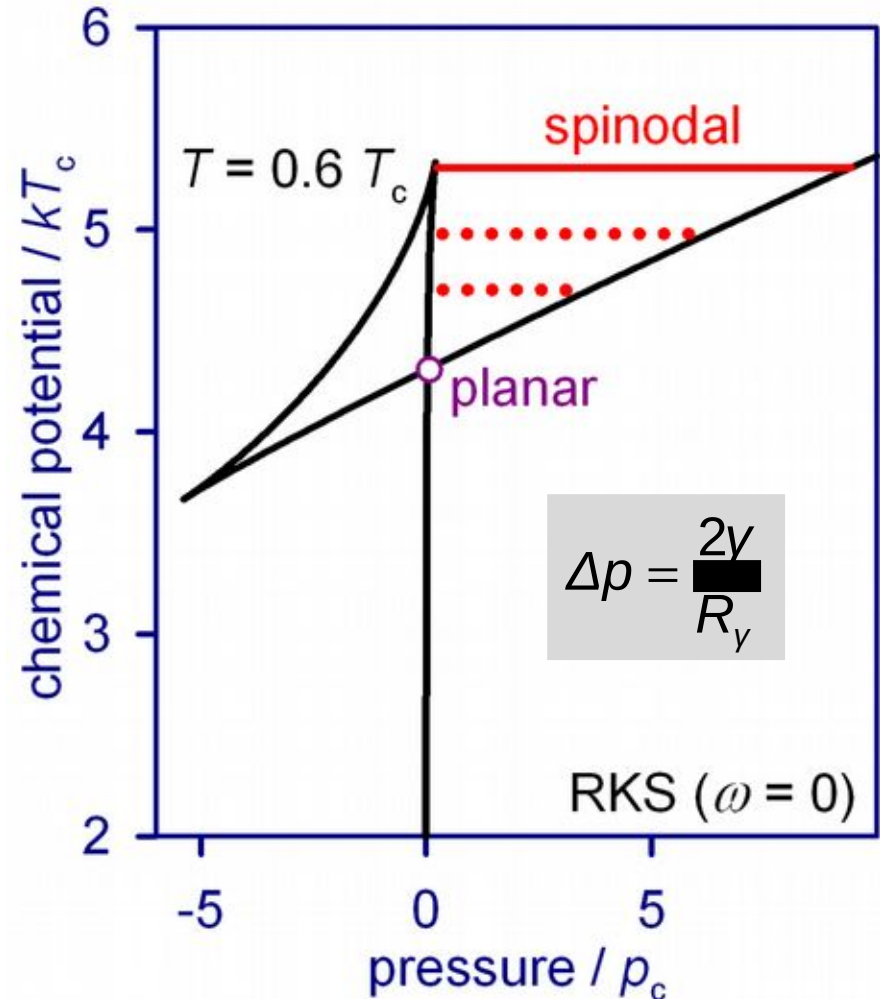


Dispersed fluid phases in equilibrium

- Droplet + metastable vapour



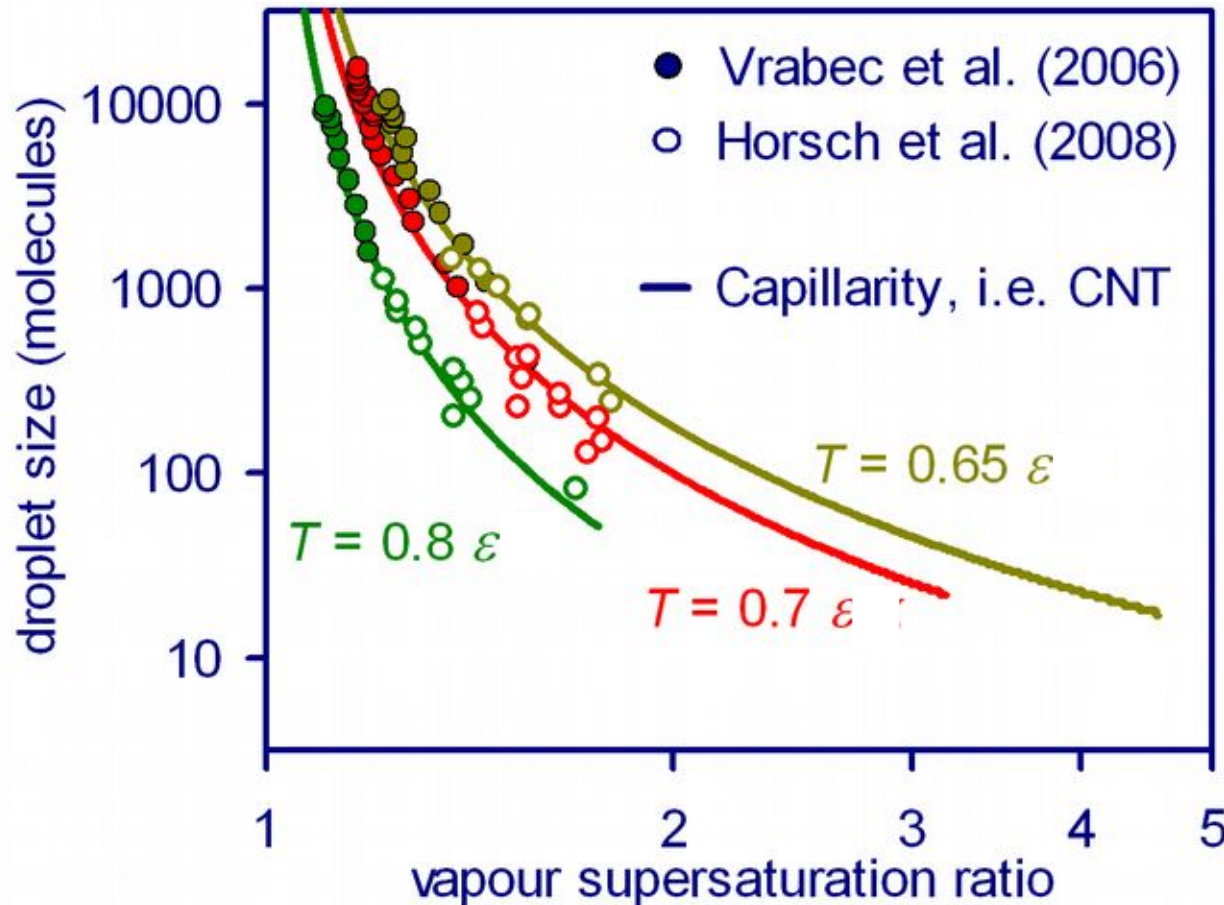
Spinodal limit: For the external phase, metastability breaks down.





Equilibrium vapour pressure of a droplet

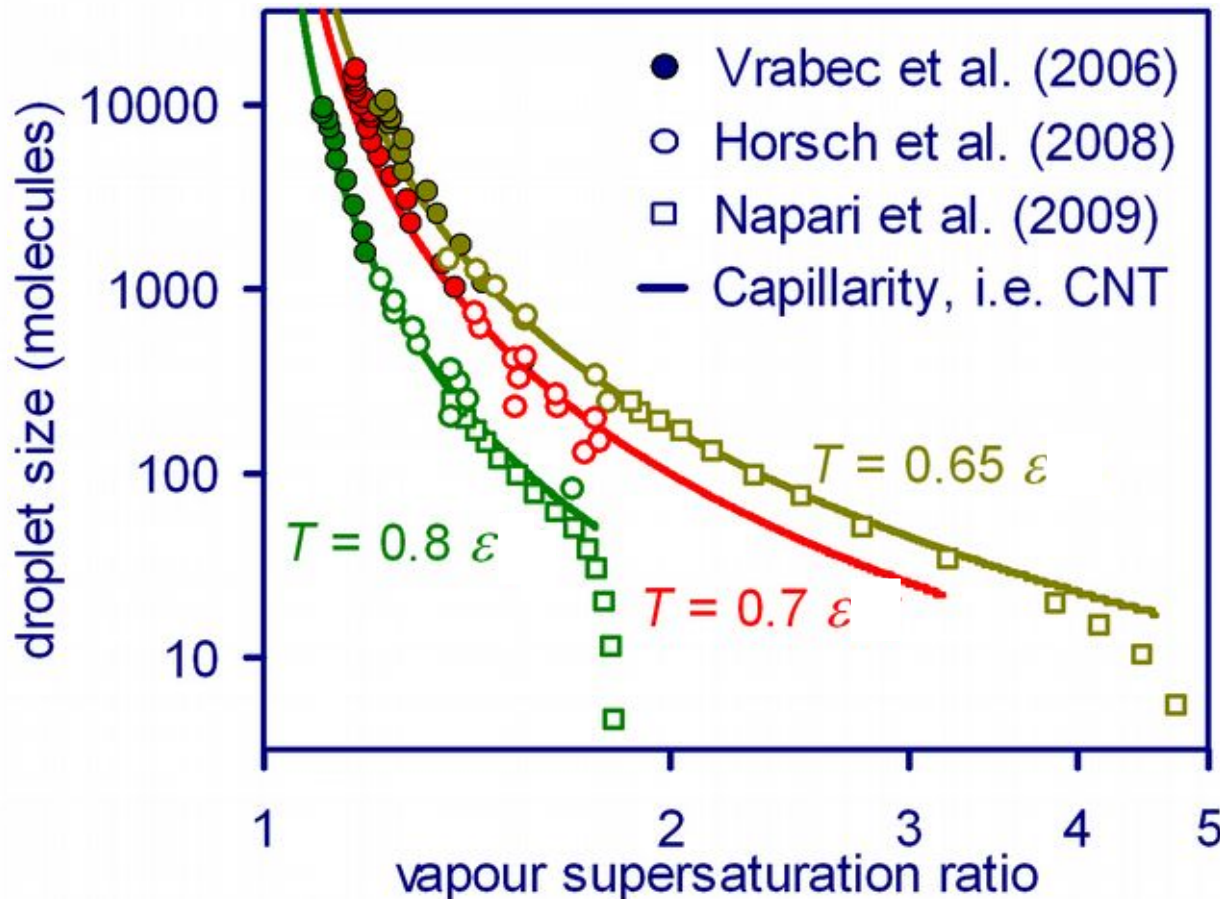
Canonical MD simulation of LJTS droplets



Down to 100 molecules: agreement with CNT ($\gamma = \gamma_0$).

Equilibrium vapour pressure of a droplet

Canonical MD simulation of LJTS droplets



Down to 100 molecules: agreement with CNT ($\gamma = \gamma_0$).

At the spinodal, the results suggest that $R_y = 2\gamma / \Delta p \rightarrow 0$. This implies

$$\lim_{R_y \rightarrow 0} \gamma = 0,$$

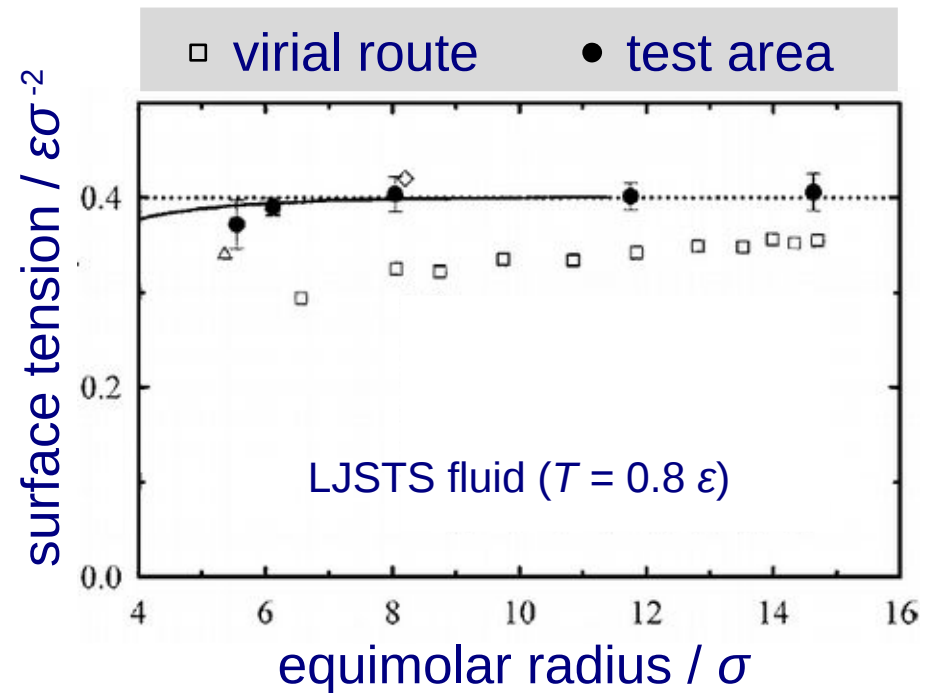
as conjectured by Tolman (1949) ...

Surface tension from molecular simulation

Integral over the pressure tensor



Test area method:
Small deformations of the volume



(Source: Sampayo et al., 2010)

N_{liq}

**Mutually contradicting
simulation results!**



Analysis of radial density profiles

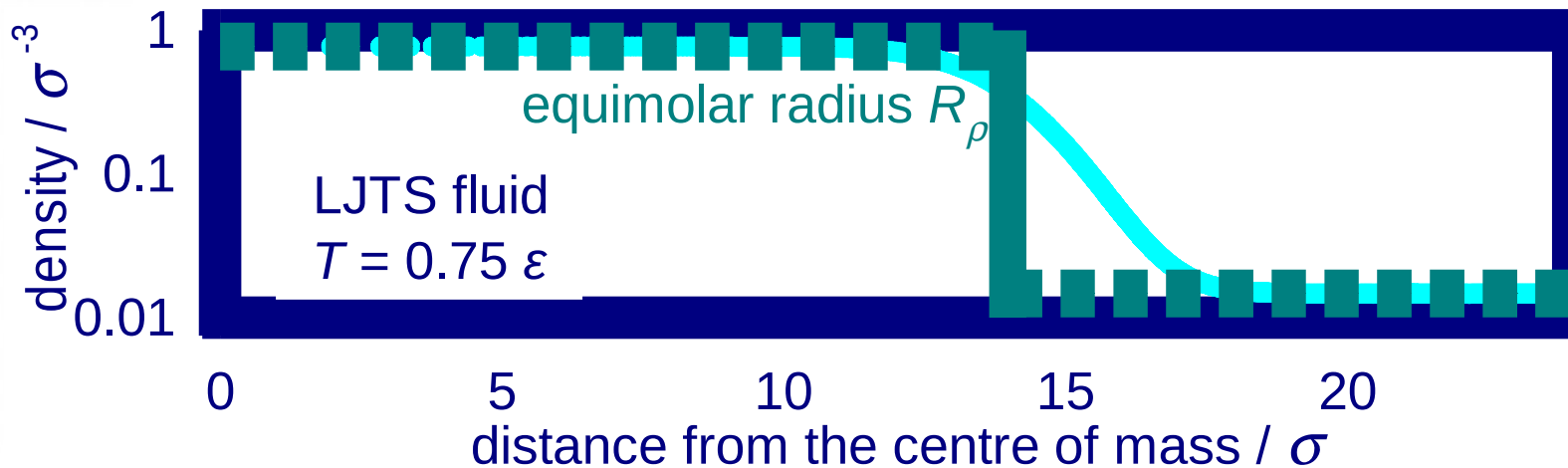
The thermodynamic approach of Tolman (1949) relies on effective radii:

- Equimolar radius R_ρ (obtained from the density profile) with

$$\Gamma = \int_0^{R_\rho} dR R^2 [\rho(R) - \rho'] + \int_{R_\rho}^{\infty} dR R^2 [\rho(R) - \rho''] = 0$$

- Laplace radius $R_\gamma = 2\gamma/\Delta p$ (defined in terms of the surface tension γ)

Since γ and R_γ are under dispute, this set of variables is inconvenient here.



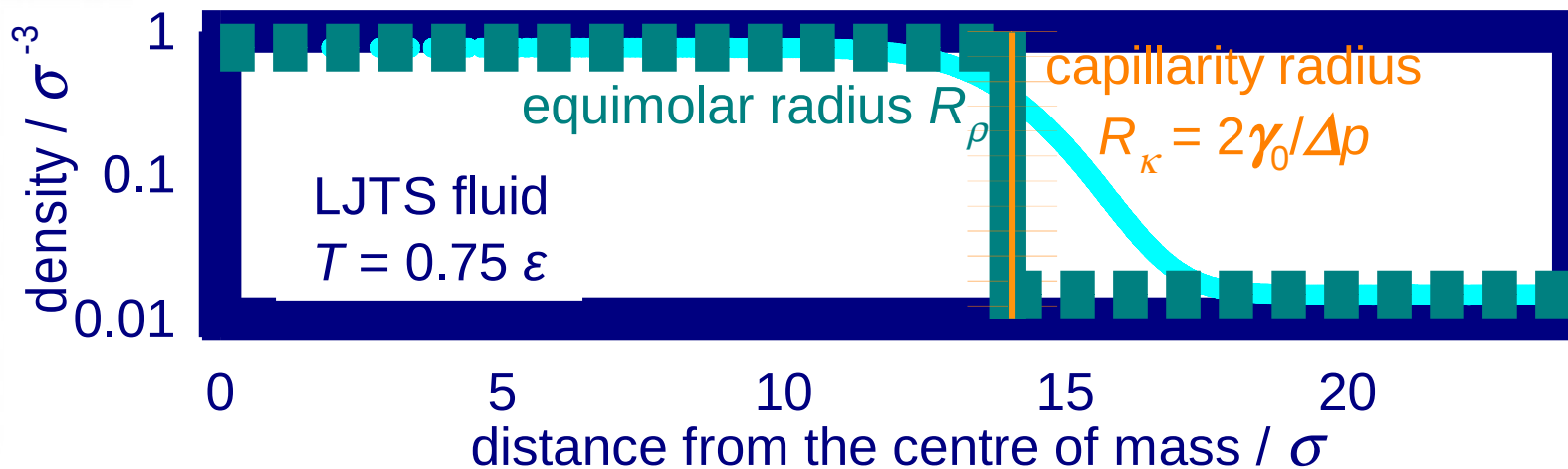


Analysis of radial density profiles

Various formal droplet radii can be considered within Tolman's approach:

- Equimolar radius R_ρ (obtained from the density profile)
- Capillarity radius $R_\kappa = 2\gamma_\infty/\Delta p$ (defined by the planar surface tension γ_∞)
- Laplace radius $R_\gamma = 2\gamma/\Delta p$ (defined by the curved surface tension γ)

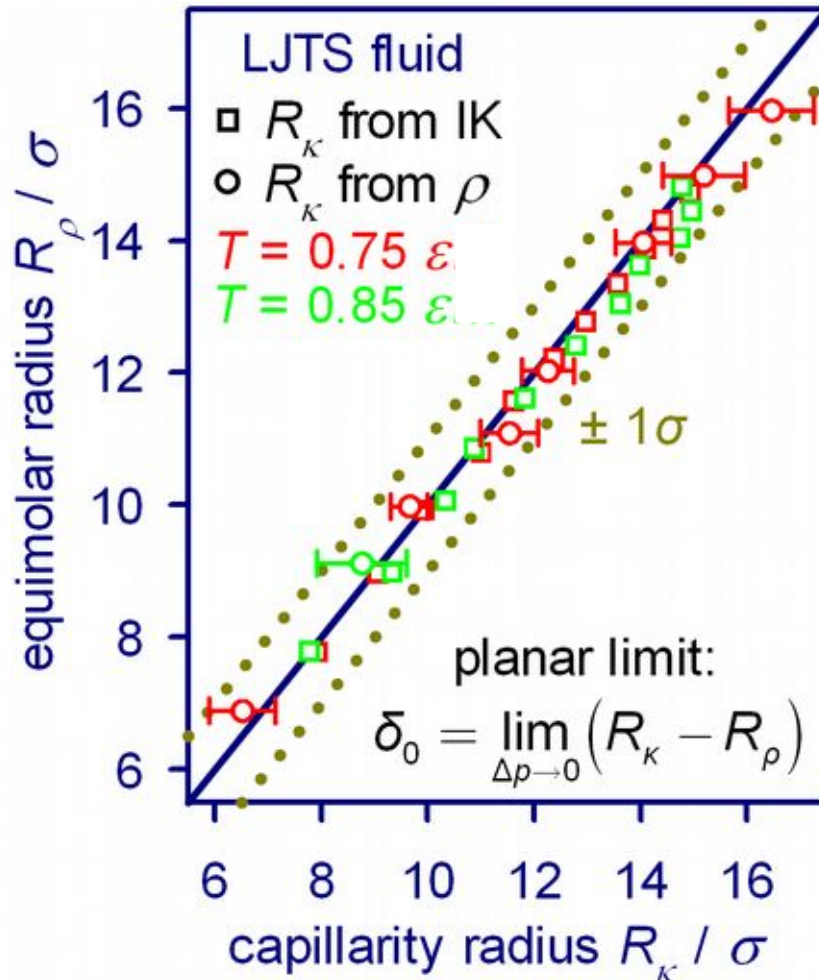
The capillarity radius can be obtained reliably from molecular simulation.



Approach: Use $\gamma/R_\gamma = \Delta p/2$ instead of $1/R_\gamma$, use $R_\kappa = 2\gamma_0/\Delta p$ instead of R_γ .

Extrapolation to the planar limit

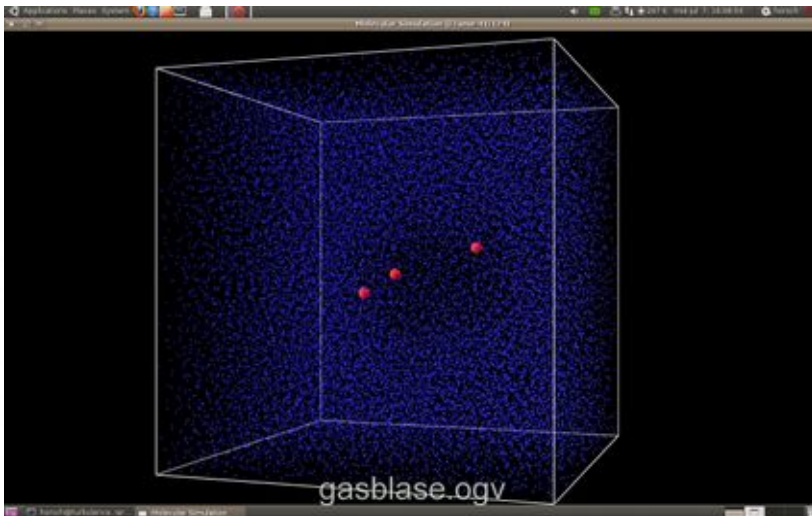
Radial parity plot



- The magnitude of the excess equimolar radius is consistently found to be smaller than $\sigma / 2$.
- This suggests that the curvature dependence of γ is weak, i.e. that the deviation from γ_∞ is smaller than 10 % for radii larger than 5σ .
- This contradicts the results from the virial route and confirms the grand canonical and test area simulations.

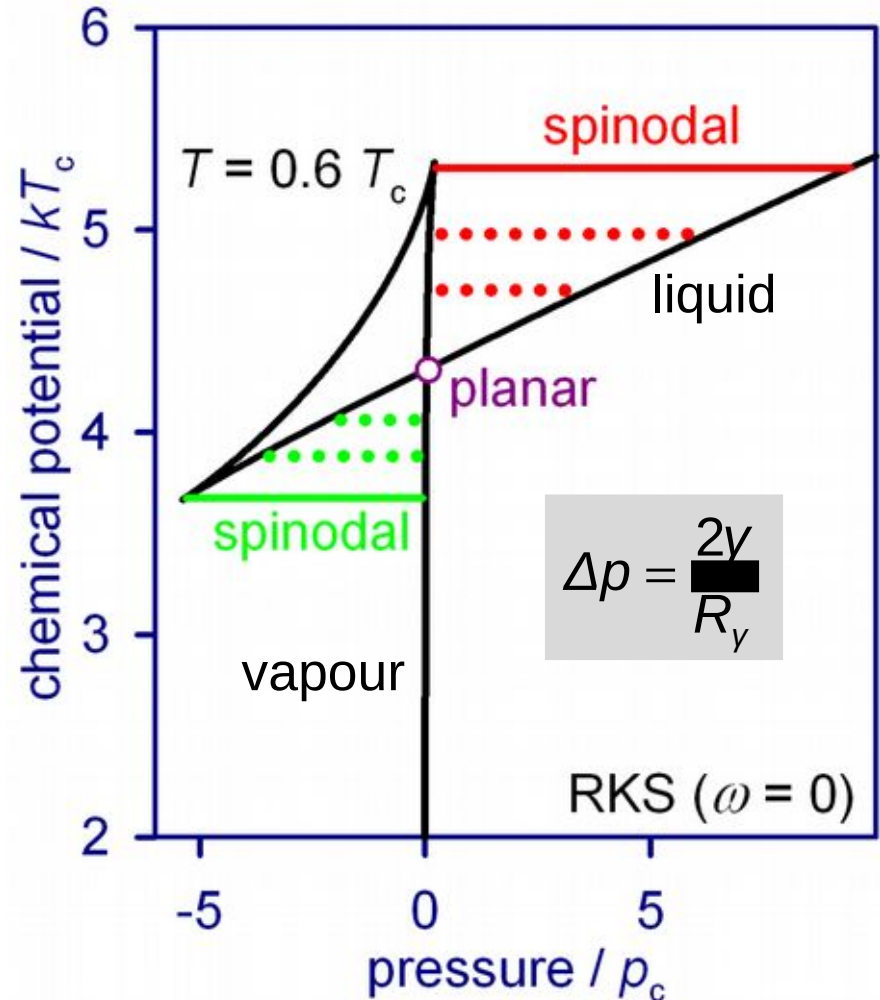
Gas bubbles in equilibrium

- Droplet + metastable vapour
- Bubble + metastable liquid



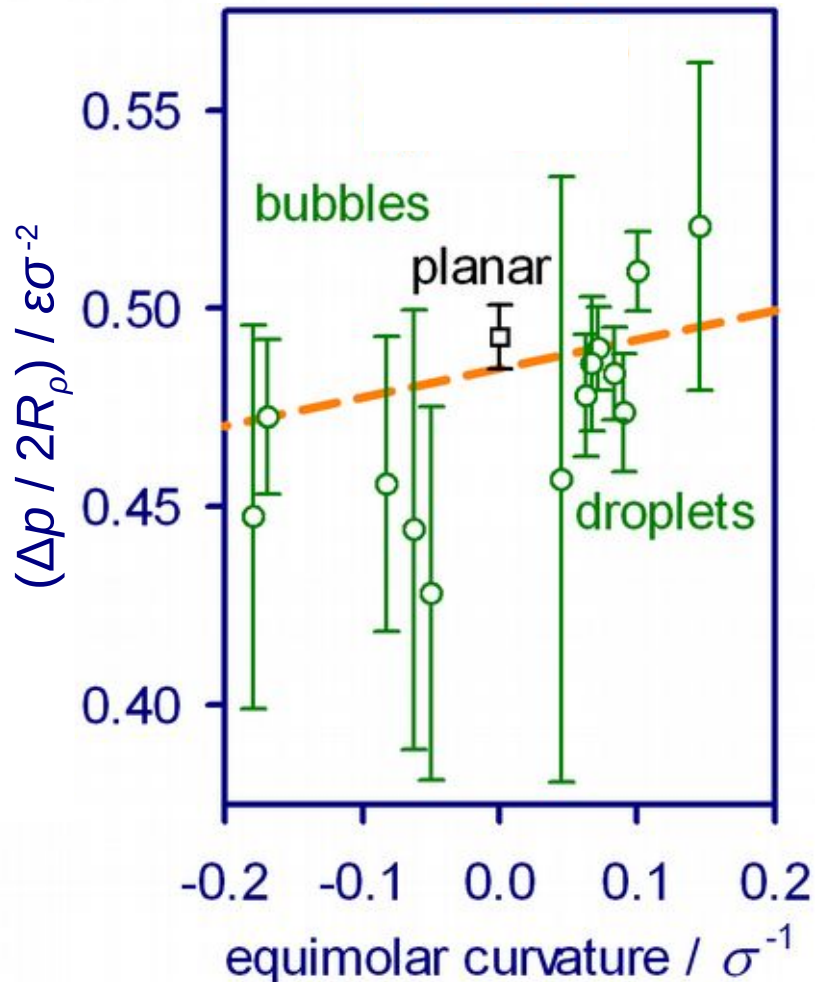
Spinodal limit: For the external phase, metastability breaks down.

Planar limit: The curvature changes its sign and the radius R_y diverges.



Interpolation to the planar limit

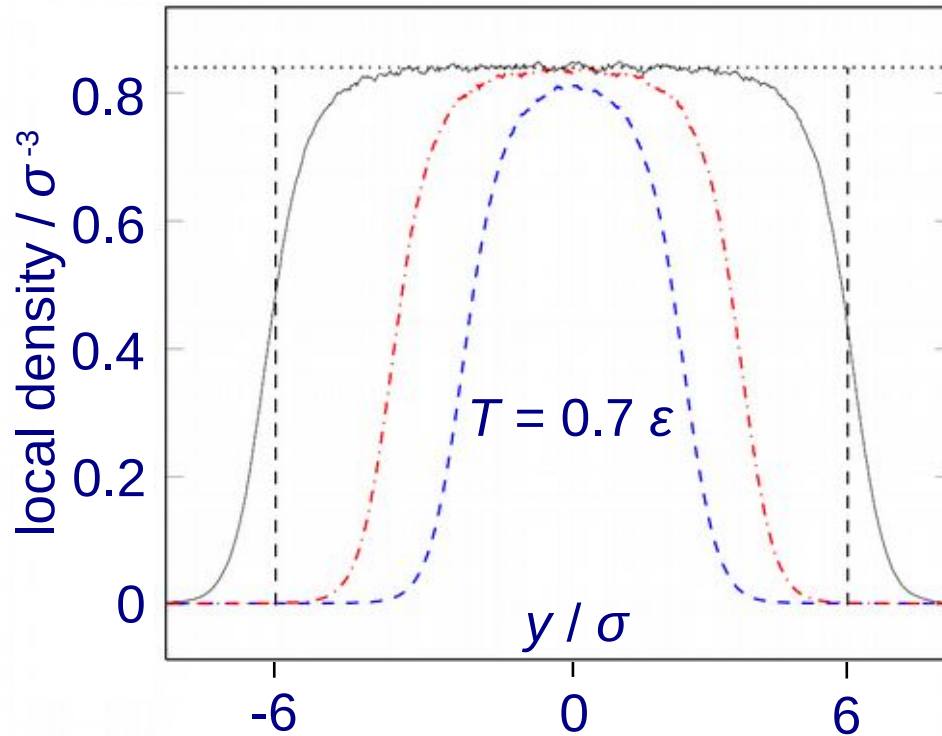
Nijmeijer diagram



- Convention: Negative curvature (bubbles), positive curvature (droplets).
- Properties of the planar interface, such as its Tolman length, can be obtained by interpolation to zero curvature.
- A positive slope of $\Delta p / 2R_\rho$ over $1/R_\rho$ in the Nijmeijer diagram corresponds to a *negative* δ , on the order of -0.1σ here, conforming that δ is *small*.
- However, $R \rightarrow 0$ for droplets in the spinodal limit for the surrounding vapour (Napari et al.) implies $\gamma \rightarrow 0$.

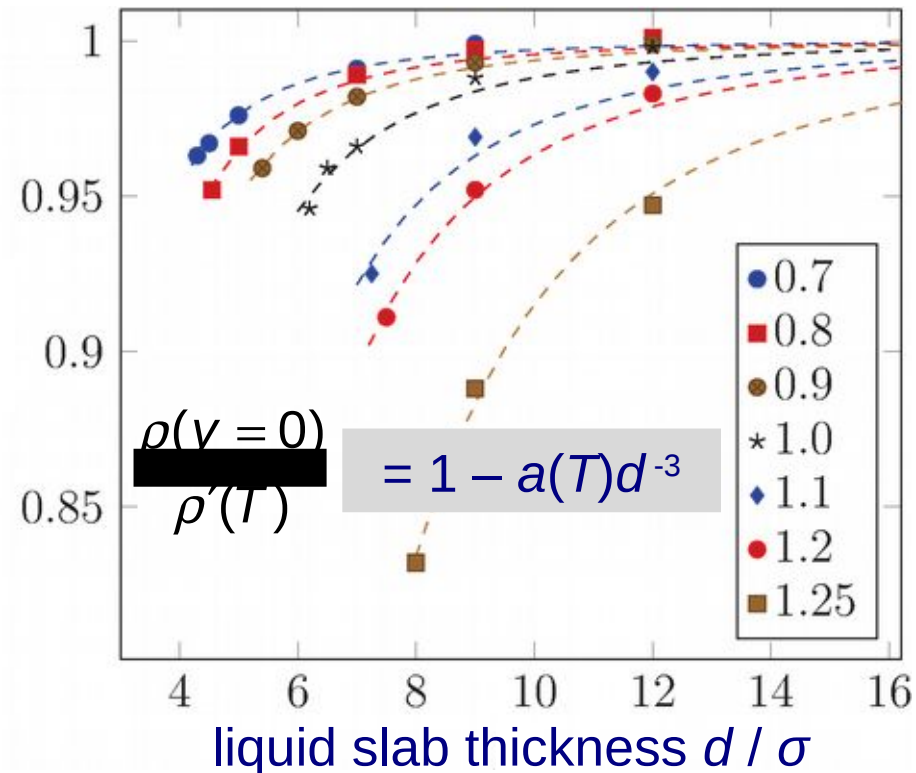


Finite size effects for planar liquid slabs



As expected, the density in the centre of nanoscopic liquid slabs deviates significantly from that of the bulk liquid at saturation.

By simulating small liquid slabs, curvature-independent size effects can be considered.

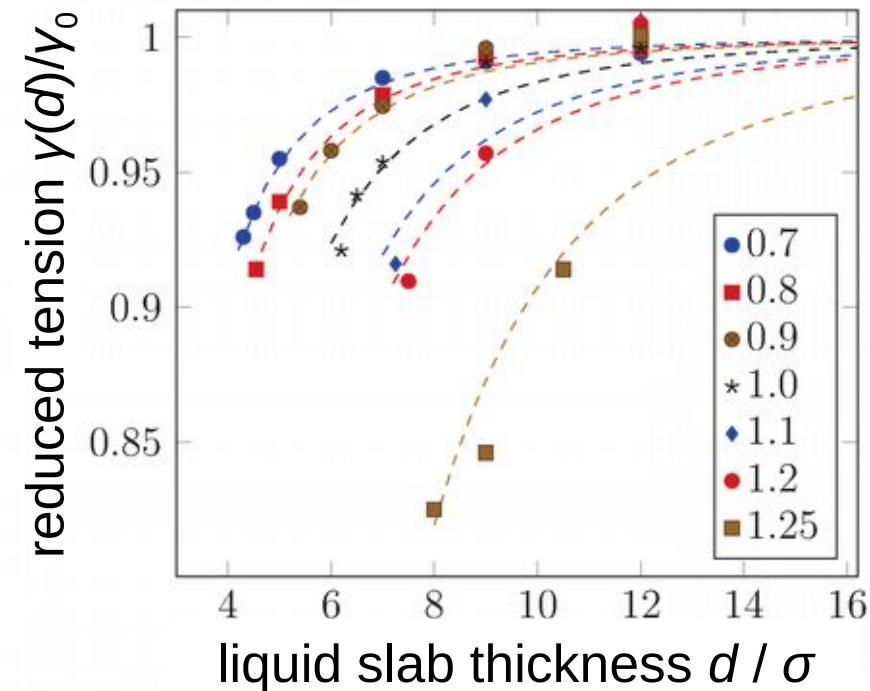




Curvature-independent size effect on γ

Surface tension for thin slabs:

Relation with $\gamma(R)$ for droplets?



Correlation: $\frac{\gamma(d, T)}{\gamma_0(T)} = 1 - \frac{b(T)}{d^3}$

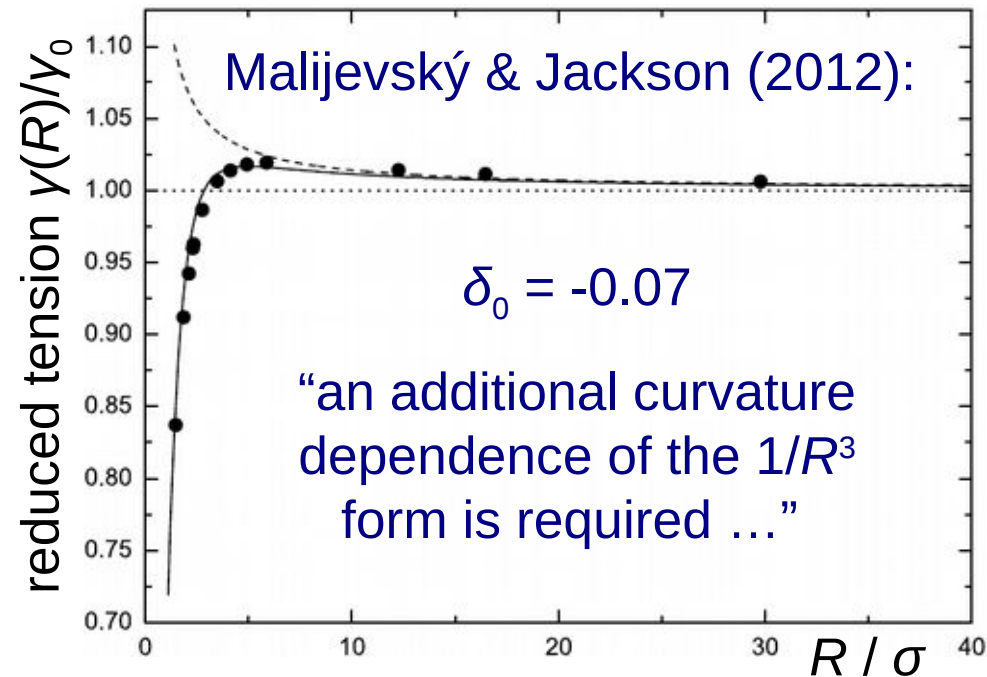
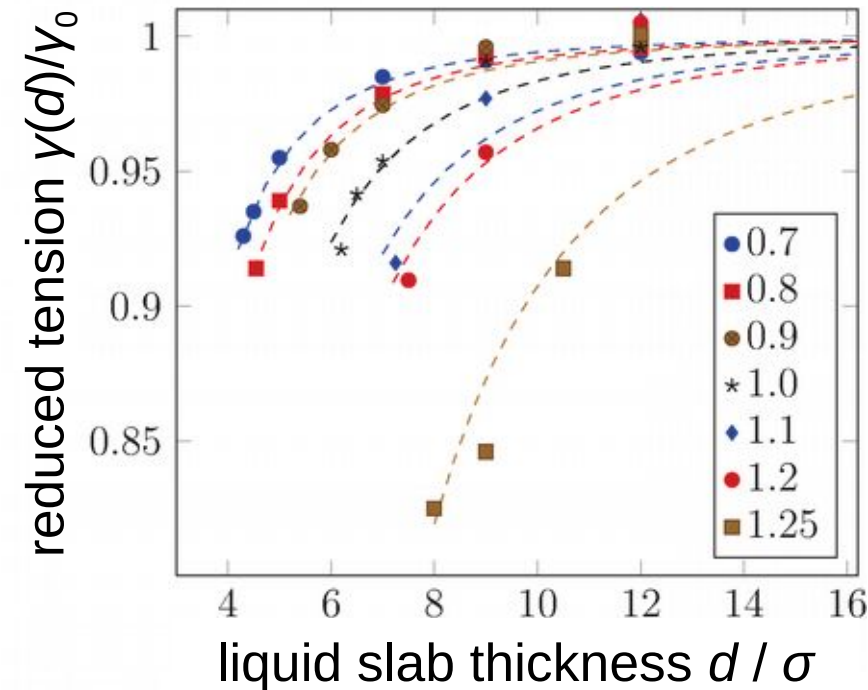


Curvature-independent size effect on γ

Surface tension for thin slabs:

Relation with $\gamma(R)$ for droplets?

δ_0 is small and probably negative



Correlation: $\frac{\gamma(d, T)}{\gamma_0(T)} = 1 - \frac{b(T)}{d^3}$



The nature of the hydrogen bond

Pauling (1960, “The Nature of the Chemical Bond”) on the hydrogen bond:

It “was for some time thought to result from the formation of two covalent bonds,” but it “is now understood that the hydrogen bond is largely ionic”

Hope: H bonds can be described by simple electrostatics (point charges).

New **IUPAC** definition (2011):

“The hydrogen bond is an attractive interaction ... from a molecule ... X—H in which X is more electronegative than H, and ... in which there is evidence for bond formation.”



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“The hydrogen bond is an attractive interaction ... from a molecule ... X—H in which X is more electronegative than H, and ... in which there is evidence for bond formation.”

“The forces involved ... include

- those of an electrostatic origin,
- those arising from ... partial covalent bond formation ...,
- and those originating from dispersion.”

Molecular modelling approaches for H...O

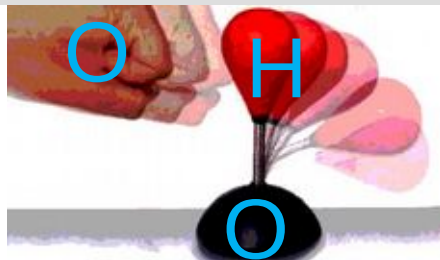
short-range square well



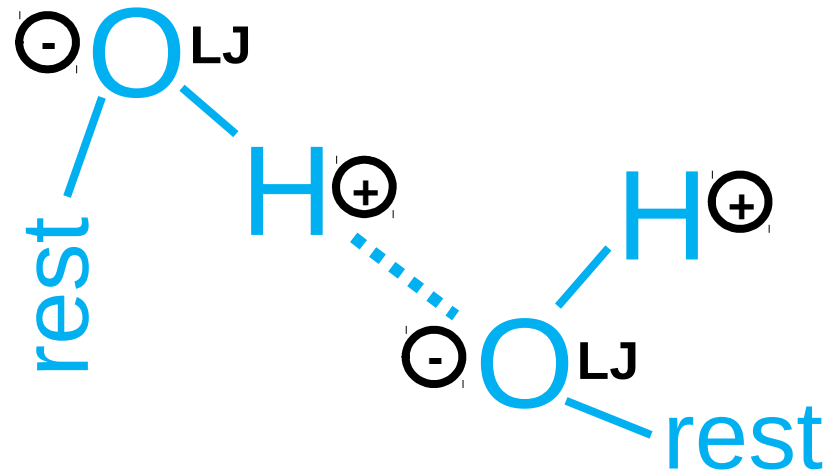
polarizable models



internal degrees of freedom



simple approach



Oxygen: LJ concentric with negative charge

Hydrogen: Positive partial charge (no LJ)

Molecular modelling approaches for H...O

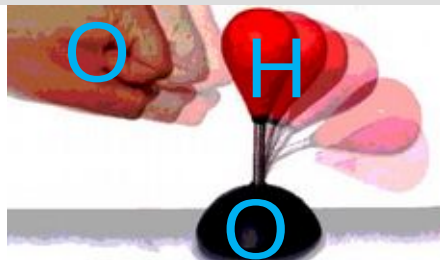
short-range square well



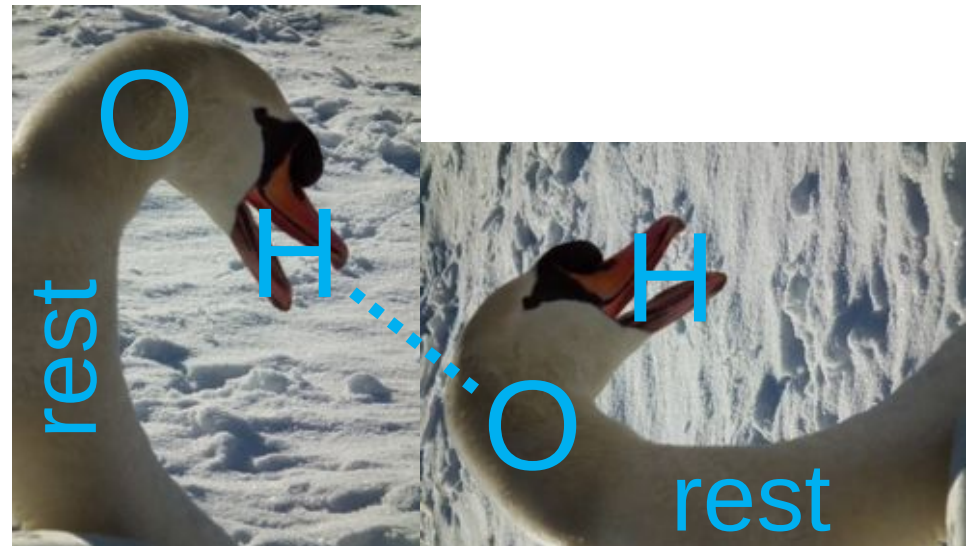
polarizable models



internal degrees of freedom



simple "beak" approach



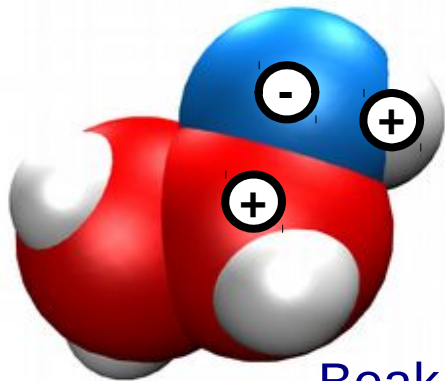
Oxygen: LJ concentric with negative charge
Hydrogen: Positive partial charge (no LJ)

Simple beak-shaped hydroxyl group model

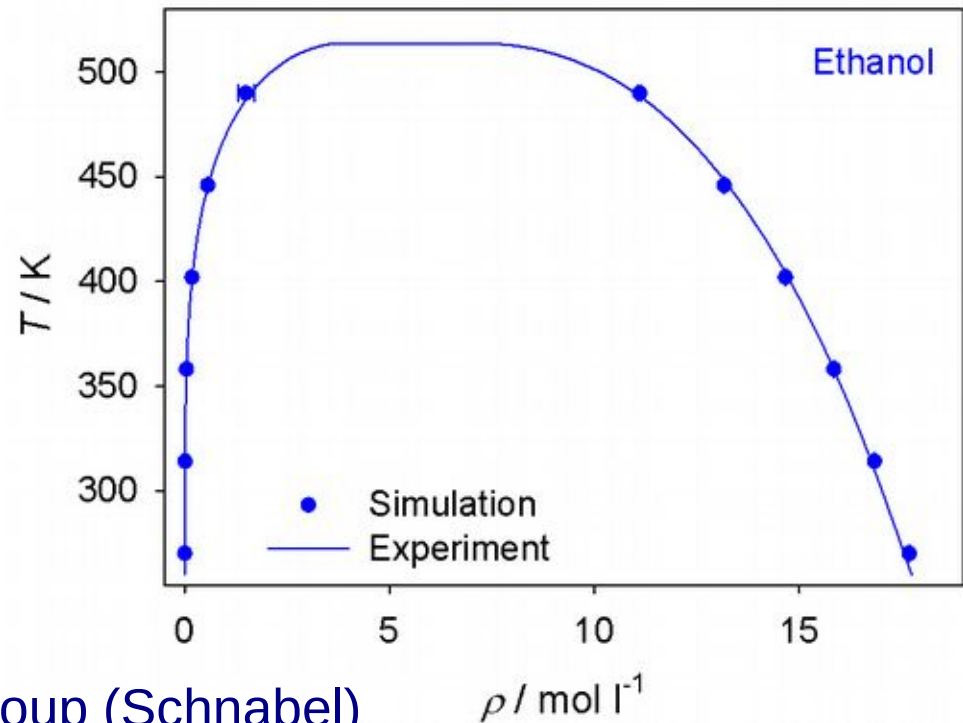
Ethanol:

- three LJ interaction sites
- three point charges

Simple electrostatic sites account for **polarity** as well as **H bonding**.



Beak-like OH group (Schnabel)

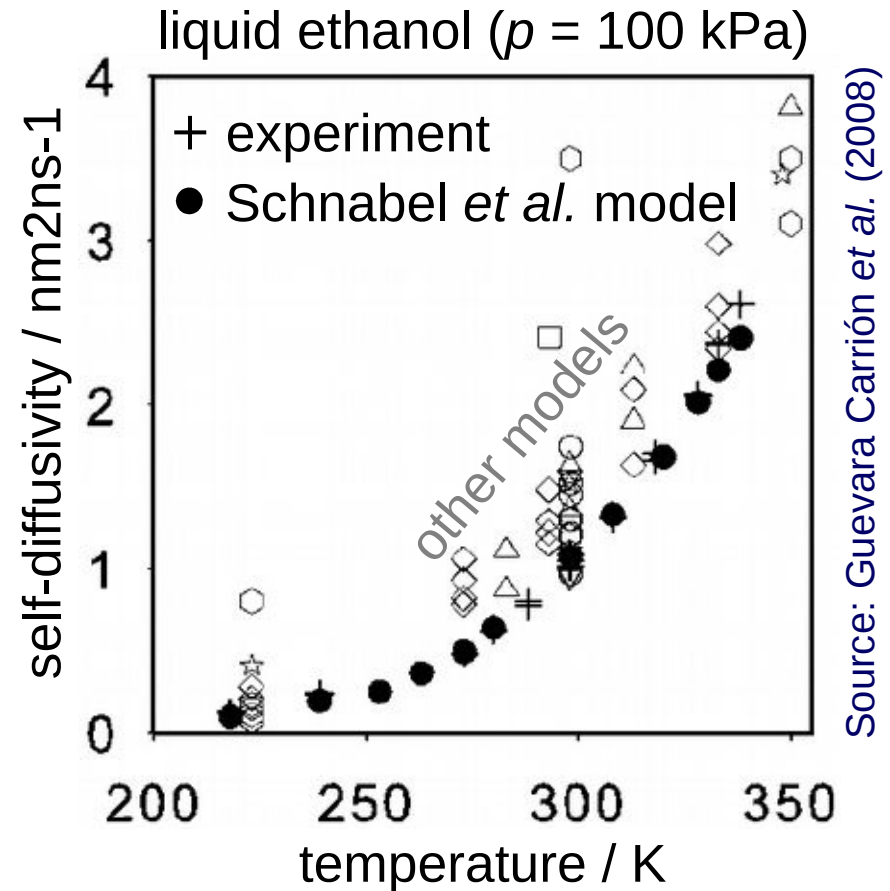
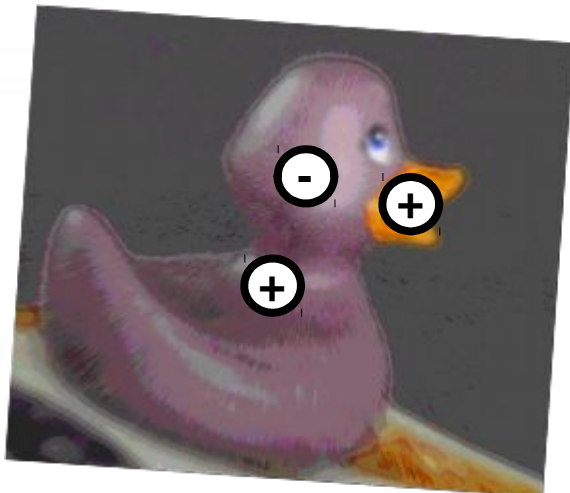


This approach is also valid for methanol and mixtures of H bonding fluids.

Simple beak-shaped hydroxyl group model

Ethanol:

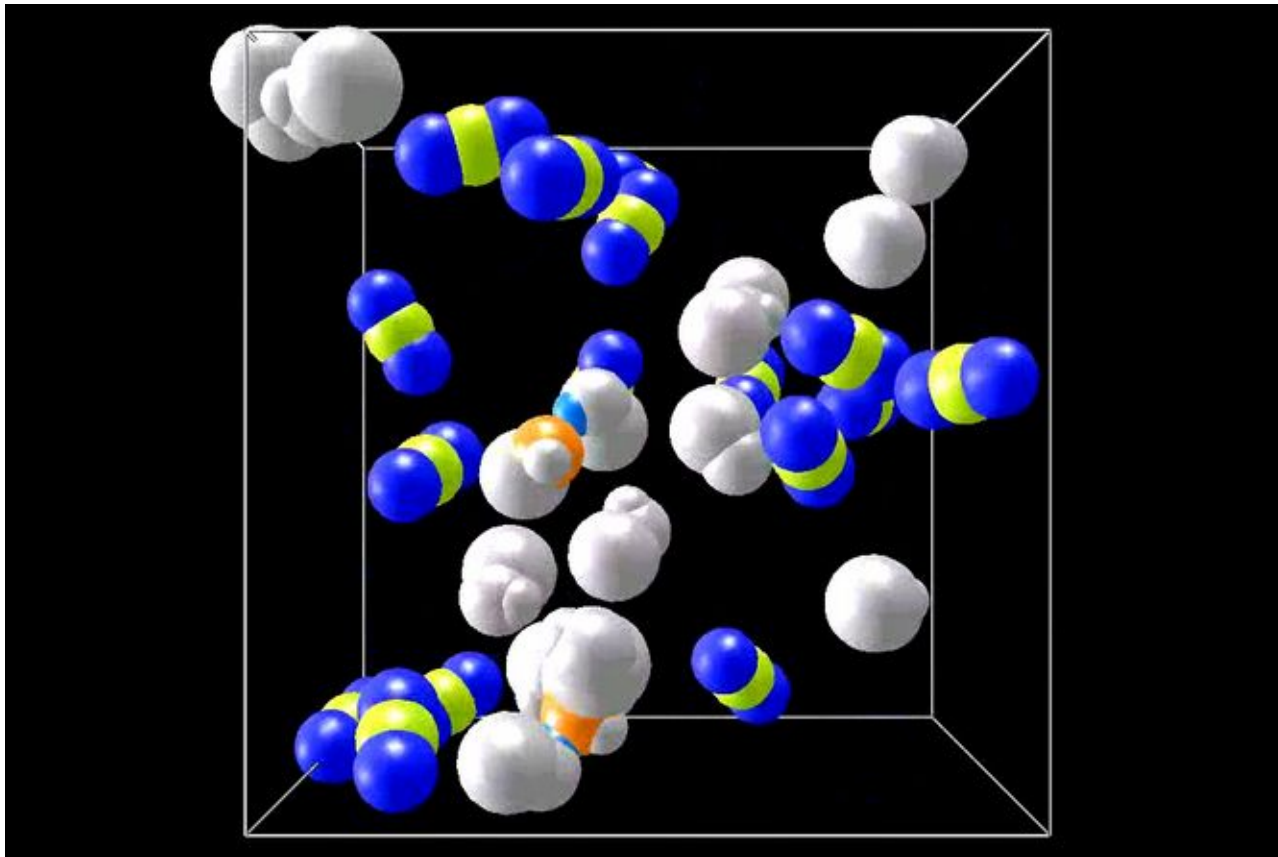
- three LJ interaction sites
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This approach is also valid for methanol and mixtures of H bonding fluids.



Hydrogen bonding in molecular simulation

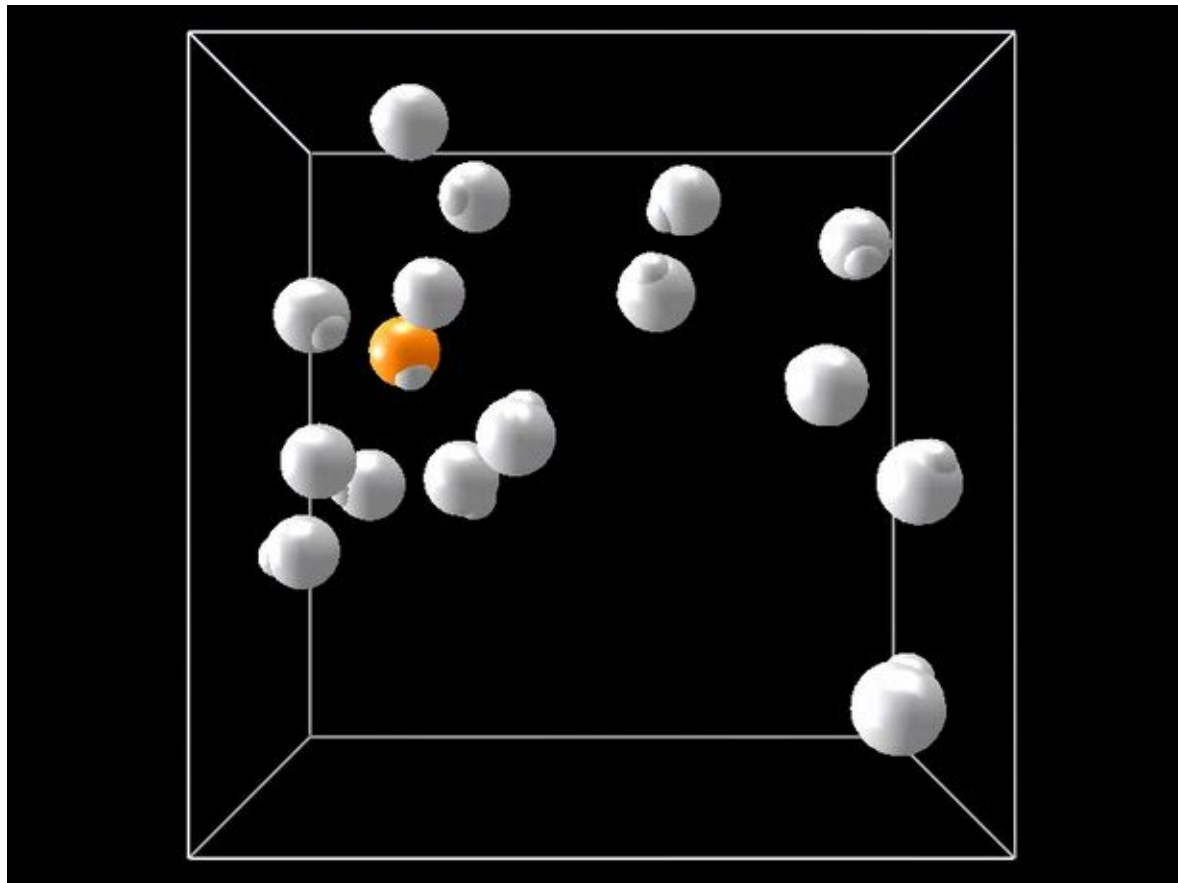


350 K
100 kPa

equimolar mixture of methanol and carbon dioxide



Hydrogen bonding in molecular simulation



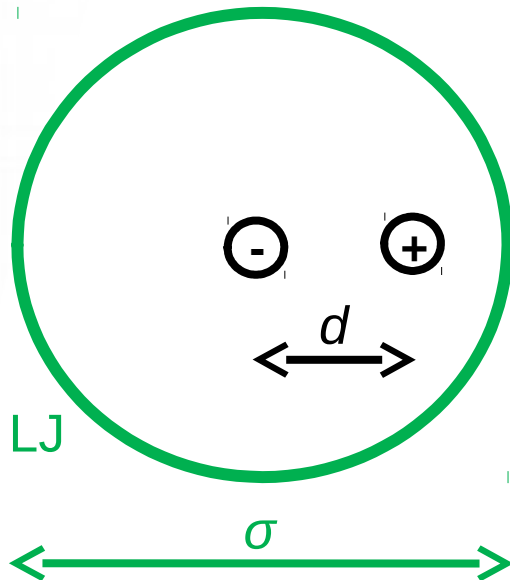
350 K
100 kPa

equimolar mixture of methanol and carbon dioxide

Zoom in: Point charge models of H bonding

The Stockmayer dipole is decomposed into two separate point charges:

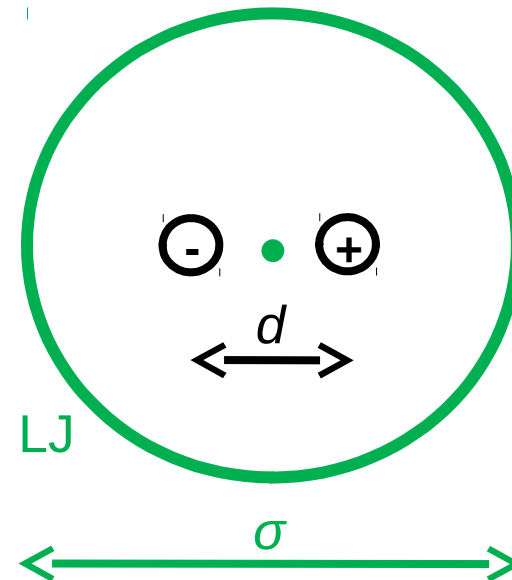
beak fluid (asymmetric)



reflects OH group structure

dipole $\mu = dq$

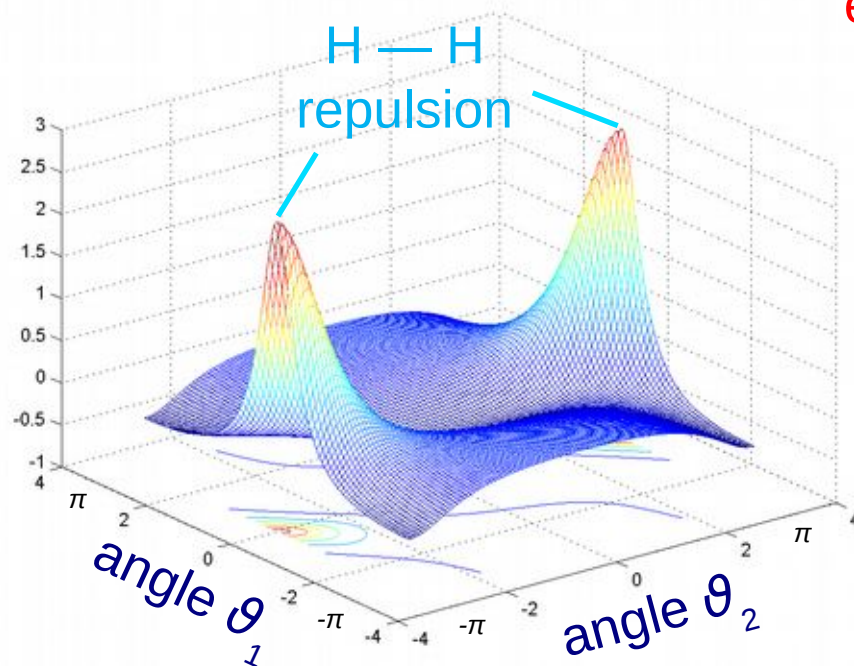
symmetric charges



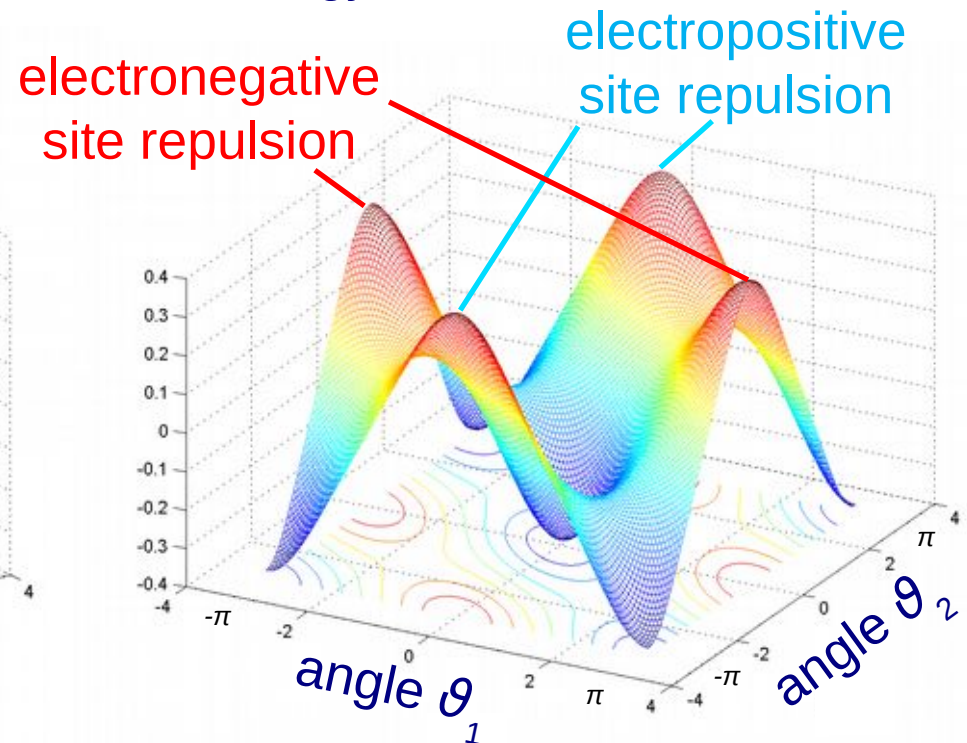
negative and positive sites are equal

Potential energy surface

Electrostatic contribution to the dimer bond energy:



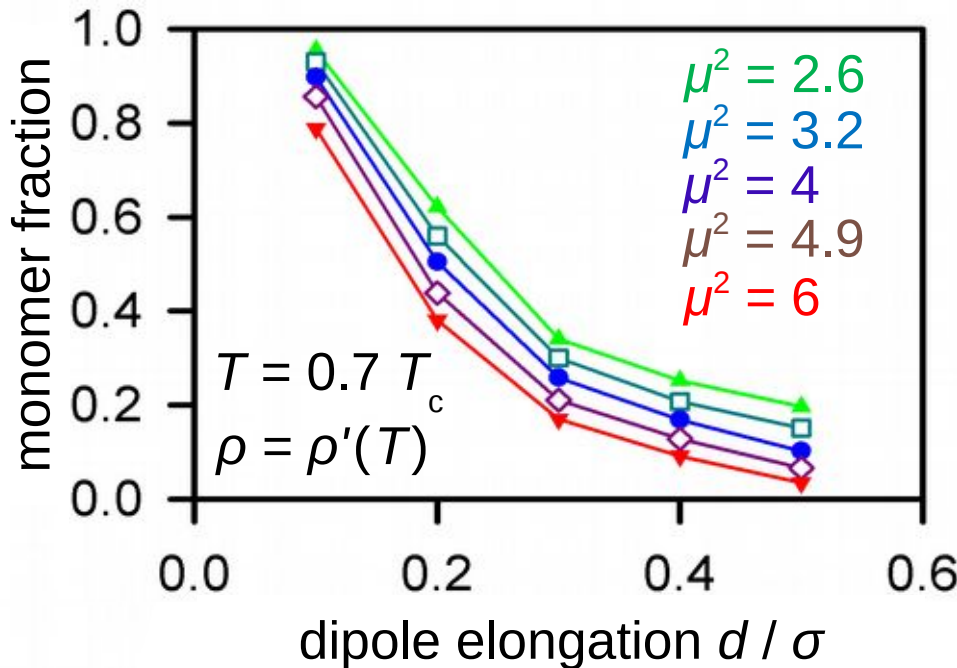
beak fluid



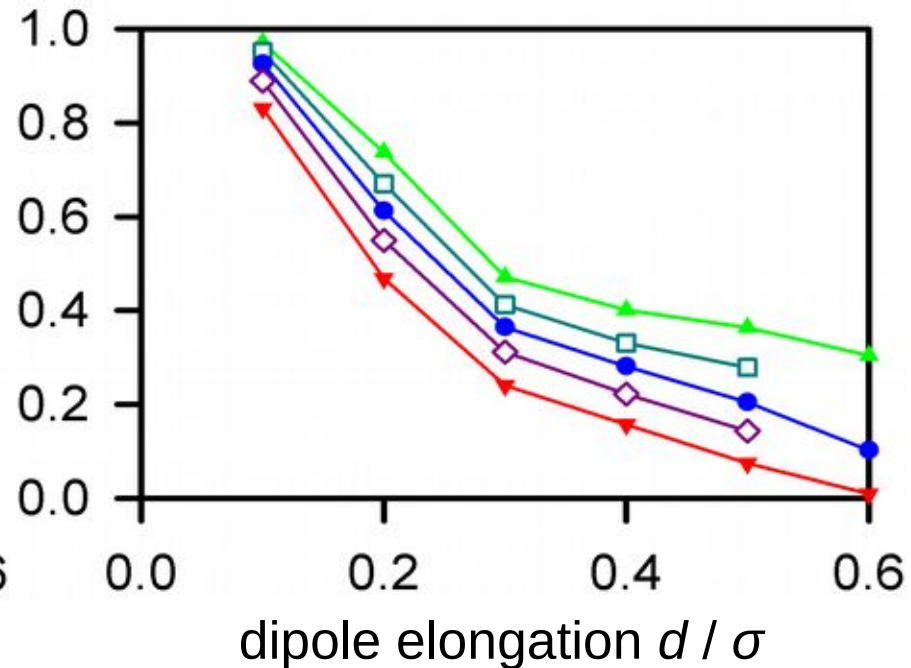
symmetric charges

Hydrogen bonds in the liquid phase

beak fluid

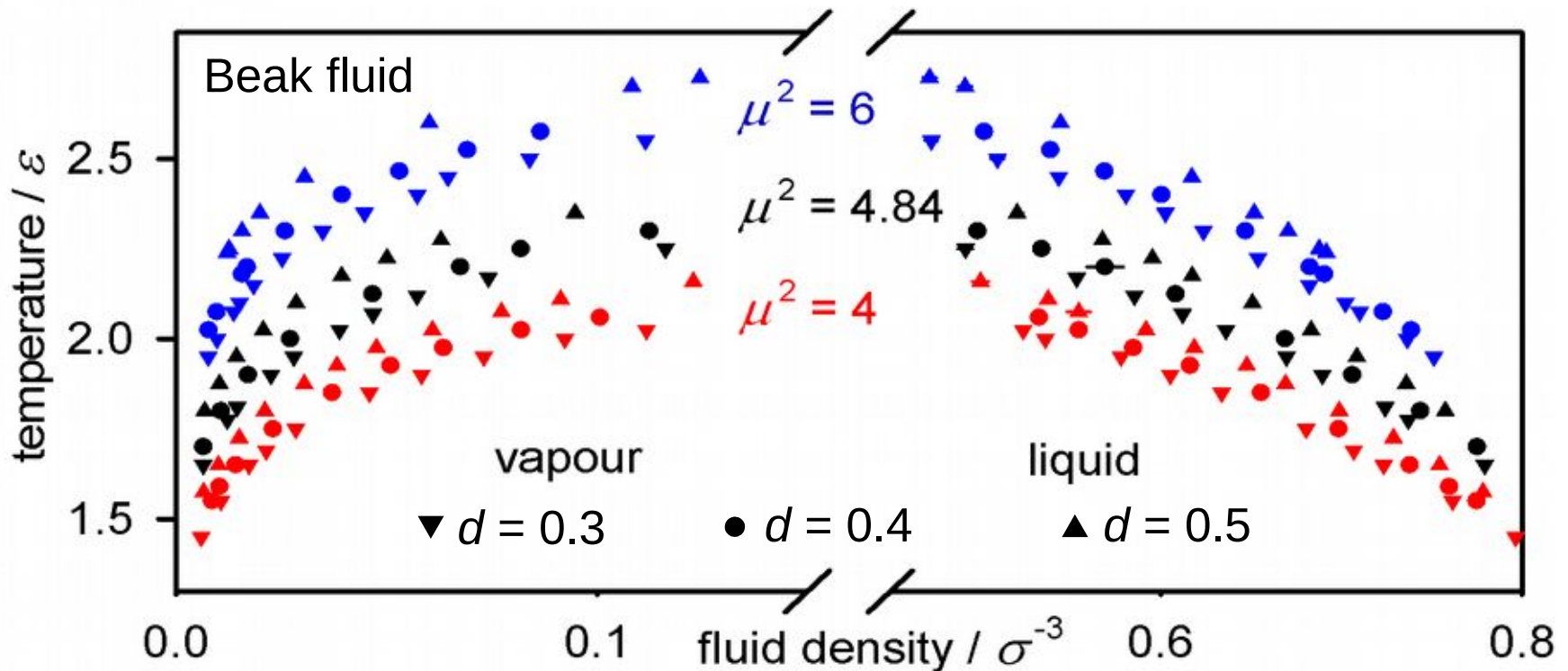


symmetric charges



As expected, hydrogen bonding depends significantly on the distance between the partial charges (and on the dipole) for both model classes.

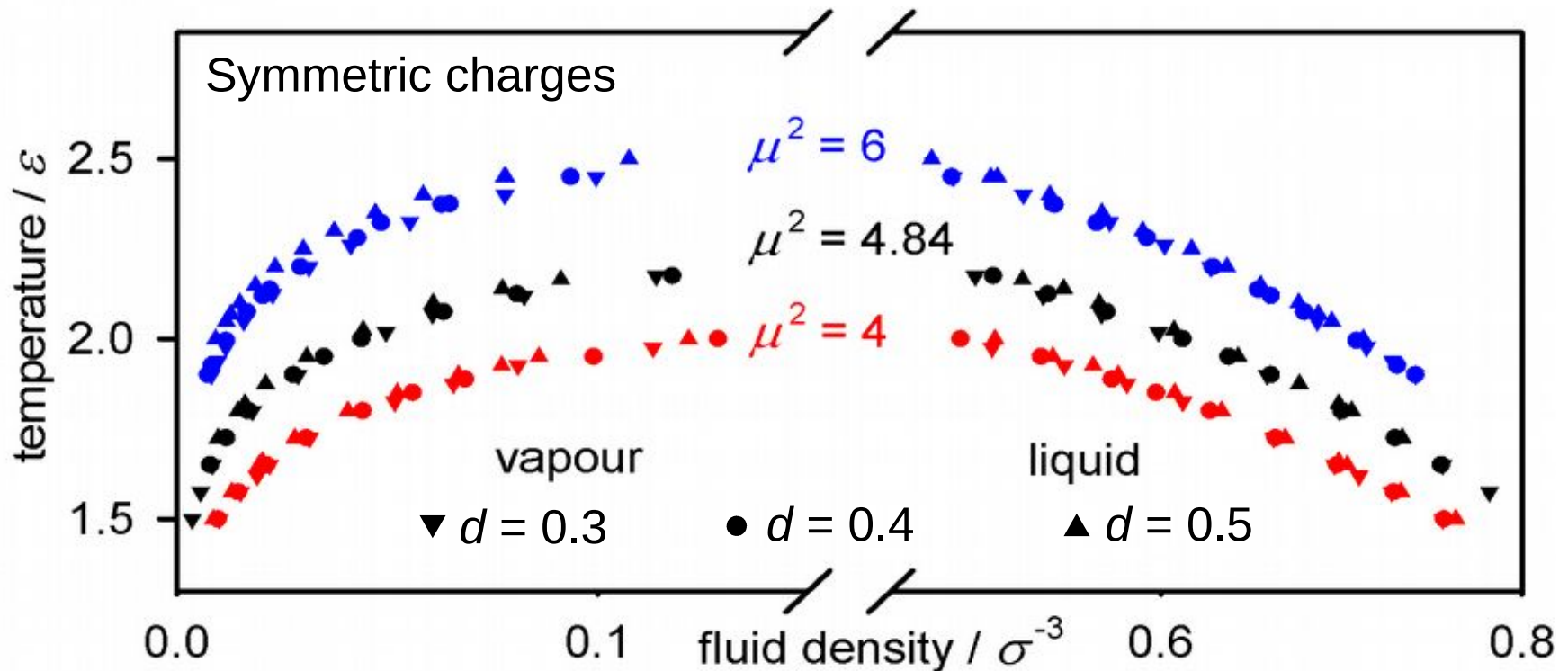
VLE of the asymmetric beak fluid



As desired, both the dipole strength μ^2 (\rightarrow polarity) and the elongation d (\rightarrow intensity of H bonding) influence the VLE behaviour.



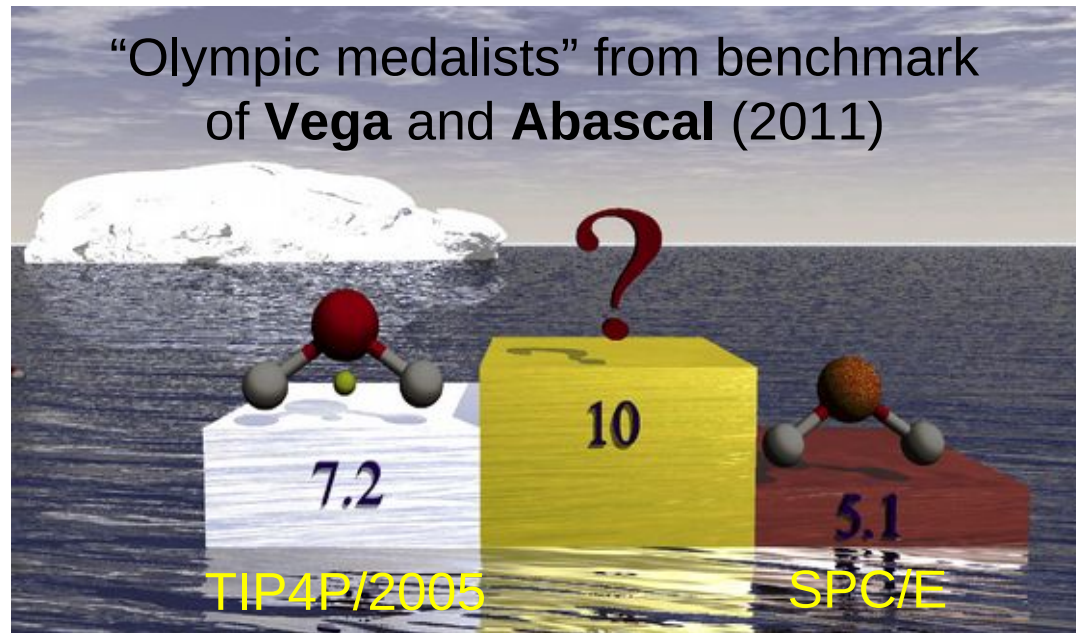
VLE of the model with preserved symmetry



The symmetric model does not capture the thermodynamics of hydrogen bonding: Phase behaviour is controlled by polarity only.

Classical molecular models of water

Water models following the simple beak approach (SPC, TIP3P, SPC/E) are quite popular. However, their overall reliability is relatively limited:

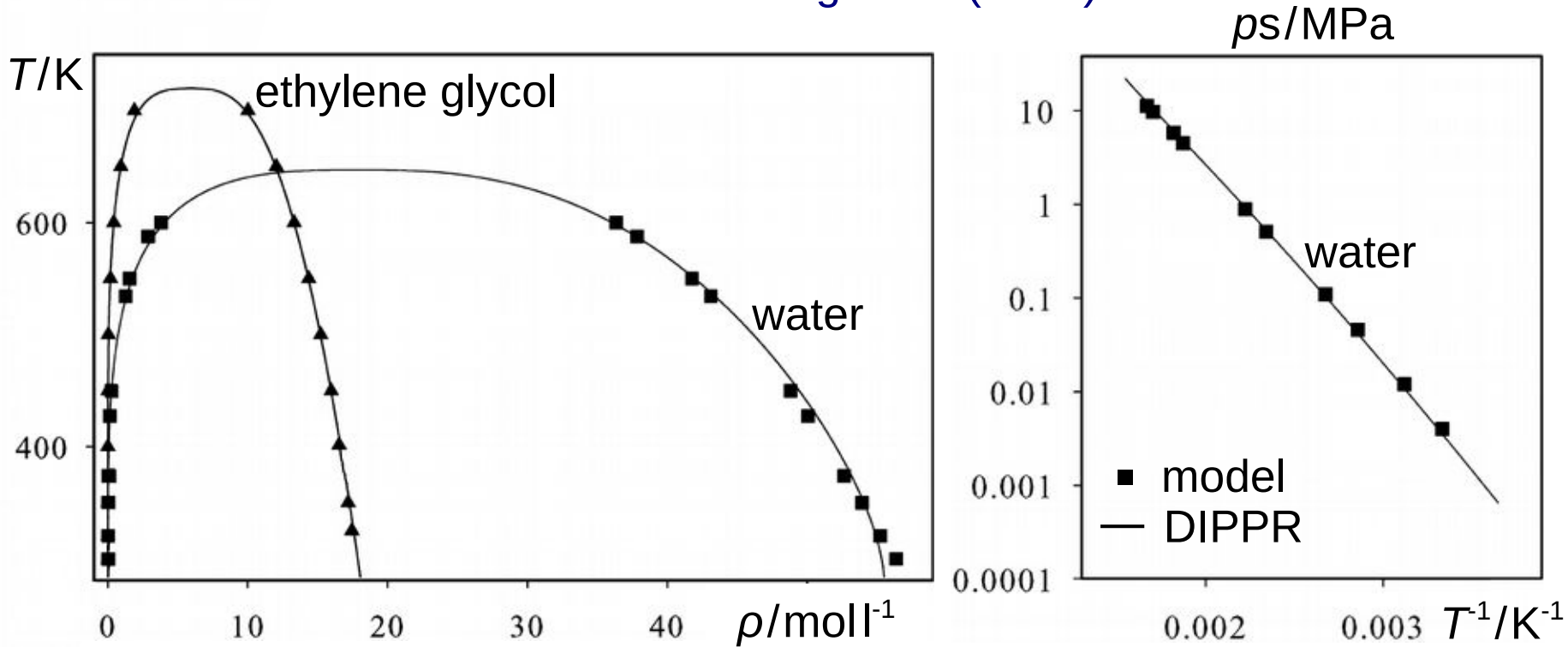


Vega and Abascal: “Neglecting **polarizability** prevents an accurate description of” pressure-related properties like $B(T)$, $p_s(T)$, and p_c .



Recent developments in modelling water

New TIP4P-like four-site model of Huang *et al.* (2012)



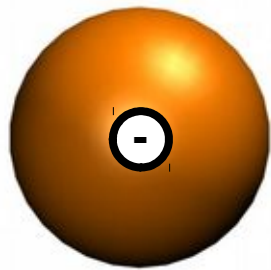
Nearly perfect agreement for critical properties, including p_c .

(However, comparably poor for the liquid density at low temperatures ...)

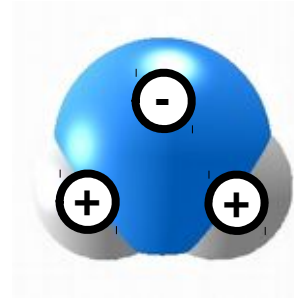


Modelling aqueous electrolyte solutions

Molecular models:



Ions
 1 CLJ
 1 point charge



Water
 1 CLJ
 3 partial charges

Literature models:

- Scattering of model parameters

Parameters for Na^+ :

$$1.9 < \sigma_{\text{Na}^+} / \text{\AA} < 4.1$$

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

Reference property:

- Density ρ

 Large deviation from experimental data!



Parameter optimization for alkali halides

Adjustable parameters:

- Ions: 1 CLJ with 1 point charge ($\pm 1e$): **2 parameters**

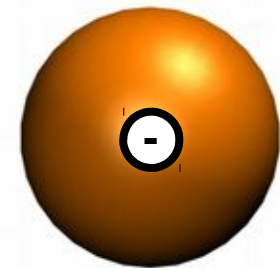
Target:

- Reduced density for varying salinity at $T = 293$ K, $p = 1$ bar

$$\rho^{\text{‰}} = \frac{\rho_{\text{solution}}}{\rho_{\text{pure solvent}}} = \rho^{\text{‰}}(\sigma_{\text{cat}}, \sigma_{\text{an}}, \epsilon_{\text{cat}}, \epsilon_{\text{an}}, X)$$

Simulation conditions:

- Monte Carlo simulations
- SPC/E water model
- Simulation code: extended version of *ms2*

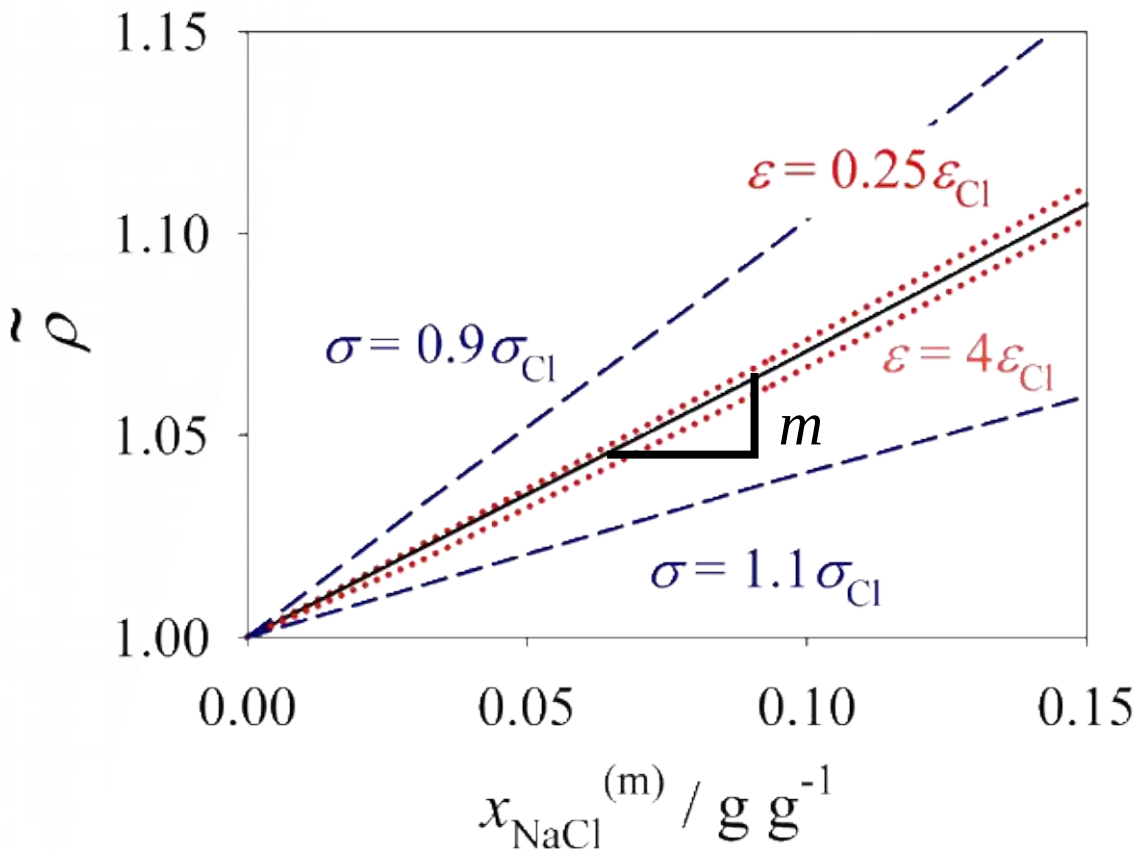


$\sigma_{\text{ion}}, \epsilon_{\text{ion}}$



Reduced density over salt concentration

Reduced density of NaCl solutions ($T = 298 \text{ K}$, $p = 1 \text{ bar}$)



Sensitivity study:

- σ_{ion} dominant
- ε_{ion} negligible

$$\rho^{\text{‰}} = \rho^{\text{‰}}(\sigma_{\text{cat}}, \sigma_{\text{an}}, x)$$

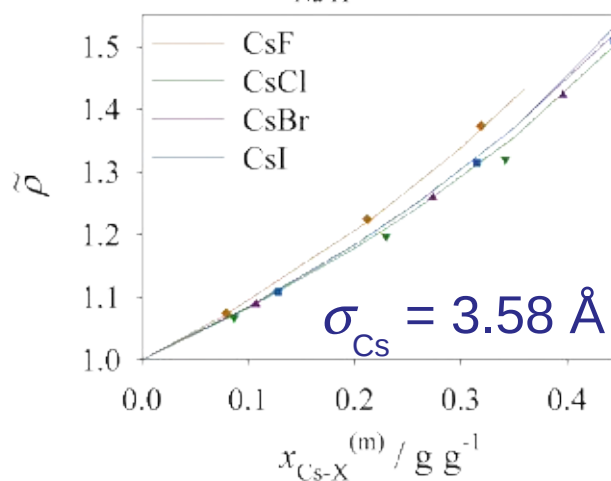
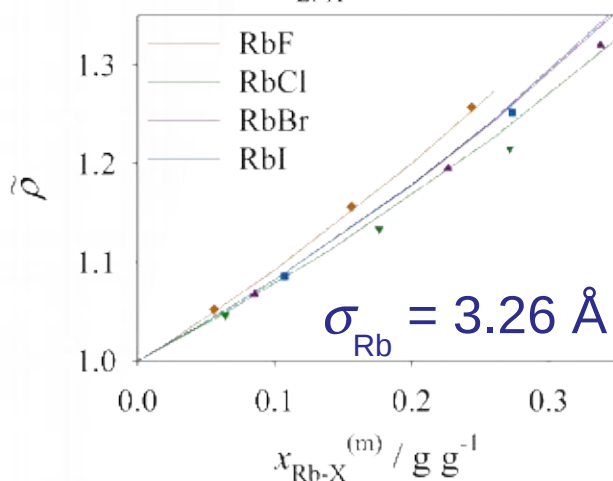
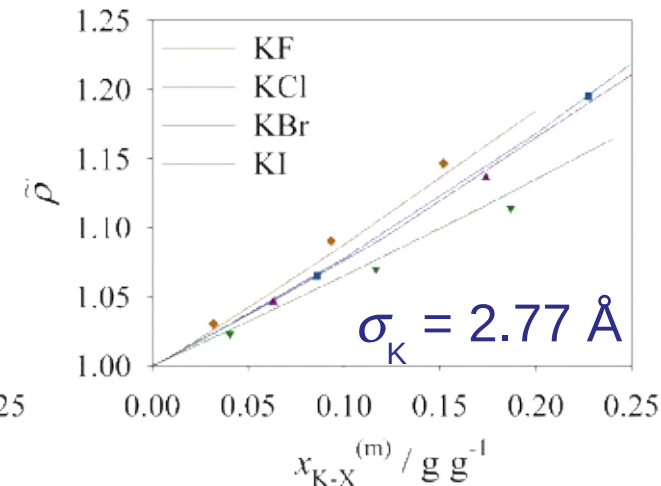
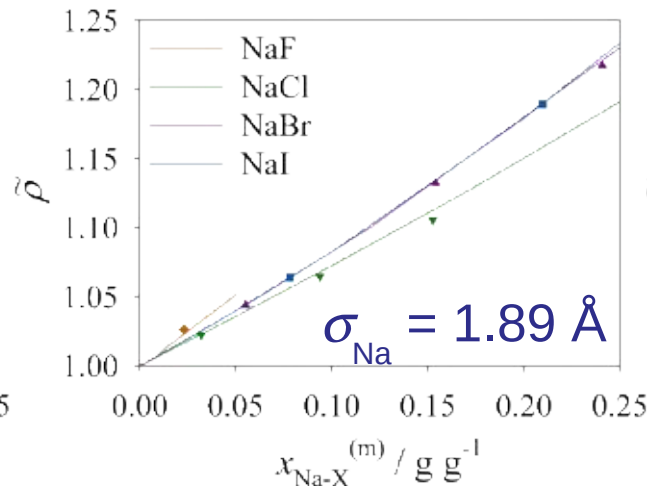
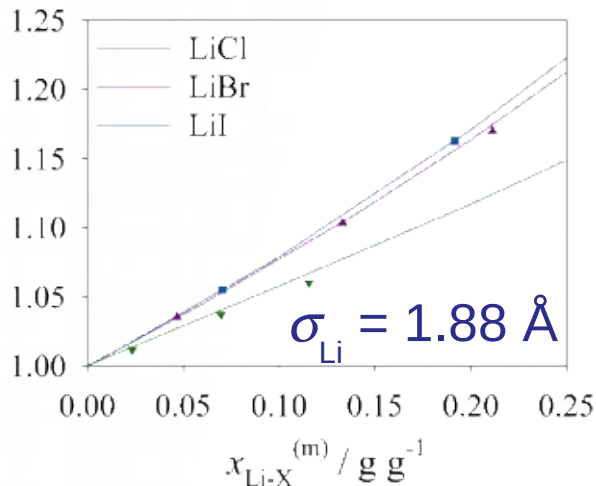
Adjustment:

$$m = \frac{d\rho^{\text{‰}}}{dx} = \frac{d\rho^{\text{‰}}}{dx}(\sigma_{\text{cat}}, \sigma_{\text{an}})$$



Aqueous electrolyte solutions: Overview

Reduced density ($T = 293 \text{ K}$, $p = 1 \text{ bar}$)



Anions

$\sigma_{\text{F}} = 3.66 \text{ \AA}$

$\sigma_{\text{Cl}} = 4.41 \text{ \AA}$

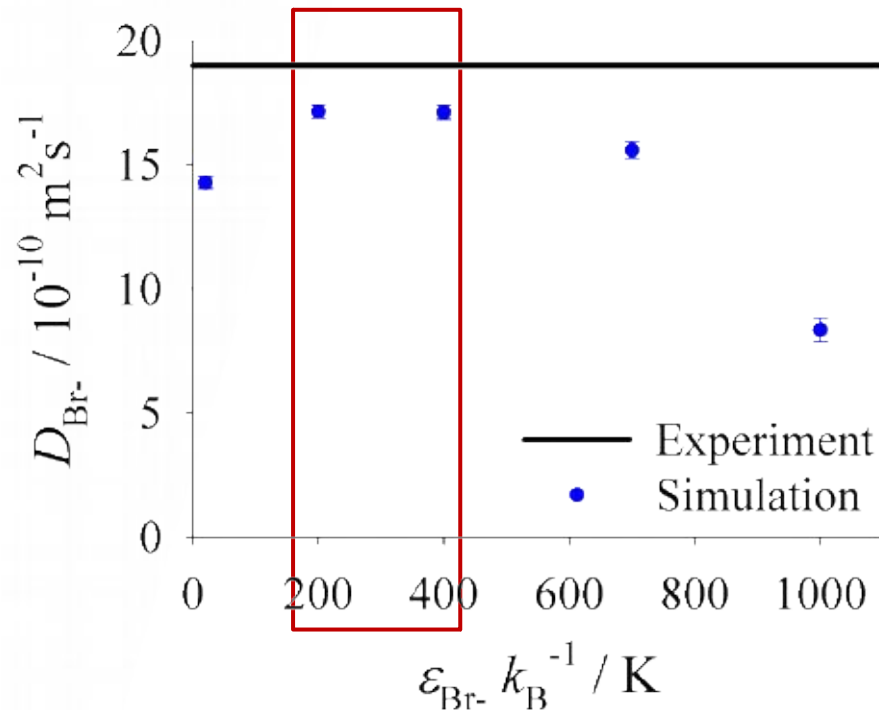
$\sigma_{\text{Br}} = 4.54 \text{ \AA}$

$\sigma_{\text{I}} = 4.78 \text{ \AA}$



Fine tuning of the molecular models

Adjustment of the LJ energy parameters ε_{ion} to the **self-diffusion coefficient** in solution ($T = 298 \text{ K}$, $p = 1 \text{ bar}$)

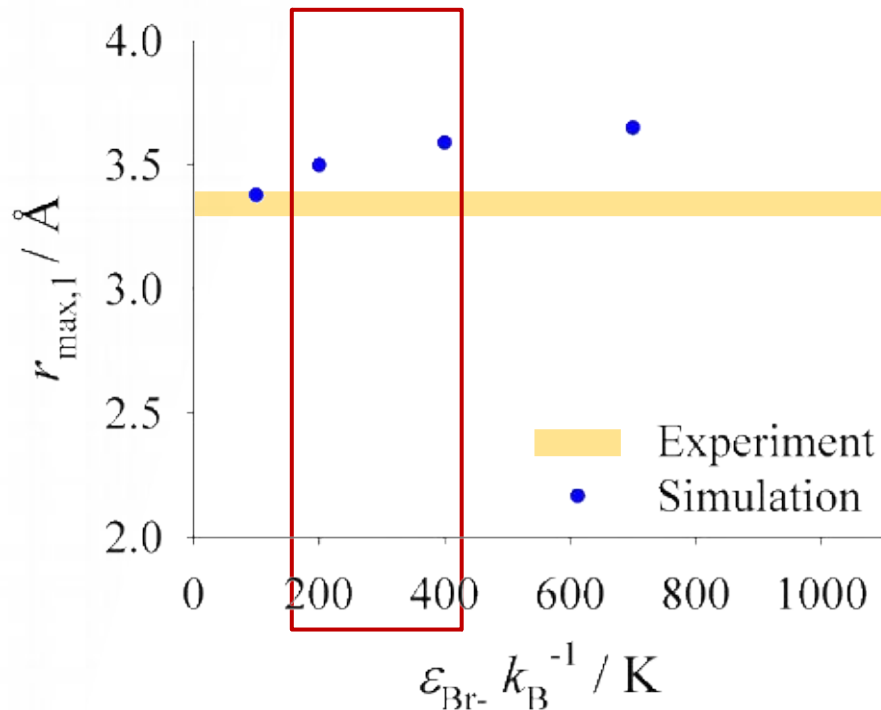


- Reasonable parameter range:
 $200 \text{ K} \leq \varepsilon_{\text{Br}^-} \leq 400 \text{ K}$
- Similar dependence of D_i on ε_i for all alkali and halide ions

(water model: SPC/E)

Fine tuning of the molecular models

Adjustment of the LJ energy parameters ϵ_{ion} to the first peak in the radial distribution function ($T = 293 \text{ K}$, $p = 1 \text{ bar}$)



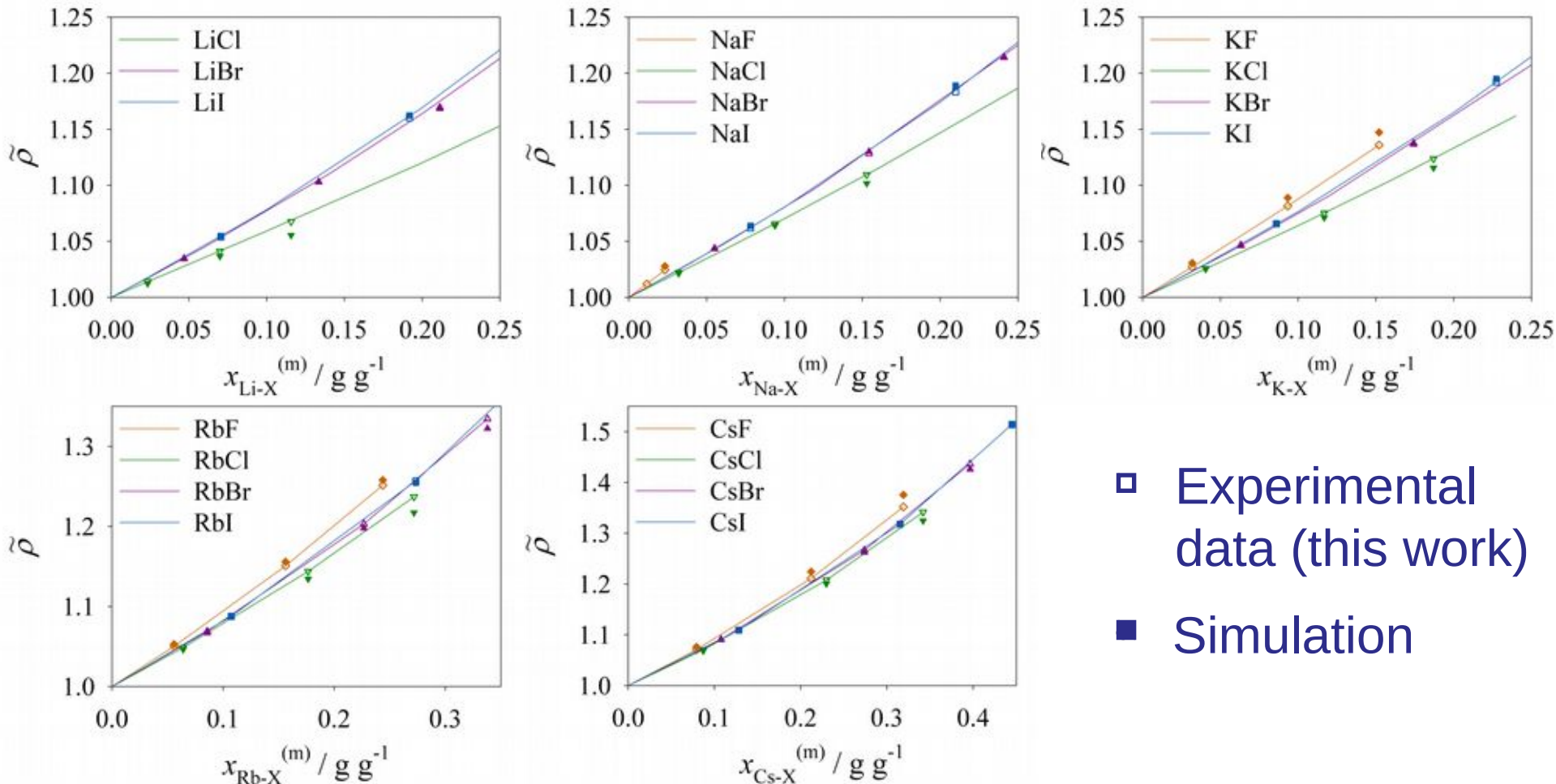
- Reasonable match:
 $\epsilon_{\text{Br}^-} = 200 \text{ K}$
- Final compromise:
 $\epsilon_{\text{cat}} = \epsilon_{\text{an}} = 200 \text{ K}$

(water model: SPC/E)



Temperature dependence of the density

Predictions for aqueous solution ($T = 333 \text{ K}$, $p = 1 \text{ bar}$)

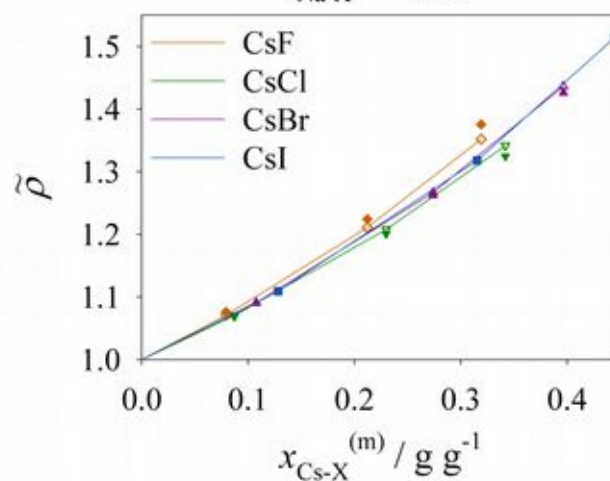
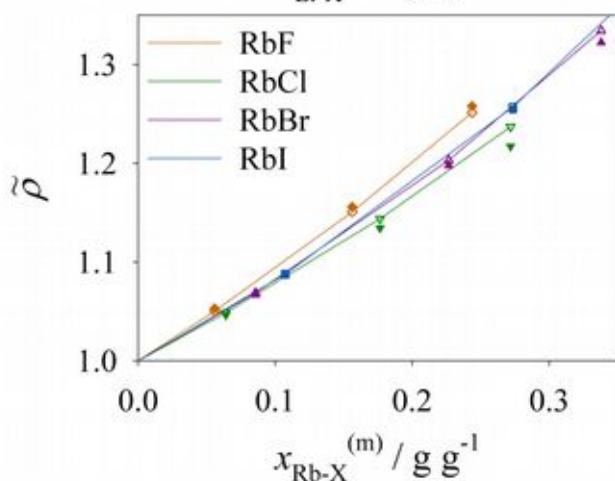
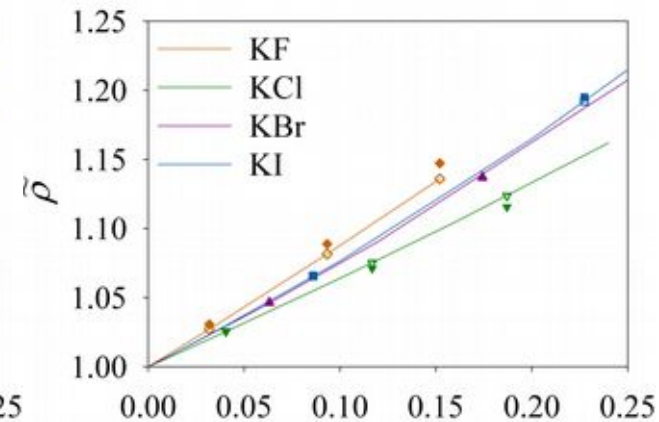
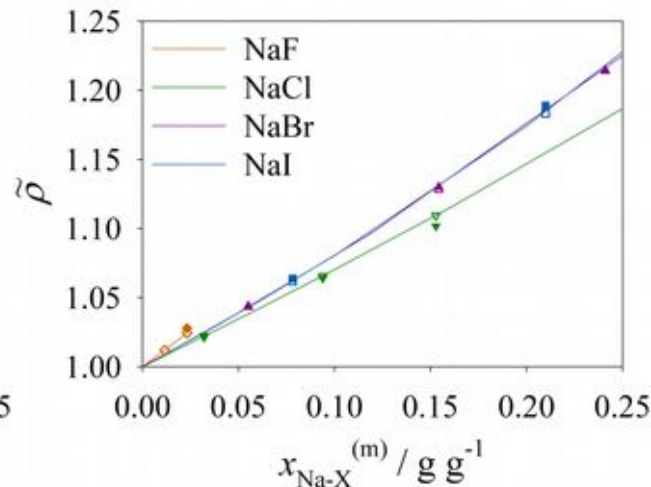
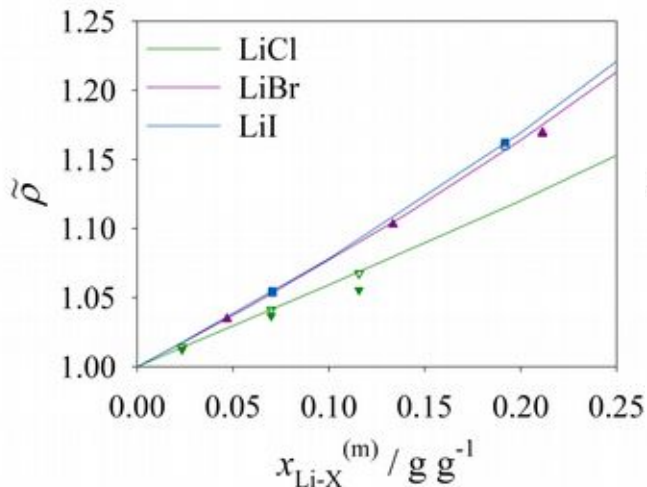


- Experimental data (this work)
- Simulation



Temperature dependence of the density

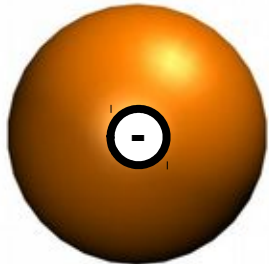
Predictions for aqueous solution ($T = 333 \text{ K}$, $p = 1 \text{ bar}$)



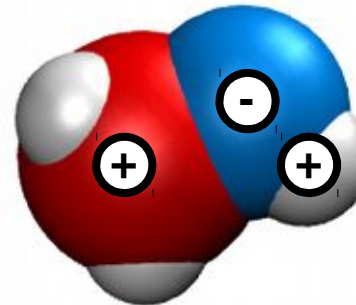


Non-aqueous electrolyte solutions (CH_3OH)

Molecular models:



Ions
 1 CLJ
 1 point charge



Methanol
 2 CLJ
 3 partial charges

Reference property:

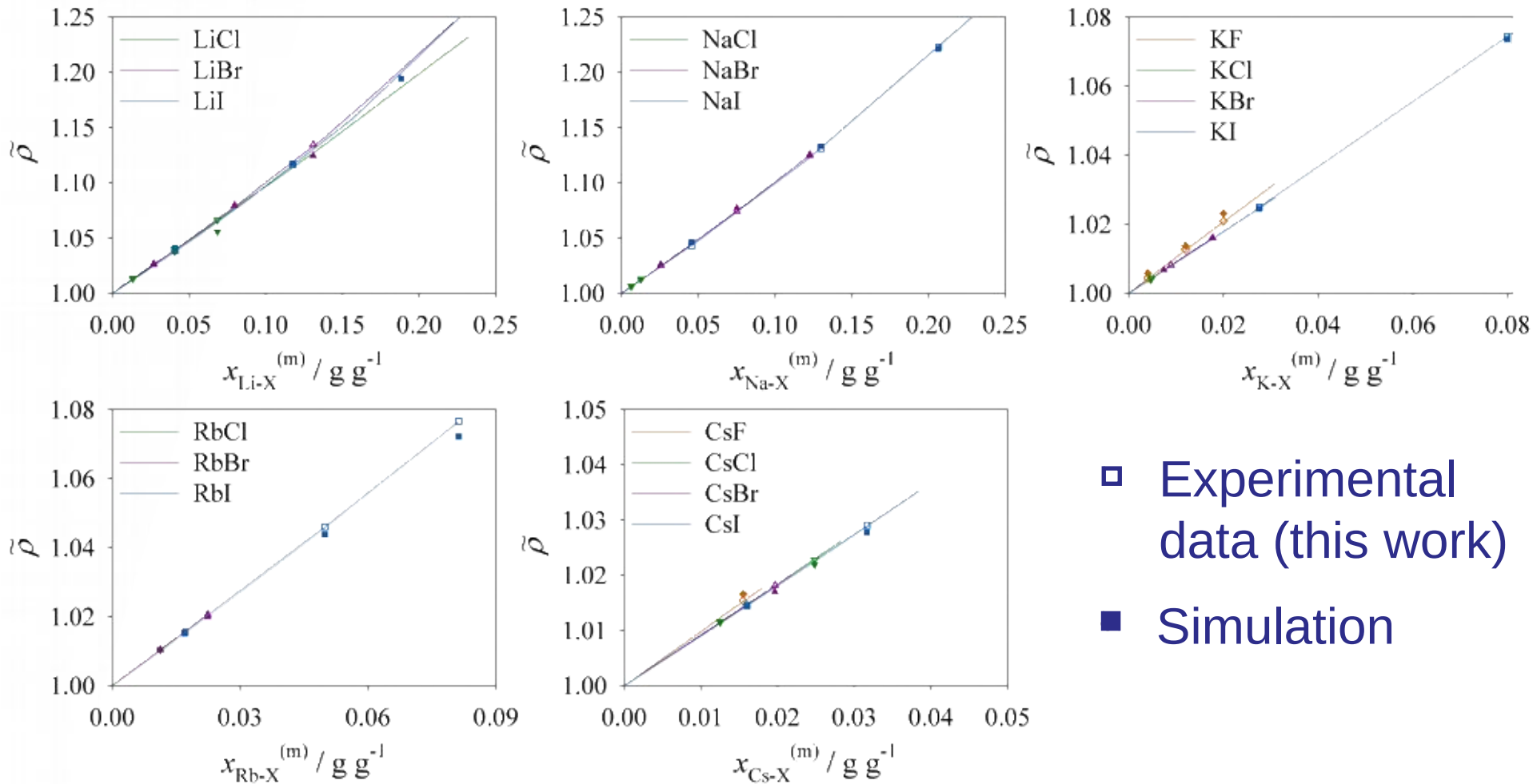
- Reduced density $\rho^{\text{‰}} = \frac{\rho_{\text{solution}}}{\rho_{\text{pure solvent}}}$

Simulation:

- MC simulations at $T = 298 \text{ K}$, $p = 1 \text{ bar}$

Methanolic electrolyte solutions

Predictions ($T = 298 \text{ K}$, $p = 1 \text{ bar}$)



- Experimental data (this work)
- Simulation



Conclusion

- Mechanical and thermodynamic routes lead to contradicting results for the curvature dependence of the **surface tension**. Present results for the **excess equimolar radius** confirm the thermodynamic route.
- The surface tension of the dispersed liquid phase is reduced due to a **curvature-independent effect** which is present in planar slabs as well as spherical droplets.
- By simulating the **beak fluid**, i.e. the OH group without a rest, it is shown that point charge models can adequately cover **polarity and hydrogen bonding** as related, but distinct effects.
- Molecular models were developed for **alkali and halide ions**, which were fitted to aqueous electrolyte solution properties and correctly predict properties of **non-aqueous solutions** as well.