SAFT γ-Mie Coarse-Grained Forcefield for the Simulation of Anionic Surfactants: Phase Behaviour

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Parameterisation of a Forcefield Using an Equation of State

► SAFT γ-Mie models the free energy based on molecular structure as function of composition, volume and temperature[1].

$$\Phi_{\text{Mie}} \propto \varepsilon[(\sigma/r)^{\lambda_r} - (\sigma/r)^{\lambda_a}]$$
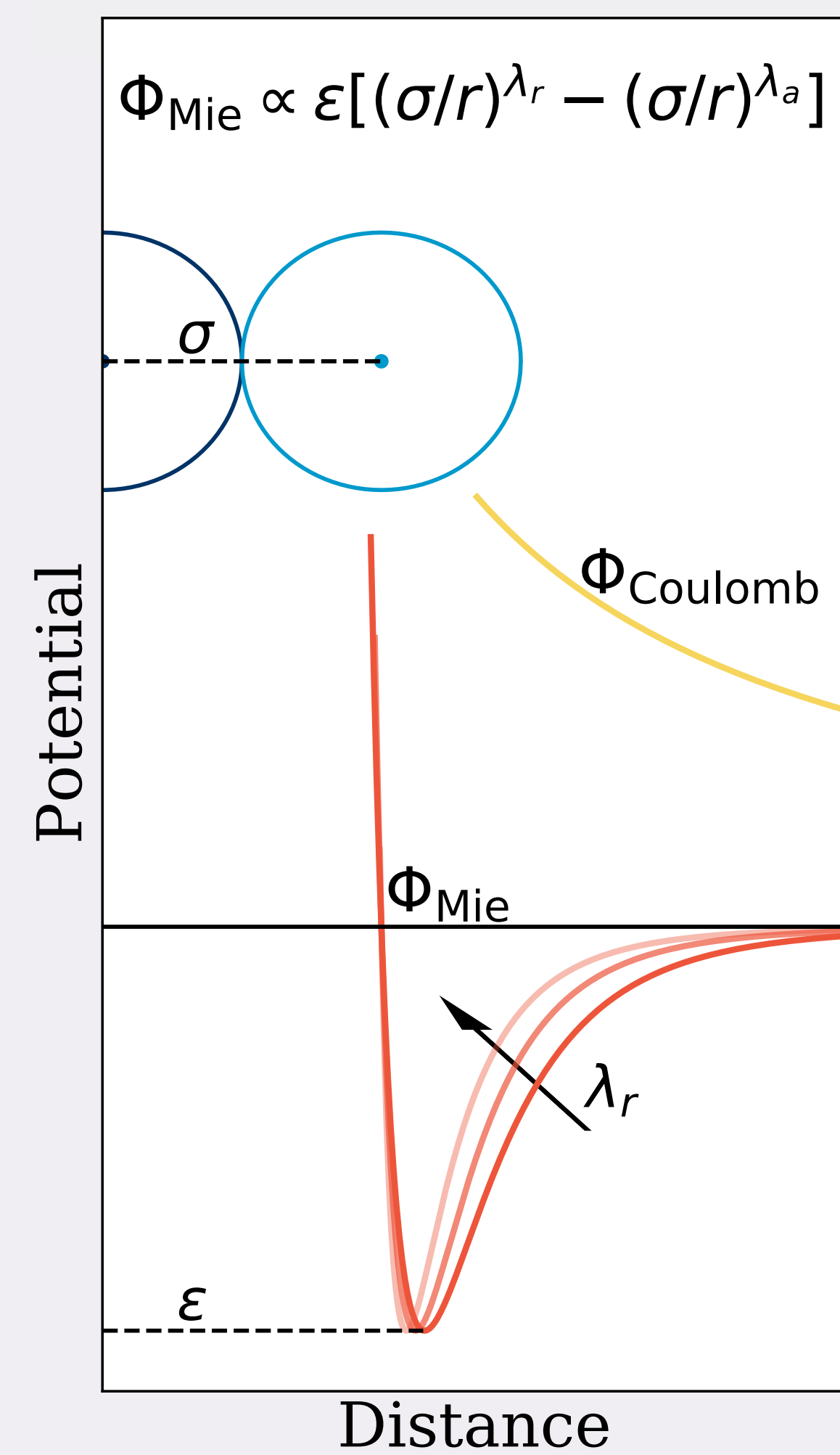
► Multiple atoms can be included into a single group — interacting via an effective potential.

► The group contribution approach honours chemical specificity resulting in transferable groups.

► Free energy contributions from charge interactions are treated with an MSA.

► Charged groups are solvated in a dielectric medium via the Born solvation process[2].

► Repulsion and dispersion interactions are treated with a high temperature expansion.

► Any thermodynamic property is accessible via simple derivatives:

$$\frac{\partial A\left(T, V, \text{N}, \epsilon, \sigma, \sigma_{\text{Born}}, \lambda_{\text{r}}, \epsilon_r\right)}{\partial N_i}\bigg|_{T,V,\text{N}_{j\neq i}} = \mu_i$$

► The interaction parameters between groups are varied to minimise the following function:

$$f = \left(X_{\text{Exp}} - X_{\text{SAFT}}(\epsilon, \sigma, \lambda_{\text{r}})\right)^2$$

► The fast evaluation of the objective function enables us to scan a wide parameter space.

Sodium Dodecyl Sulfate

► HSO$_4$- is used as head group along with alkane beads[6] to model SDS.

► Bonded interaction are parameterised via bottom-up approaches.

► Pre-assembled micelles in NaCl solution show first promising results:
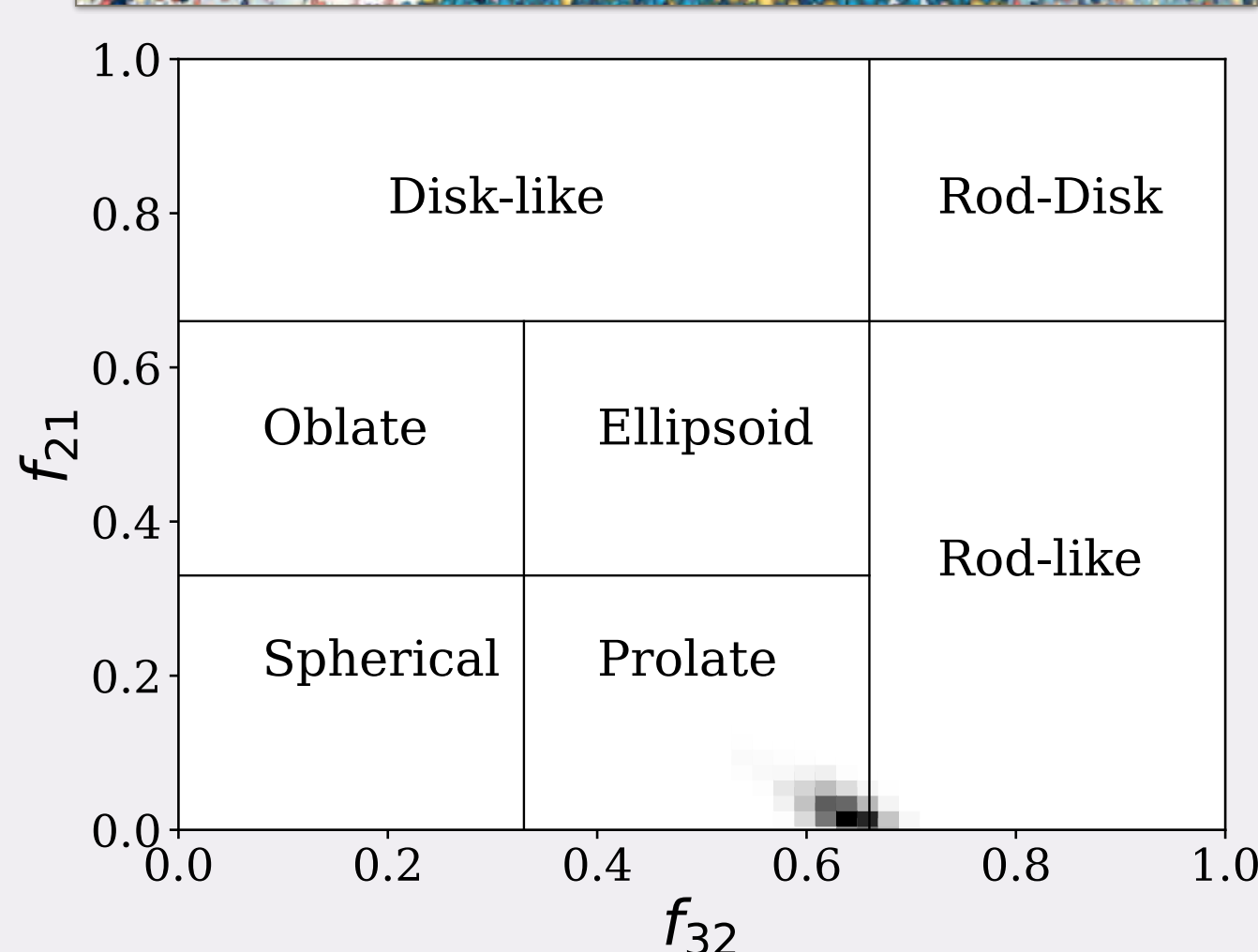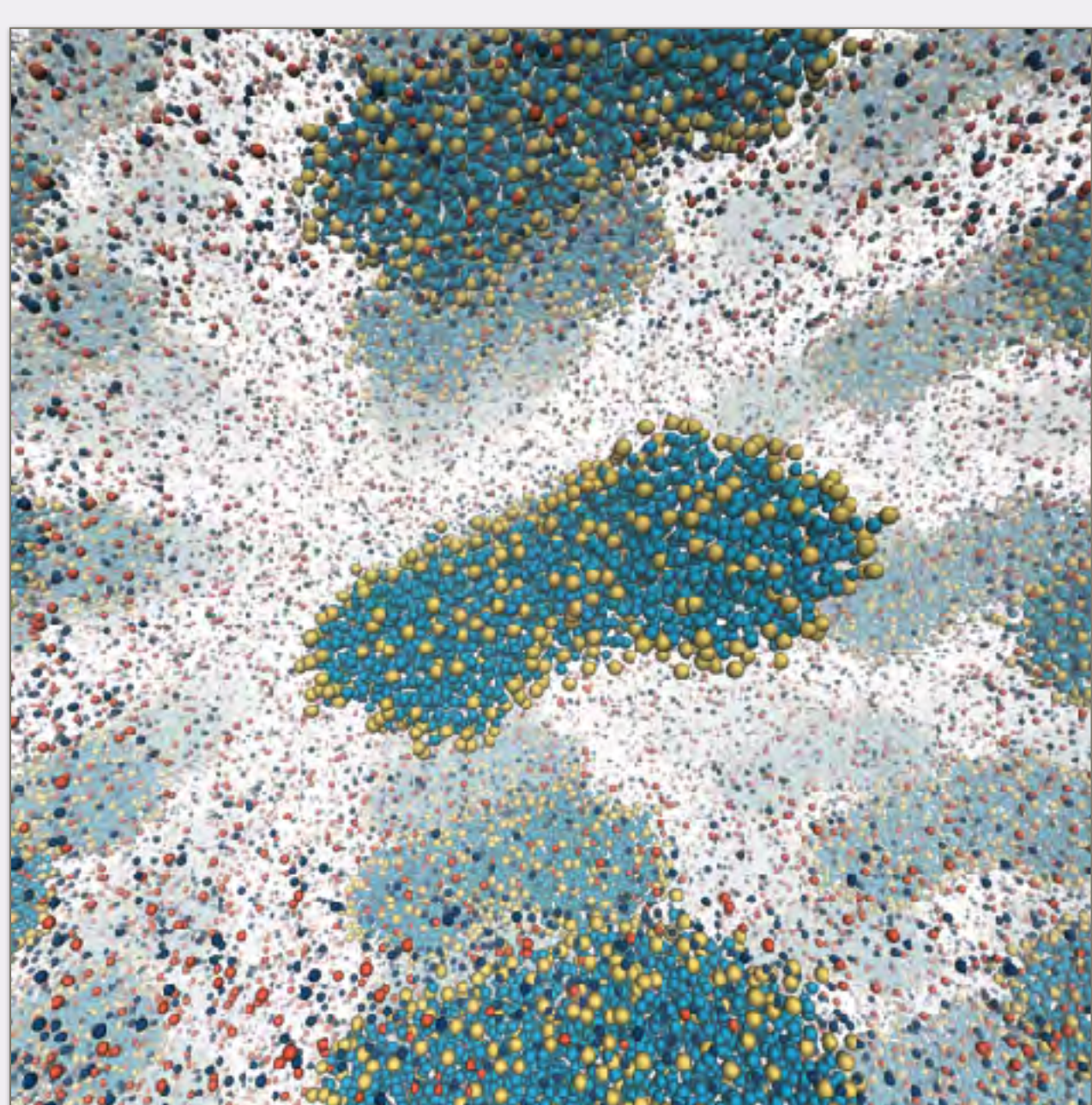
Adopted from: David J. Bray Bray, Annalaura Del Regno and Richard L. Anderson, Molecular Simulation, 46:4, 308-322 (2020).

A Model for Strong Electrolytes

► Ions (e.g. Na+, HSO$_4$-) are modelled as point charges + Mie soft cores, water as Mie segment[3].

► Literature values are assigned to $\sigma, \epsilon_{\text{self}}, \lambda_{\text{a/r}}, \sigma_{\text{Born}}$[4].

► Charge — charge interactions are screened via a dielectric constant correlation for water.

► Central point for optimisation is the Mie interaction strength between water and the ions.

► Osmotic coefficients for a range of alkali metal halide salts are fitted simultaneously.

► Simulation of the osmotic pressure[5] and density confirms the applicability for various salts at low to high molalities and temperatures between 25 and 60 °C.
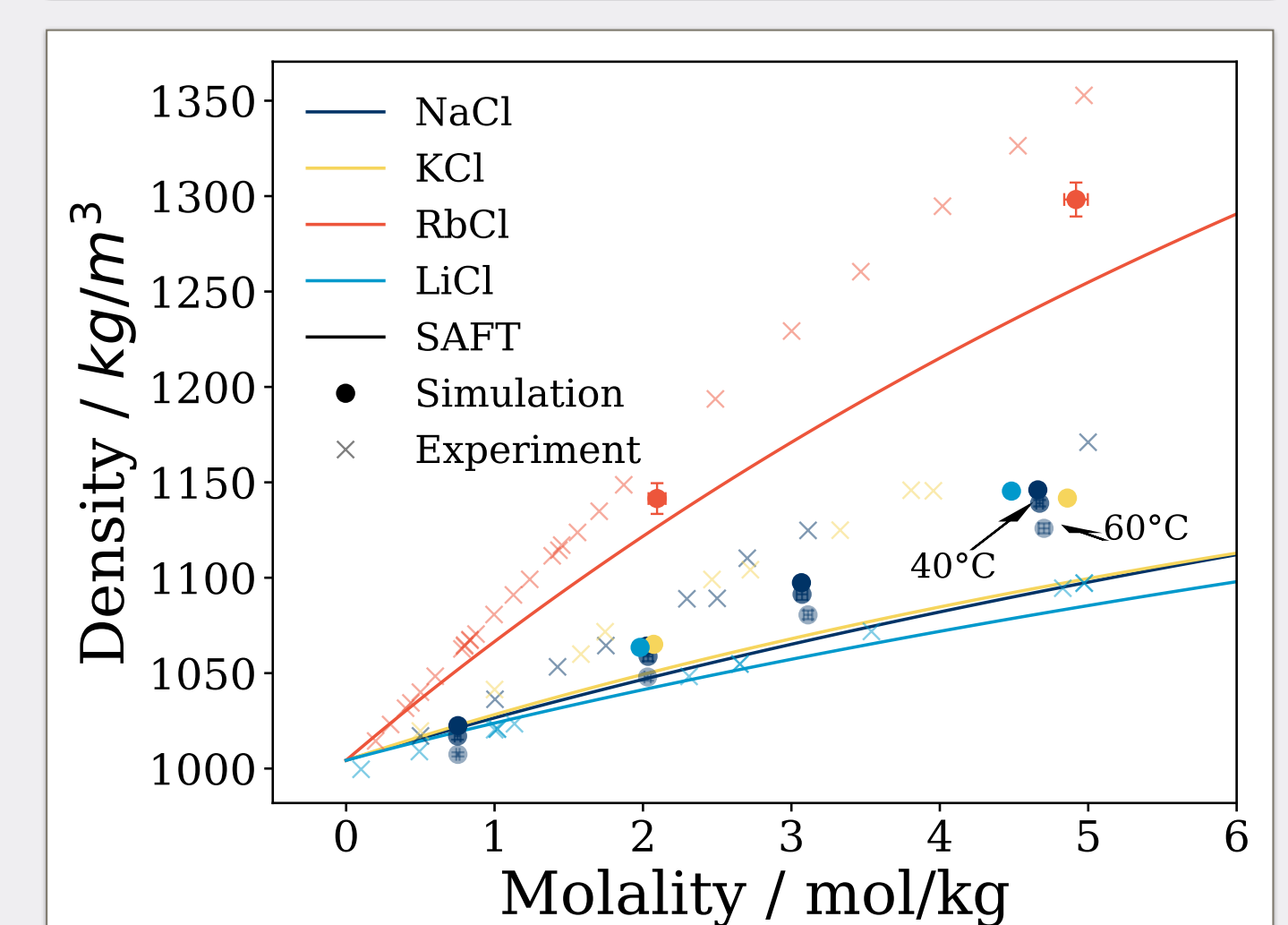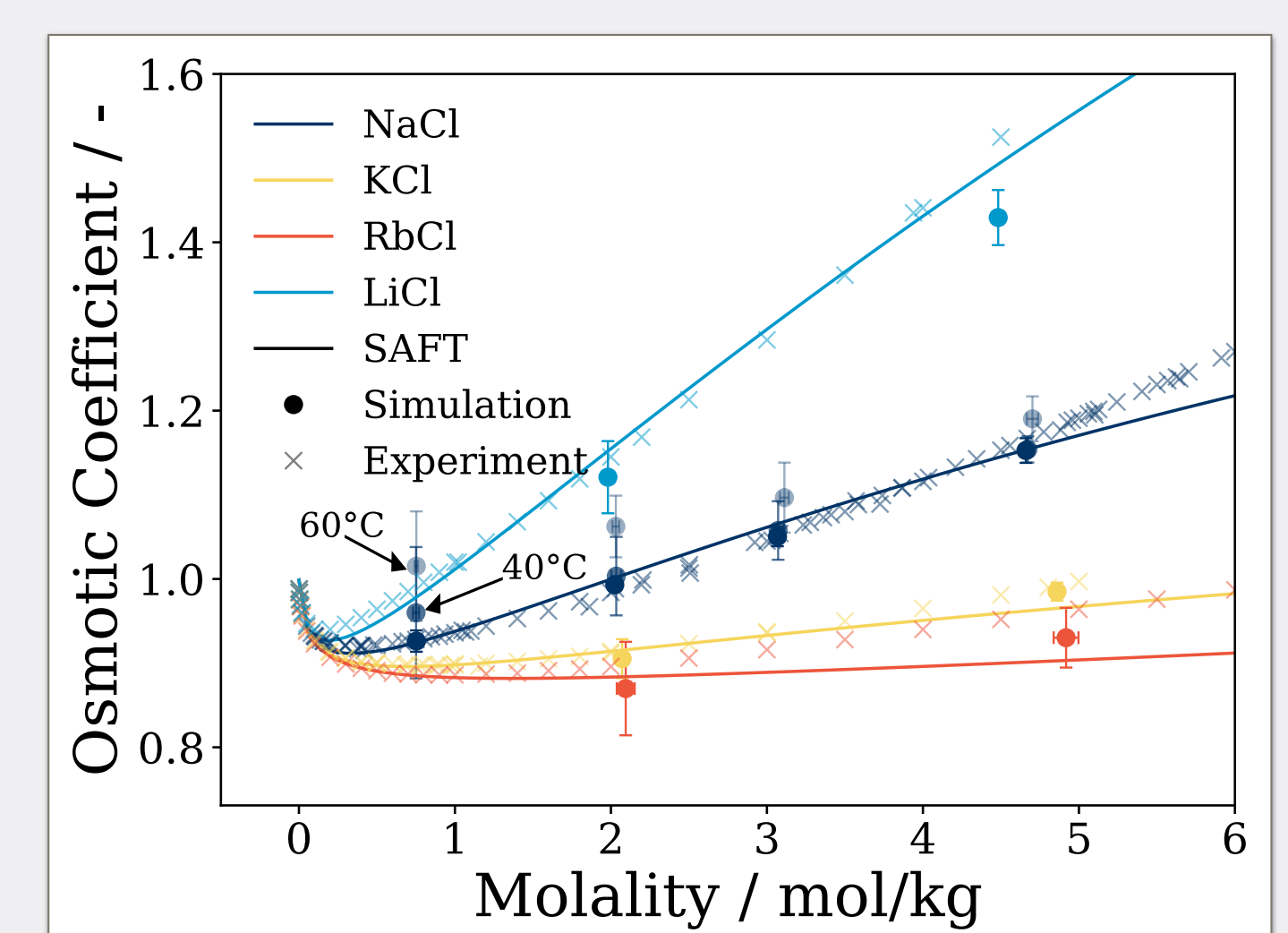
Conclusion, Future Work and Challenges

► The SAFT γ-Mie coarse graining workflow was successfully extended to strong electrolytes.

► The osmotic coefficient as measure of the solvent activity has been proven to be a suitable target property for charged species.

► Additional head groups need to be parameterised, tested and compared to experimental data of surfactants.

► Artefacts due to non-polar water and implicit screening pose a challenge for simulation of larger aggregates.

References:
1. Papaioannou *et al.*, J. Chem. Phys. 140, 054107 (2014).
2. Rashin and Honig, J. Phys. Chem. 89, 5588-5593 (1985).
3. Lobanova *et al.*, Mol. Phys., 113:9-10, 1228-1249 (2015).
4. Eriksen *et al.*, Mol. Phys., 114:18, 2724-2749 (2016).
5. Kohns *et al.*, J. Chem. Phys. 144, 084112 (2016).
6. Rahman *et al.*, J. Phys. Chem. B 122, 9161-9177 (2018).