

1. Motivation

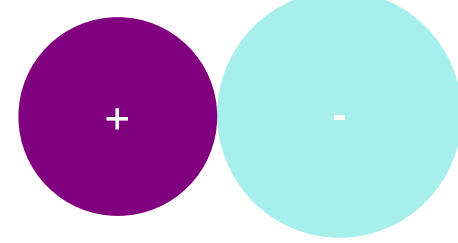
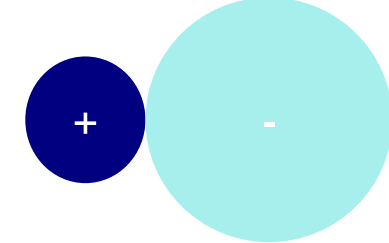
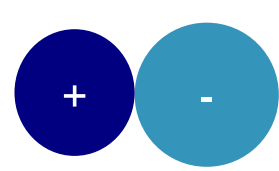
• Studying mixed electrolytes is important for applications in batteries, desalination, CO₂ sequestration, etc.

• Collins: Law of Matching Water Affinities [1]

• Upon ion pairing, ion-water interactions are broken while ion-ion interactions and new water-water interactions are formed.

Kosmotrope: Small, charge dense, high water affinity

Chaotrope: Large, charge diffuse, low water affinity



Kosmotrope-Kosmotrope: Ion pairing favoured due to strong ion-ion interaction

Kosmotrope-Chaotrope: Ion pairing disfavoured due to strong ion-water interactions

Chaotrope-Chaotrope: Ion pairing favoured due to strong water-water interactions

• Extension of model to mixed electrolytes not previously investigated.

• Challenges:

Classical Force Fields do not offer adequate accuracy and require extensive parametrisation for mixed systems.

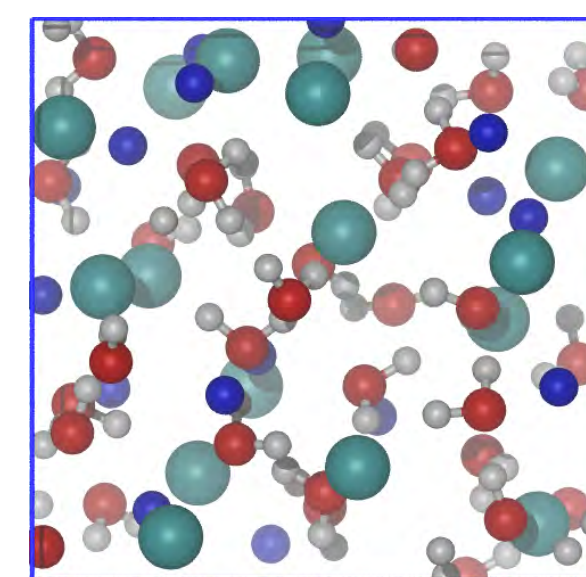
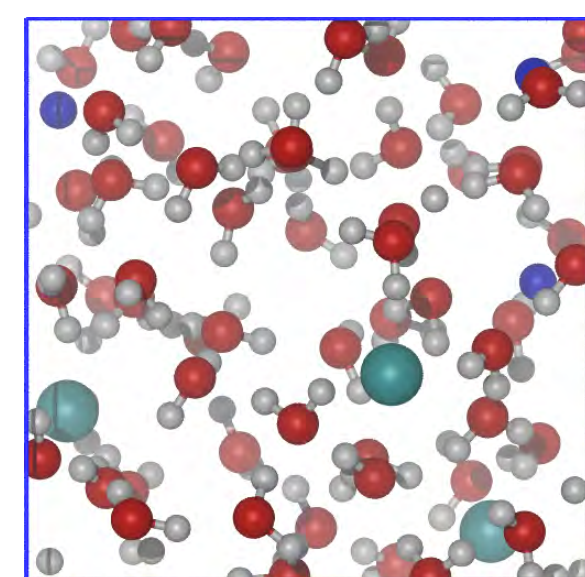
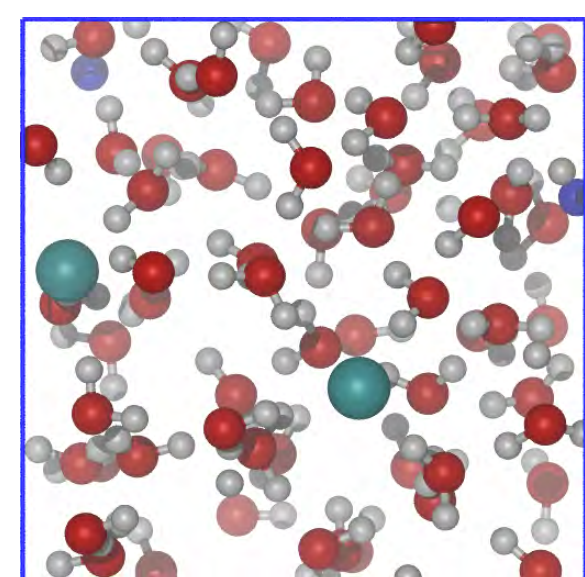
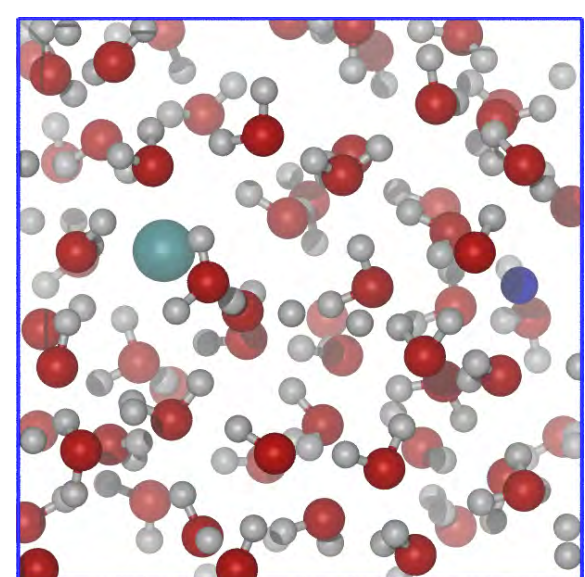
Ab initio Molecular Dynamics is far too computationally expensive.

2. Methods

Solution: Machine Learning Potentials (MLPs) combine accuracy of *ab initio* methods with superior computational efficiency

Training

Compositions used to train model (M = Li, Na, K)



62:1 Water: MCl

60:2 Water: MCl

58:3 Water: MCl

32:16 Water: MCl

Structures of aqueous electrolyte solutions

Simulations of systems using newly trained MLP

Density Functional Theory (DFT) calculations as model input

MLP reproducing DFT potential energy surface

• MACE-MP-0 used as foundation model, subsequently fine-tuned with DFT data (revPBE-D3) [2].

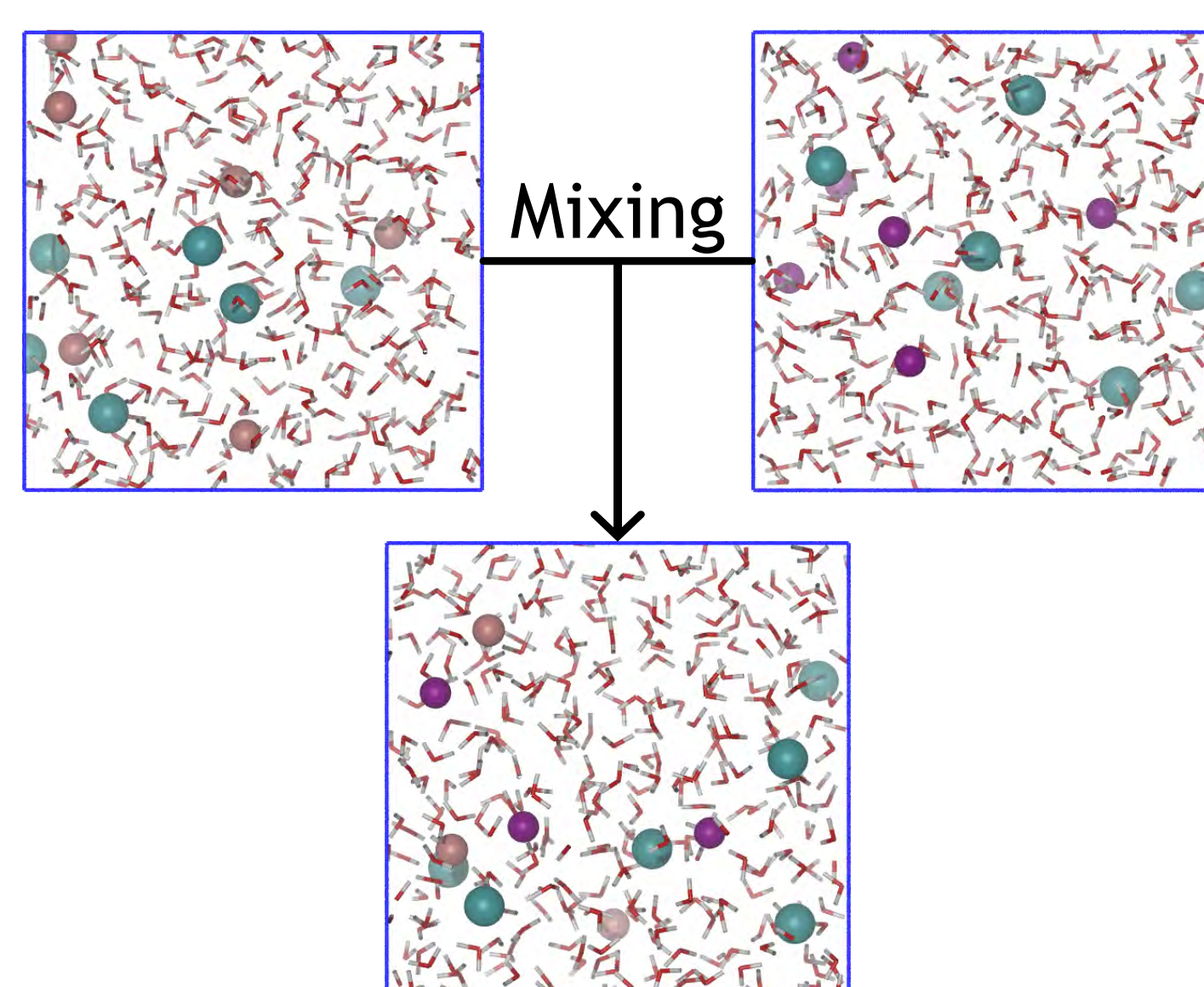
• Simulations carried out in NpT ensemble.

• Simulation pressure: 1 bar

• Simulation temperature: 300 K

Simulations

NpT simulations of larger simulation unit cells (332 water molecules, 6 ion pairs, 1 M) were carried out using the fine-tuned model.



Unmixed LiCl, NaCl and KCl 1 M solutions as well as 50:50 mixtures of the above were simulated.

3. Results

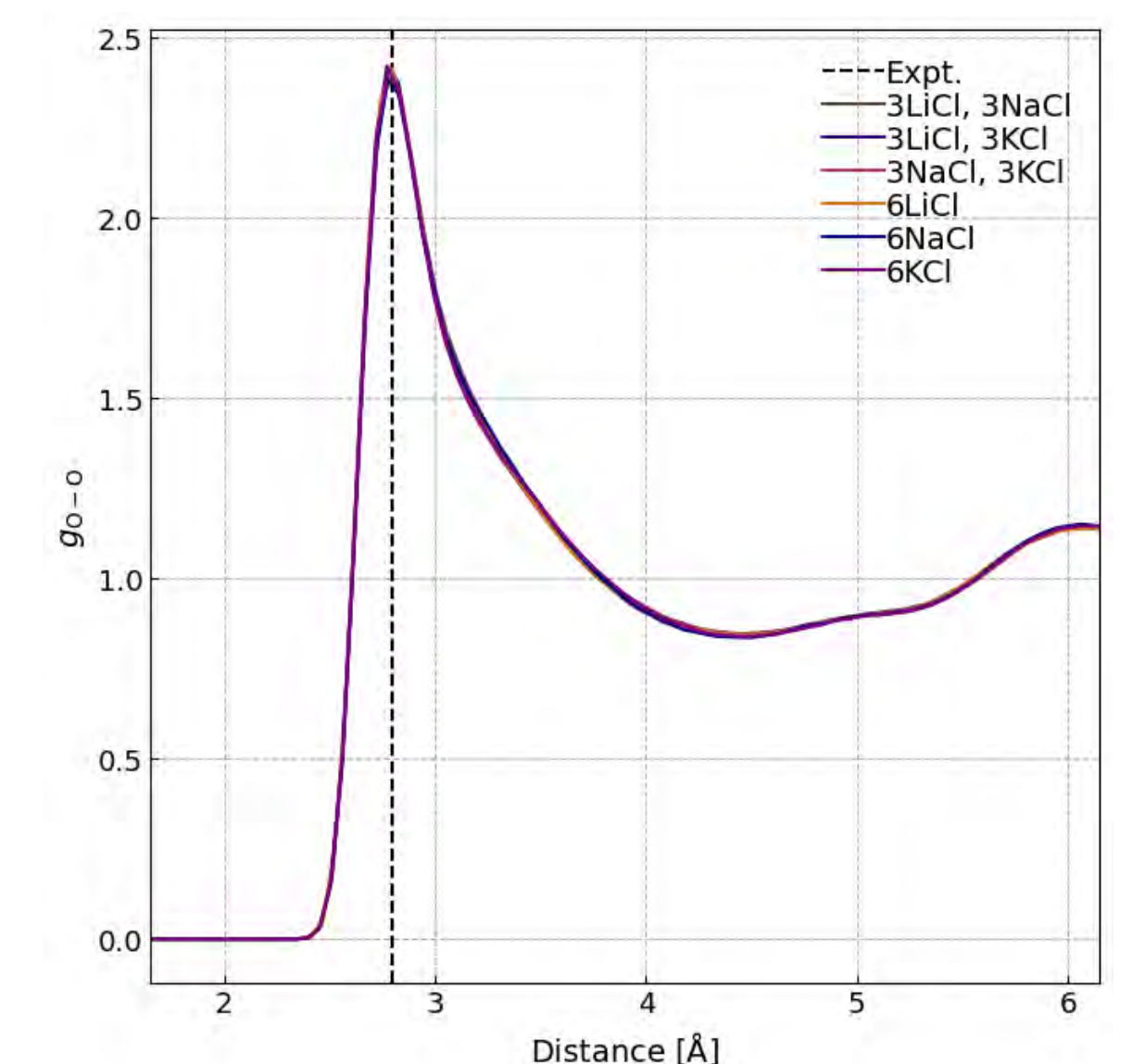
How well does our model do?

	Energy RMSE (meV/atom)	Force RMSE (meV/Å)
Mixed Compositions	0.59	31.2
Unmixed Compositions	0.52	30.5

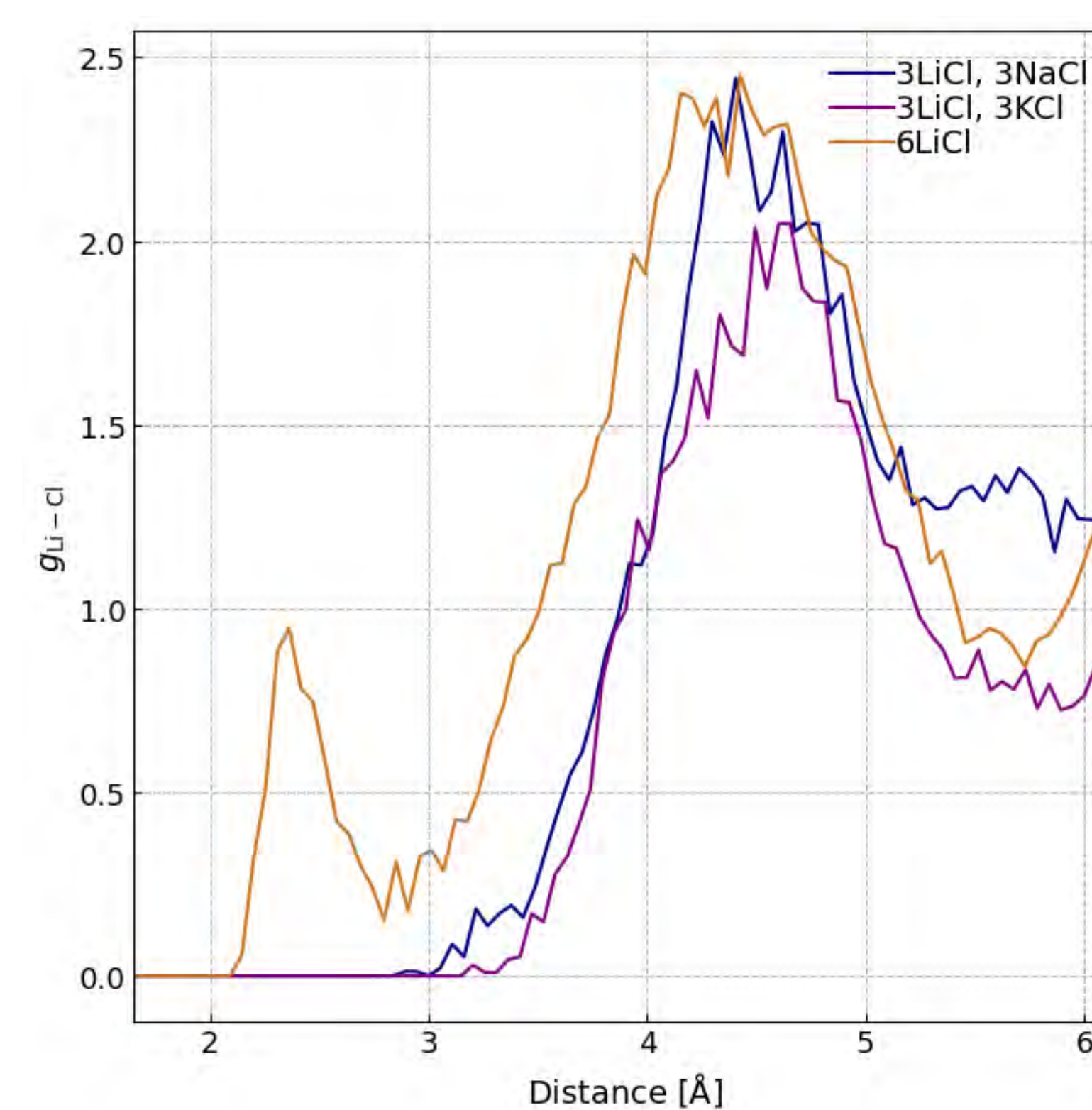
The model performs very well in describing the energies and forces of our systems, with the relevant errors being quite low.

Similar errors for both mixed and unmixed compositions despite only fine-tuning on simple electrolytes.

The bulk water structure as determined by experiment is accurately reproduced by our model [3].



Insights into ion pairing



Is ion pairing for a given ion the same in mixed solutions as that in simple solutions?

The radial distribution functions (RDFs) for Li⁺ and Cl⁻ are shown in the plot on the left for the following compositions:

- 1 M LiCl (yellow)
- 0.5 M LiCl, 0.5 M NaCl (navy)
- 0.5 M LiCl, 0.5 M KCl (purple)

K⁺ and Na⁺ known to be more chaotropic than Li⁺ and exhibit similar water affinities to Cl⁻ [1]. As such, these ions are expected to preferentially form ion pairs with Cl⁻.

Disappearance of peak between 2 and 3 Å indicates *no contact ion pair formation* between Li⁺ and Cl⁻ - consistent with Collins' theory.

Warning!



• RDFs are not converged: greater simulation times are required to reduce errors.

• Simulations exhibit unusually high densities: Likely an issue with barostat sensitivity.

4. Conclusions

• A machine learning potential for mixed aqueous electrolytes involving Li⁺, Na⁺, K⁺ and Cl⁻ was developed.

• Ion pairing exhibits non-additive behaviour consistent with Collins' Law of Matching Water Affinities.

5. References

[1] Collins, K. D. Charge Density-Dependent Strength of Hydration and Biological Structure. *Biophys. J.* **1997**, *72*, 65–76.

[2] Batatia, I. et al. A foundation model for atomistic materials chemistry. *ArXiv*, 2024, 2401.0096; <https://arxiv.org/abs/2401.0096>.

[3] Bouazizi, S.; Nasr, S. Local Order in Aqueous Lithium Chloride Solutions as Studied by X-ray Scattering and Molecular Dynamics Simulations. *J. Mol. Struct.* **2007**, *837*, 206–213.