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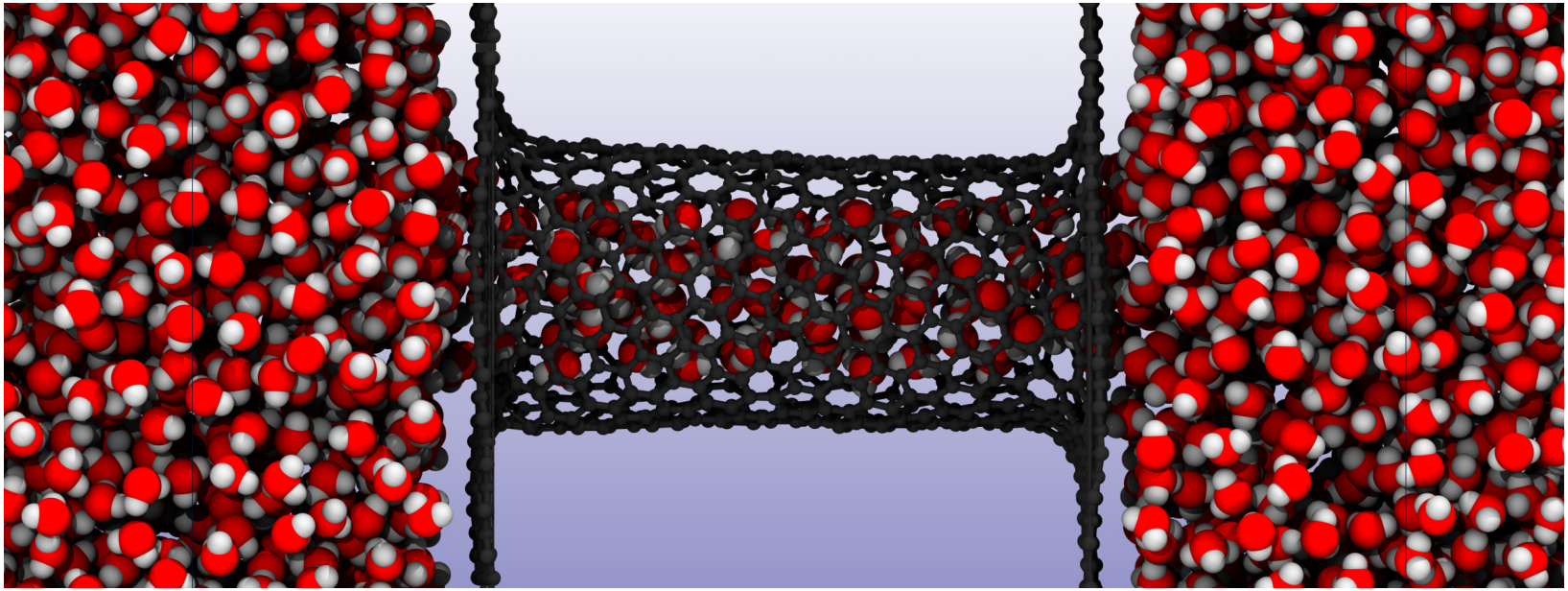
Committee neural network potentials control generalization errors and enable active learning

Christoph Schran | University of Cambridge | Jun 23, 2022

Water in Complex Environments

Interfacial Water and Water under Confinement



Relevance

- Nano filtration[1]
- Osmotic energy conversion[2]
- Desalination[3]

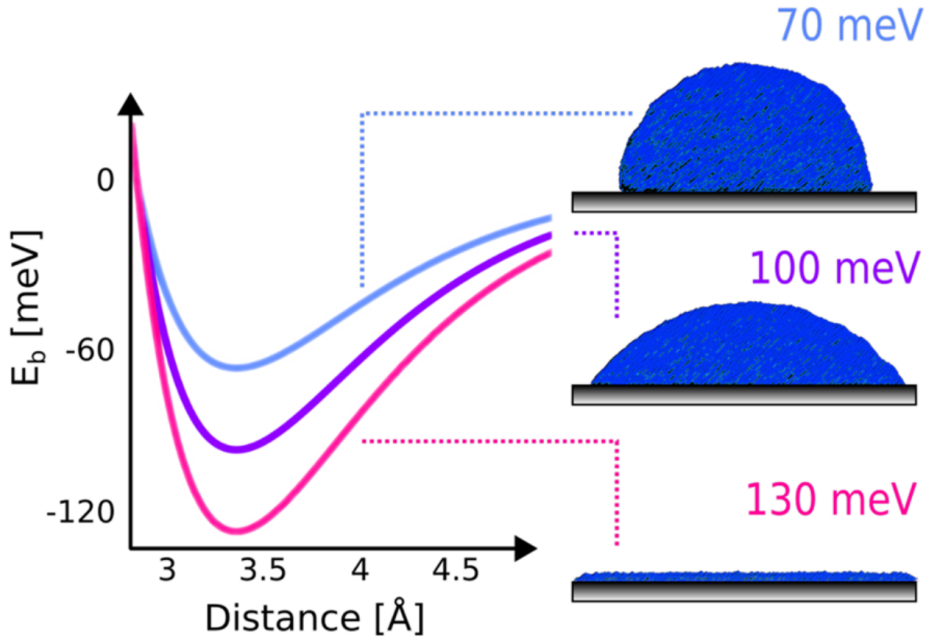
Open Questions

- Water mobility and reactivity
- Material dependence
- Confinement effect

[1] Holt, J. K. et al. Science **2006**, *312*, 1034–1037.
[2] Siria, A. et al. Nature **2013**, *494*, 455–458.
[3] Shannon, M. A. et al. Nature **2008**, *452*, 301–310.

Simulation of Water in Complex Environments

We can't afford to make errors...



Complex materials need...

- high accuracy (sensitive properties)
- large system sizes and long simulation time

Ab initio methods

+ High accuracy
– Expensive / slow

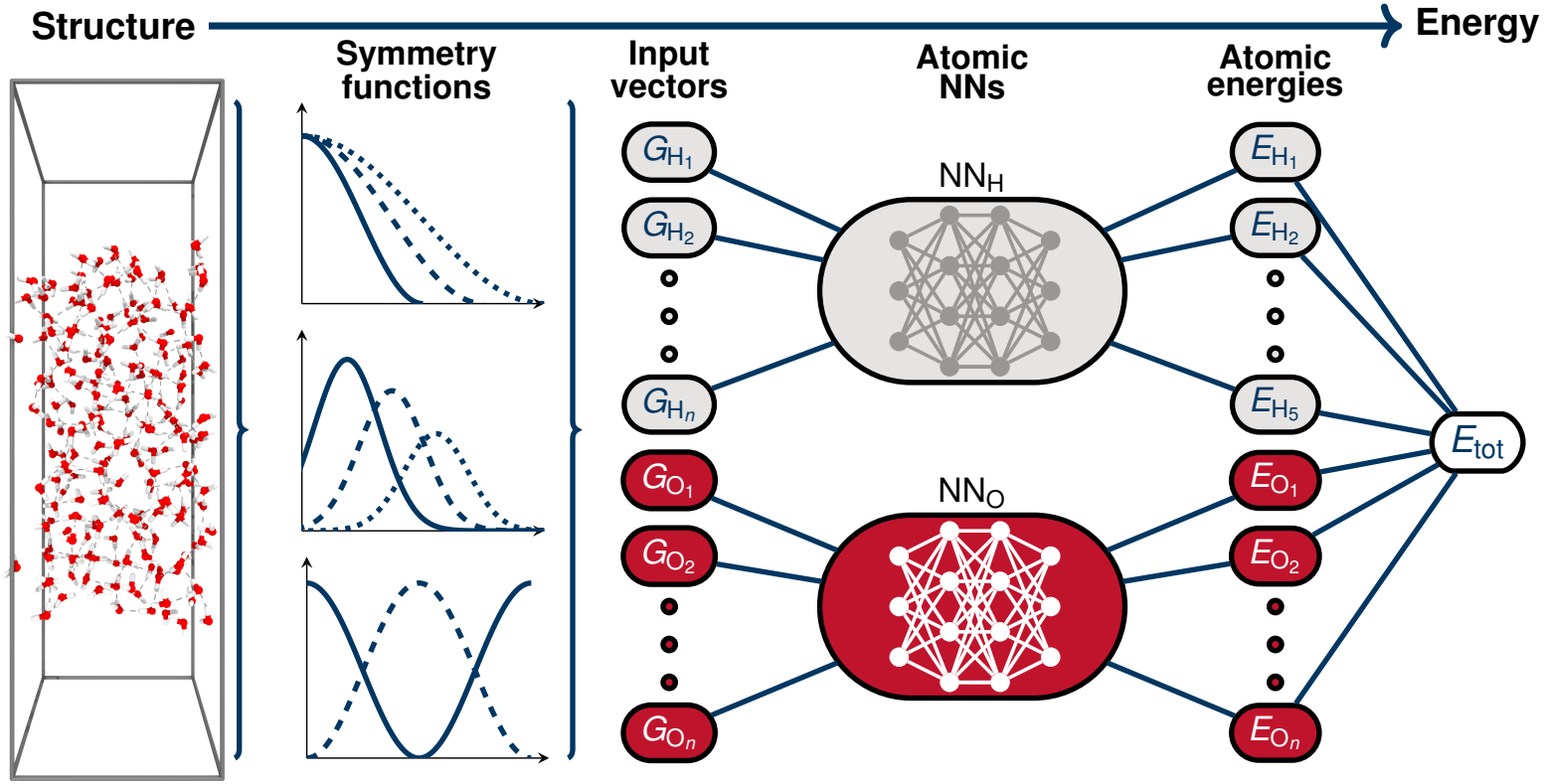
Force field methods

+ Large system sizes
– Not accurate enough

➡ Use machine learning to get the best of both worlds:
High accuracy + fast evaluation

[1] Brandenburg, J. G. et al. J. Phys. Chem. Lett. **2019**, *10*, 358–368.

High–dimensional Neural Network Potentials



- Analytical structure–energy relation[1][2]
- Transform structure via atom centered symmetry functions[3]
- Use in simulations: CP2K and Lammps

[1] Behler, J.; Parrinello, M. Phys. Rev. Lett. **2007**, *98*, 146401.
[2] Behler, J. Angew. Chemie - Int. Ed. **2017**, *56*, 12828–12840.
[3] Behler, J. J. Chem. Phys. **2011**, *134*, 074106.

Committee Neural Network Potentials

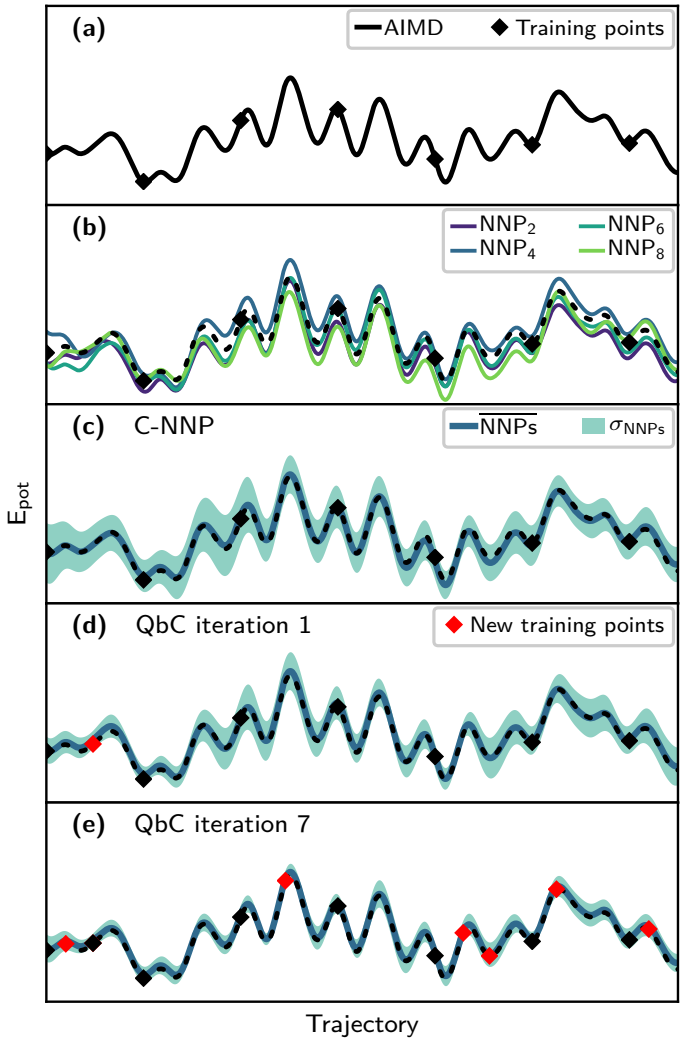
Simple but Powerful Extension

$$E^{\text{C-NNP}} = \frac{1}{n_{\text{NNP}}} \sum_{i=1}^{n_{\text{NNP}}} E_i^{\text{NNP}}$$

$$\vec{F}^{\text{C-NNP}} = \frac{1}{n_{\text{NNP}}} \sum_{i=1}^{n_{\text{NNP}}} \vec{F}_i^{\text{NNP}}$$

Advantages[1][2][3][4]:

- More accurate prediction
- Estimation of uncertainty
- Reduced overfitting
- Active learning via QbC
- Efficient with shared descriptors



[1] Schran, C.; Brezina, K.; Marsalek, O. J. Chem. Phys. **2020**, *153*, 104105.
[2] Gastegger, M.; Behler, J.; Marquetand, P. Chem. Sci. **2017**, *8*, 6924–6935.
[3] Musil, F.; Willatt, M. J.; Langovoy, M. A.; Ceriotti, M. J. Chem. Theory Comput. **2019**, *15*, 906–915.
[4] Smith, J. S. et al. J. Chem. Phys. **2018**, *148*, 241733.

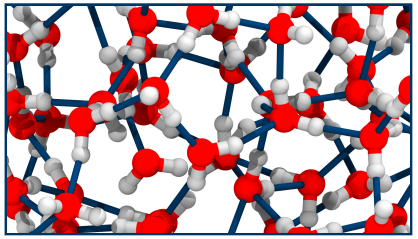
Active Learning for Water
Query by Committee

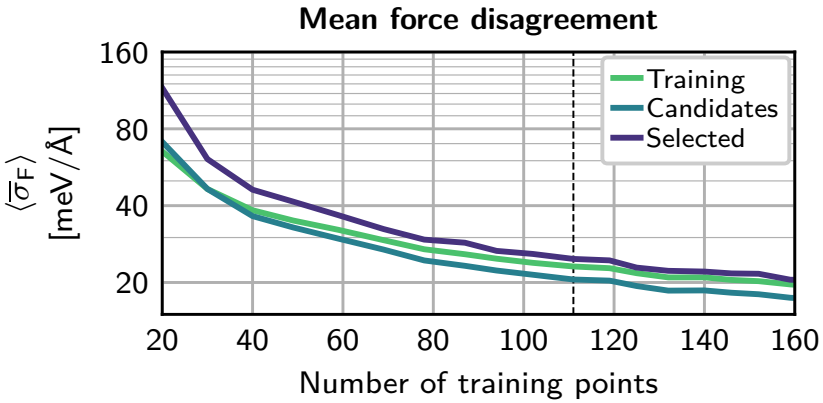
Starting point: AIMD water (revPBE0-D3) at 300K

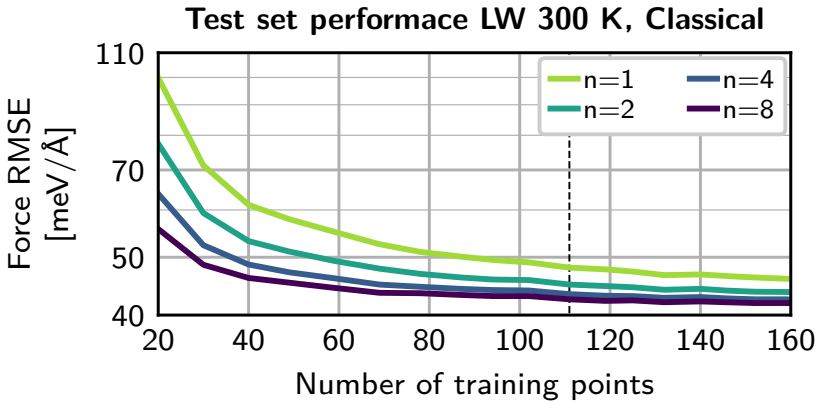
- Start with 20 random structures
- Use force disagreement to select new training points
- 10 new points per iteration

➡ Committee average is much better predictor

➡ Convergence is reached after roughly 100 points







[1] Schran, C.; Brezina, K.; Marsalek, O. J. Chem. Phys. **2020**, *153*, 104105.

C-NNPs: Robust and Accurate

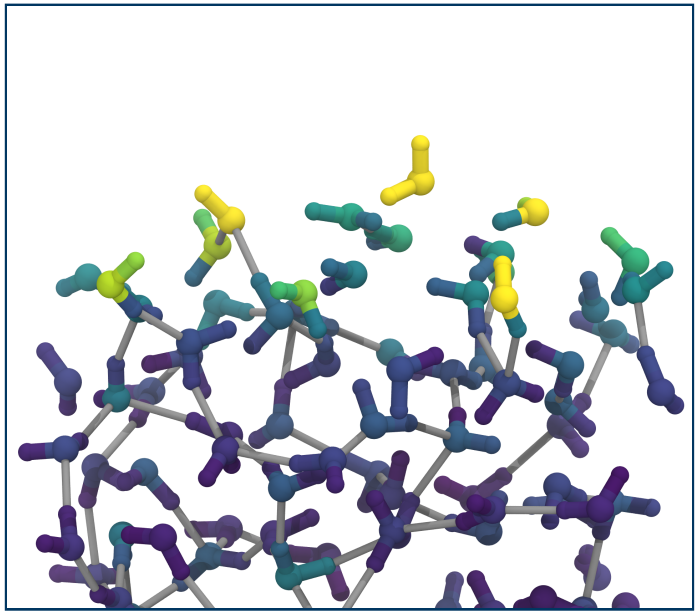
Tests on First Generation

Bulk water model trained to 100 points can:

- Treat higher T up to 500 K
- Simulate ice, gas phase clusters and interfaces

➡ Committee disagreement shows weakness of model

- Disagreement is directly related to error[1]



Force disagreement at the water-air interface

[1] Musil, F.; Willatt, M. J.; Langovoy, M. A.; Ceriotti, M. J. Chem. Theory Comput. **2019**, *15*, 906–915.

C-NNPs: Controlling the Stability

Biasing the Disagreement

Small disagreement = stable and accurate model

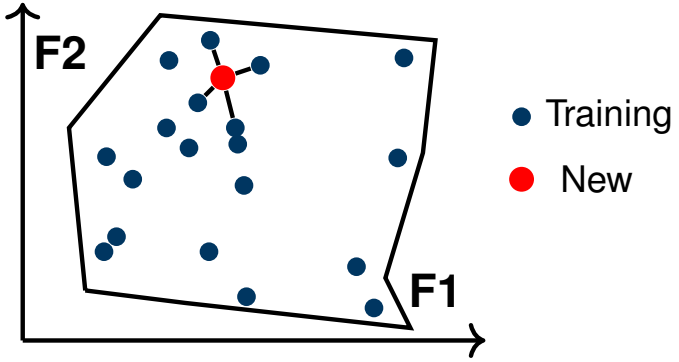
- Define simple biasing potential acting on energy disagreement

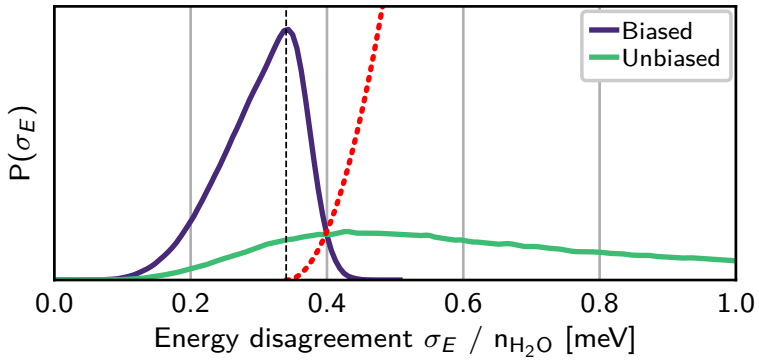
➡ Erect barrier around area with small error

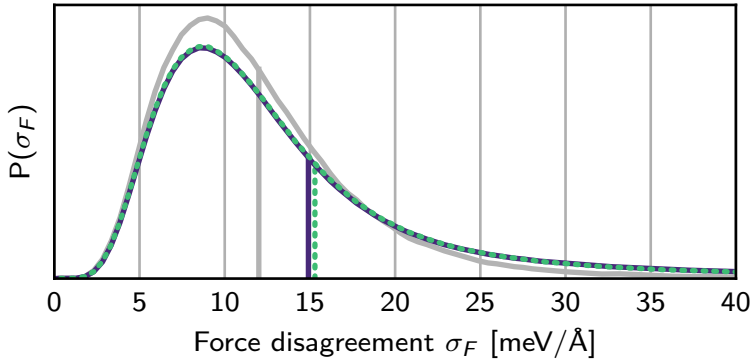
- Force disagreement not perturbed

➡ Mild influence on dynamics

$$E^{(\mathrm{b})} = \theta(\sigma_E - \sigma_0)\frac{1}{2}k^{(\mathrm{b})}(\sigma_E - \sigma_0)^2$$

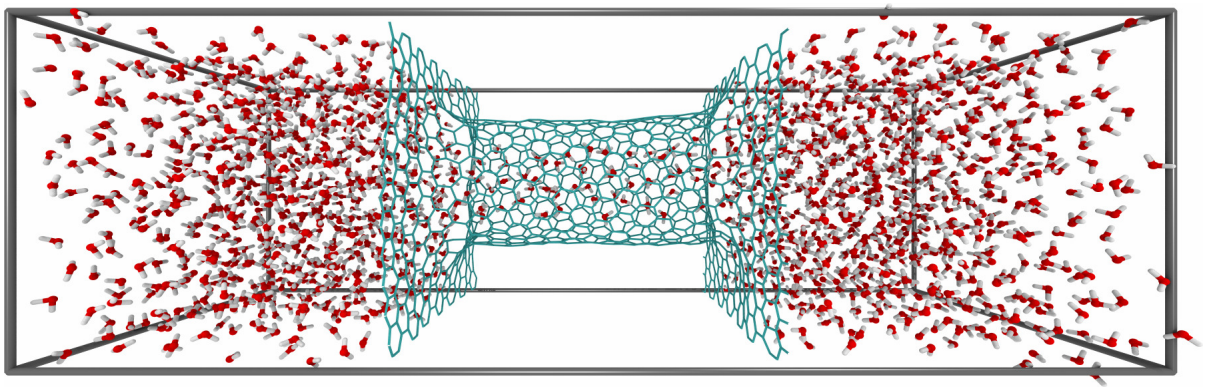






[1] Schran, C.; Brezina, K.; Marsalek, O. J. Chem. Phys. **2020**, *153*, 104105.

Rapid development of MLPs for complex aqueous systems

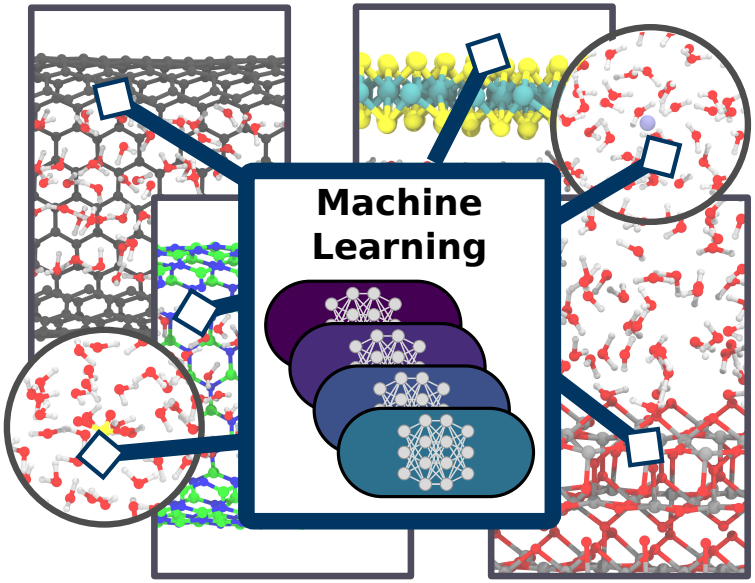


Machine Learning Potentials Made Simple

Build end-to-end framework for complex systems in simple manner.

Conceptual Idea

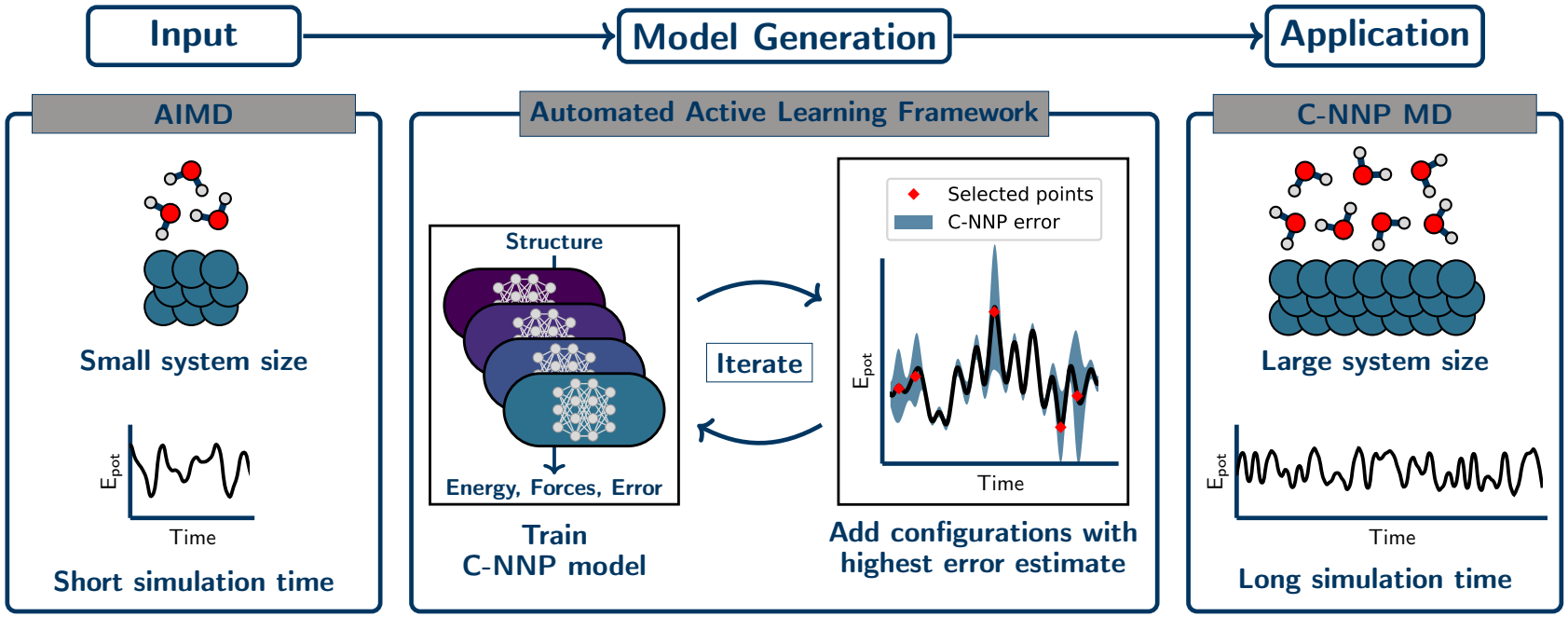
- Concentrate on specific thermodynamic condition
- Remove as much user input as possible
- Automate most of the development steps
- Establish automated validation scheme



➡ Training and simulation codes are open source + machine learning framework is made available

[1] Schran, C. et al. Proc. Natl. Acad. Sci. **2021**, *118*.

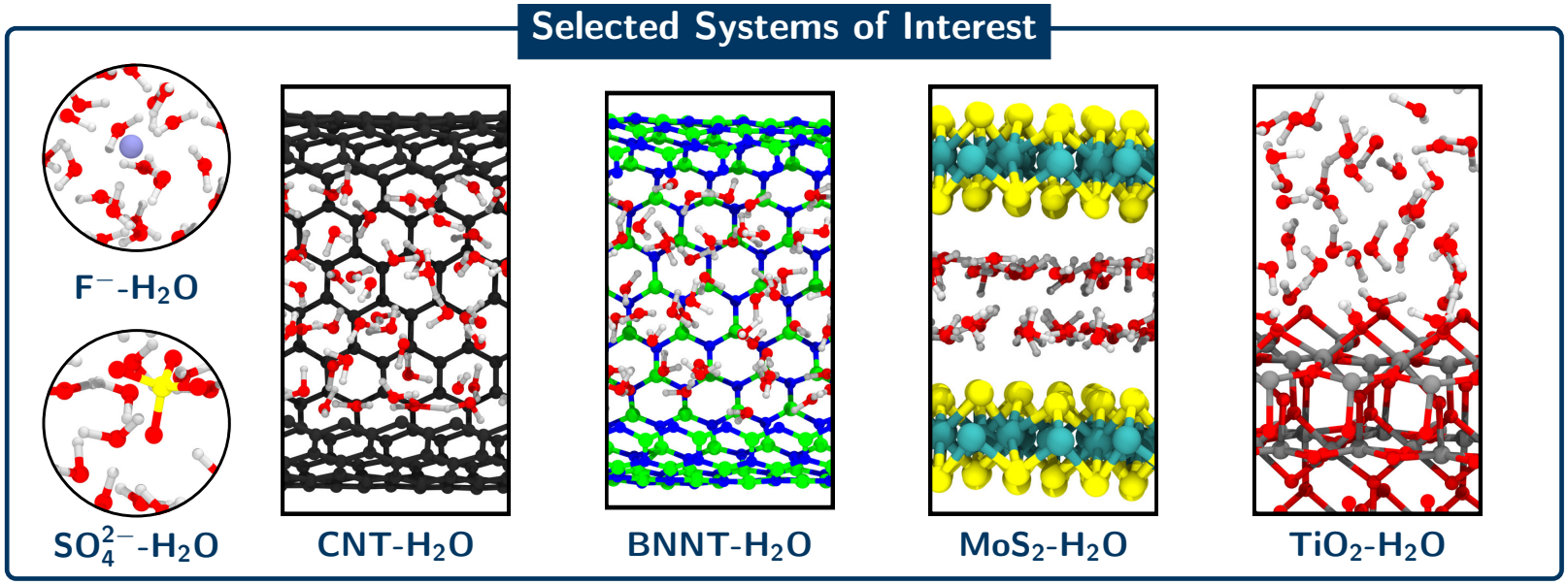
Machine Learning Potentials made simple



Rapid Development

- Use small scale AIMD trajectory (30 ps)
- Perform active learning
- Apply model for large scale C-NNP simulations

C-NNPs for Water in Complex Environments



➡ C-NNP models for all 6 systems by identifying ≈300 structures from AIMD simulations

Validation of the Models

How to validate >6 models?

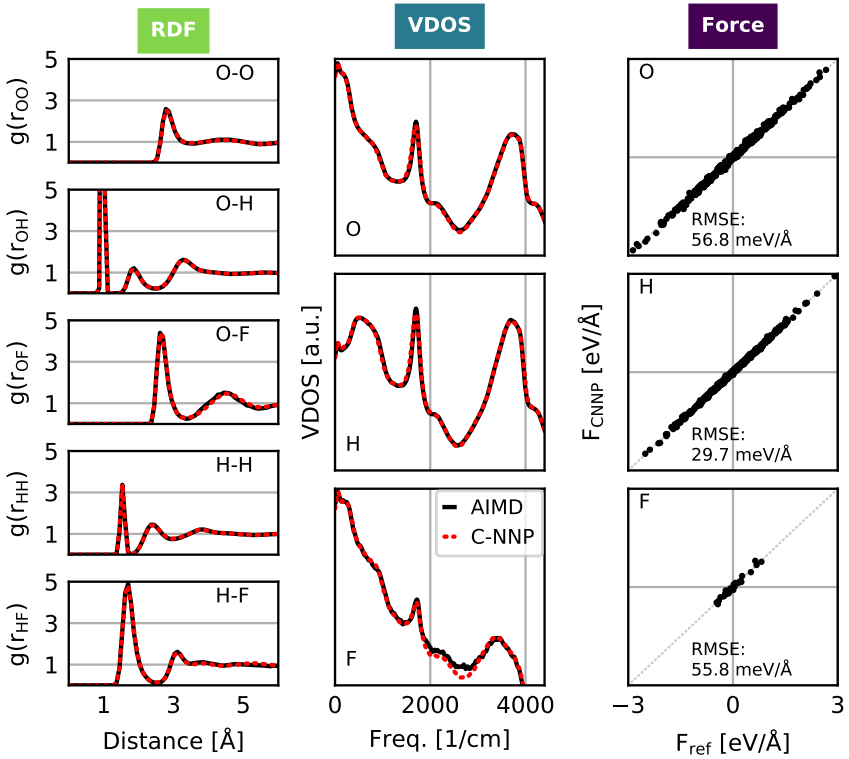
Automated testing:

1. Structural properties: RDFs
2. Dynamical properties: VDOS
3. ML properties: Force RMSE

Reduce to score (0-100%)

Scoring for RDFs and VDOS compared to AIMD:

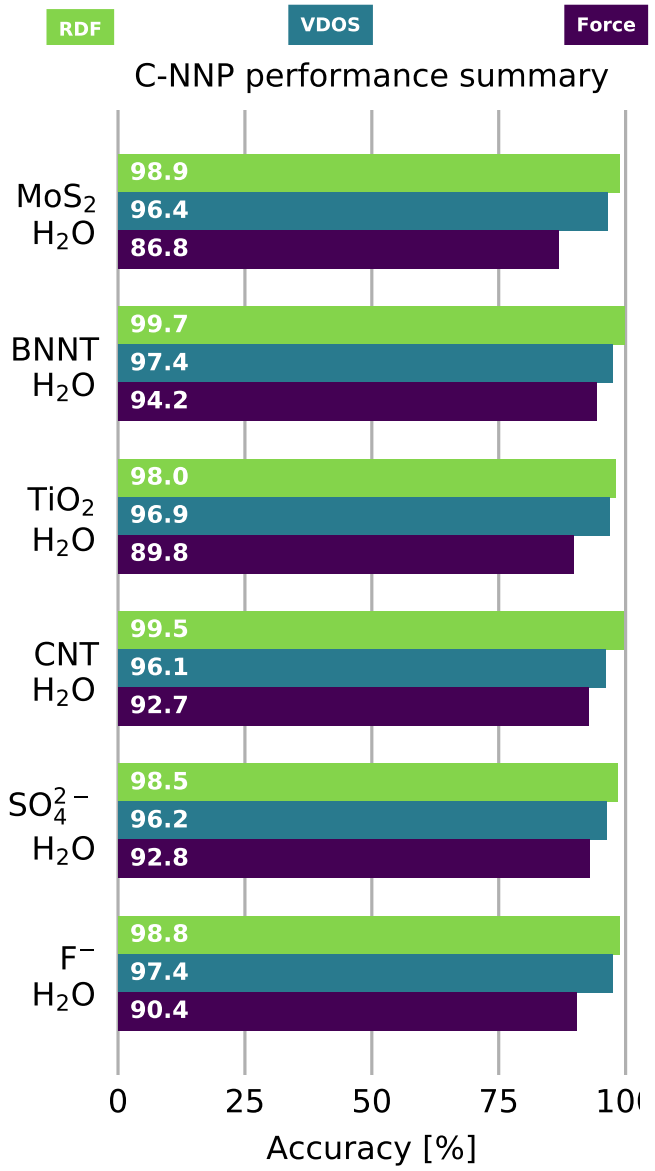
$$d = \frac{\int_{-\infty}^{+\infty} |\rho_P(x) - \rho(x)| \, \mathrm{d}x}{\int_{-\infty}^{+\infty} \rho_P(x) \mathrm{d}x + \int_{-\infty}^{+\infty} \rho(x) \mathrm{d}x}$$



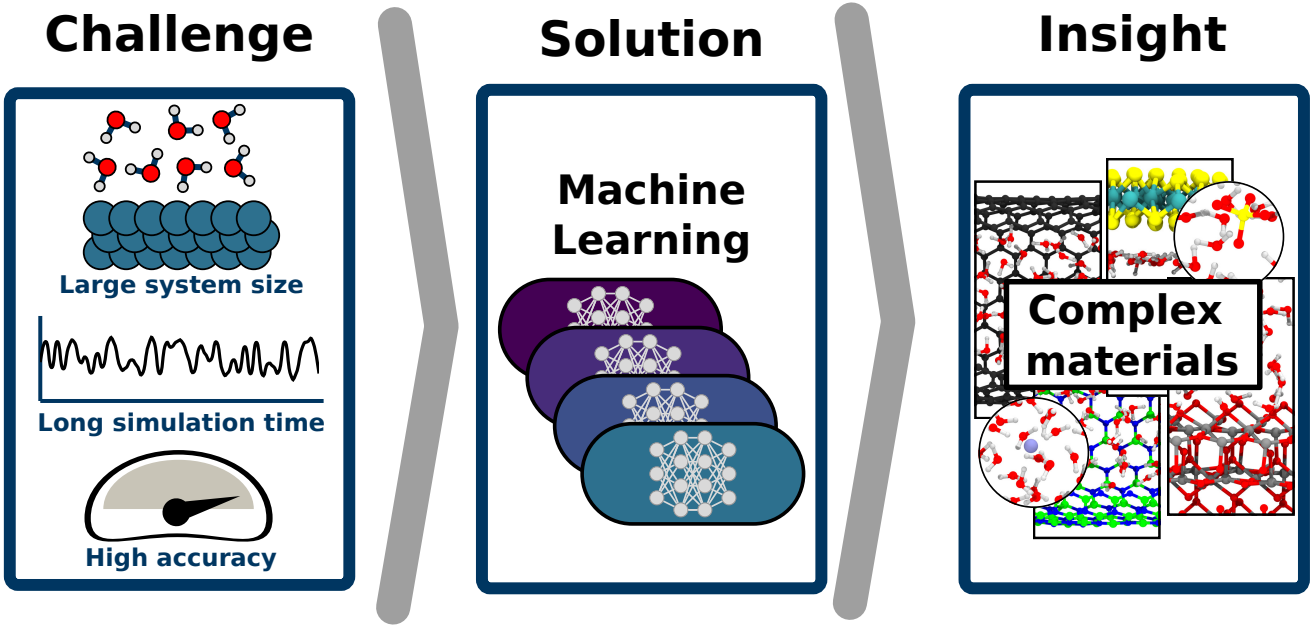
Validation of the Models

Accuracy overview

- All properties are reproduced very accurately
- Similar accuracy for all diverse systems
- Other properties (Hbonding, density profiles, water orientation) are also in very good agreement with reference



Summary



MLPs made simple

- Accurate and efficient description
- Data-driven and automated generation

➡ Open-source development including tutorials:

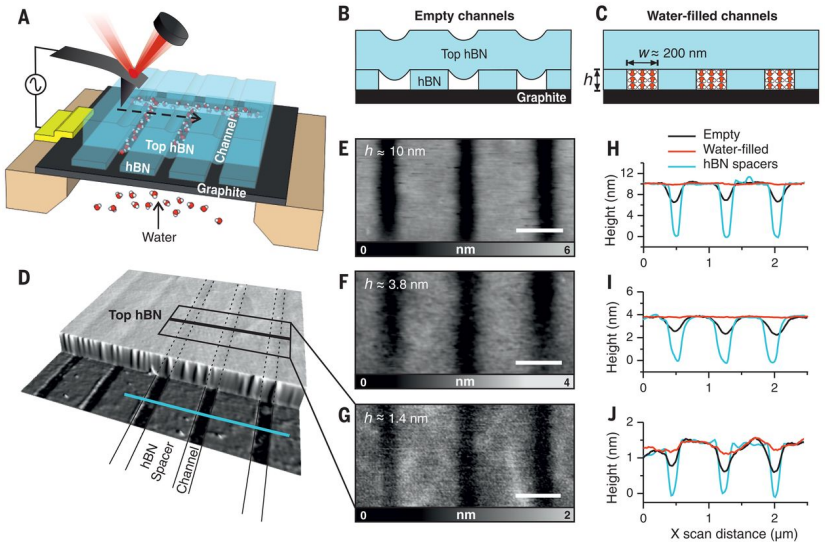
https://github.com/Marsalek-Group/aml

[1] Schran, C. et al. Proc. Natl. Acad. Sci. **2021**, *118*.

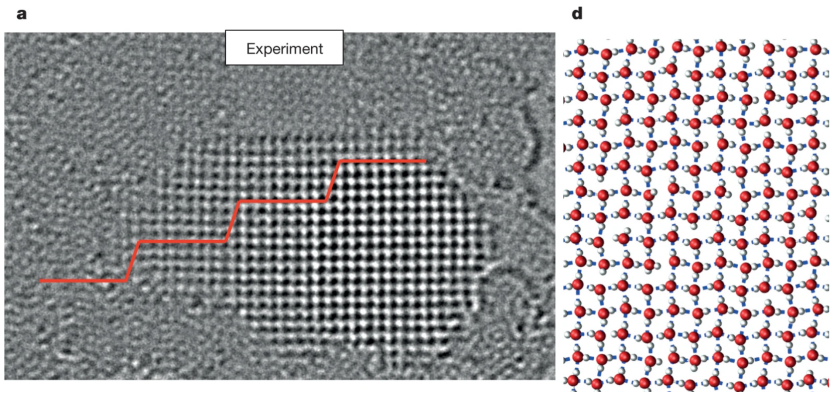
Application: Phase behavior of monolayer confined water

Motivation

Experimental fabrication of hydrophobic capillaries with nanoscale dimensions



Measurement of anonymously low dielectric constant of nanoconfined water[1]



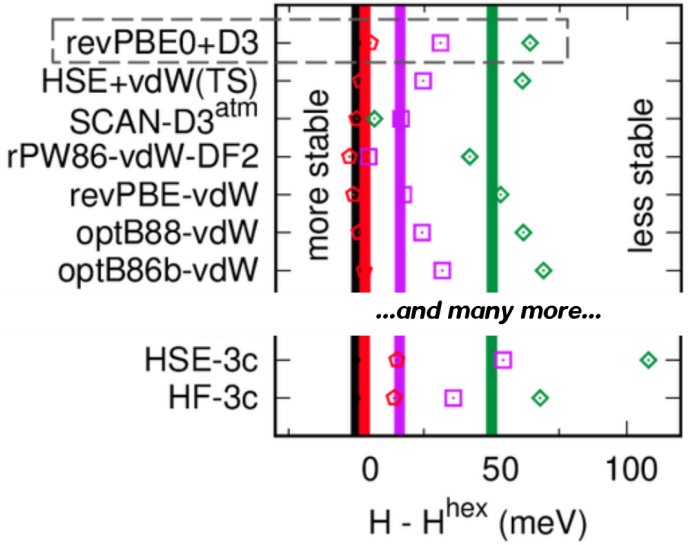
Possible existence of a square ice phase[2]

- ➡ Remarkably different properties of nanoscale water
- ➡ Provide molecular level understanding as foundation for technological application

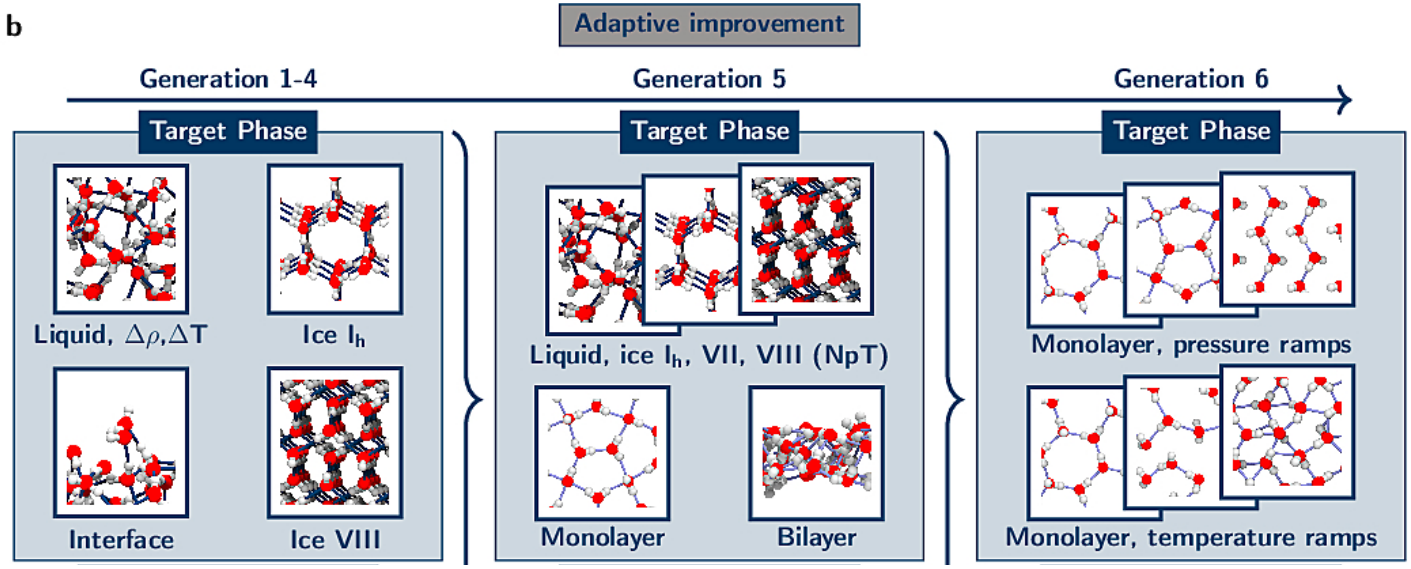
[1] Fumagalli, L. et al. Science **2018**, *360*, 1339–1342.
[2] Algara-Siller, G. et al. Nature **2015**, *519*, 443–445.

Development of a Mono-layer Water Model

Quantum Monte Carlo guided MLP



1. Use QMC to select DFT functional
2. Train MLP to DFT
3. RSS for all metastable phases
4. Free energy methods for phase diagram



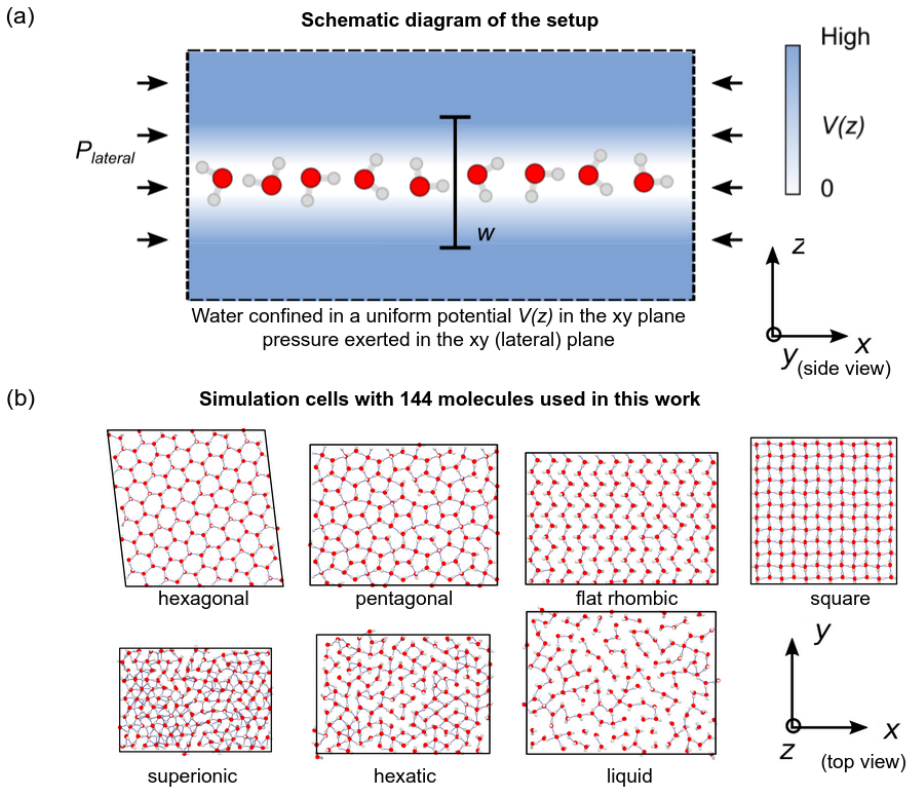
Simulations of Monolayer confined water

Setup

- Lennard-Jones confinement potential fitted to QMC data
- Lateral pressure
- 144 molecules per unit cell

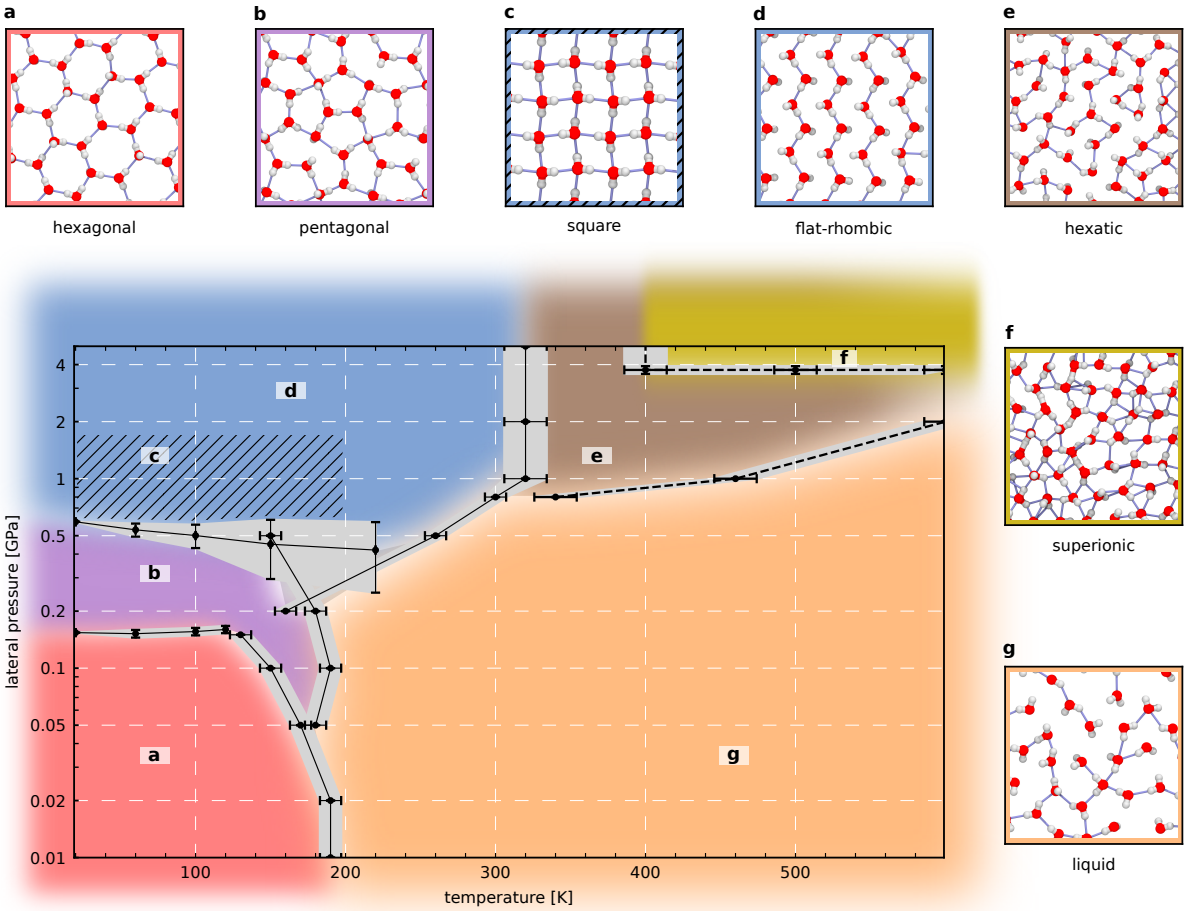
Simulation techniques

- Random structure search to find stable ordered phases
- Thermodynamic integration to compute free energy
- Coexistence simulations to locate solid-liquid boundaries



Phase Diagram of Monolayer Confined Water

Rich phase behavior and unique properties



- Unique “hexatic” phase which is neither liquid nor solid
- Superionic behavior beyond 4 GPa and 400 K

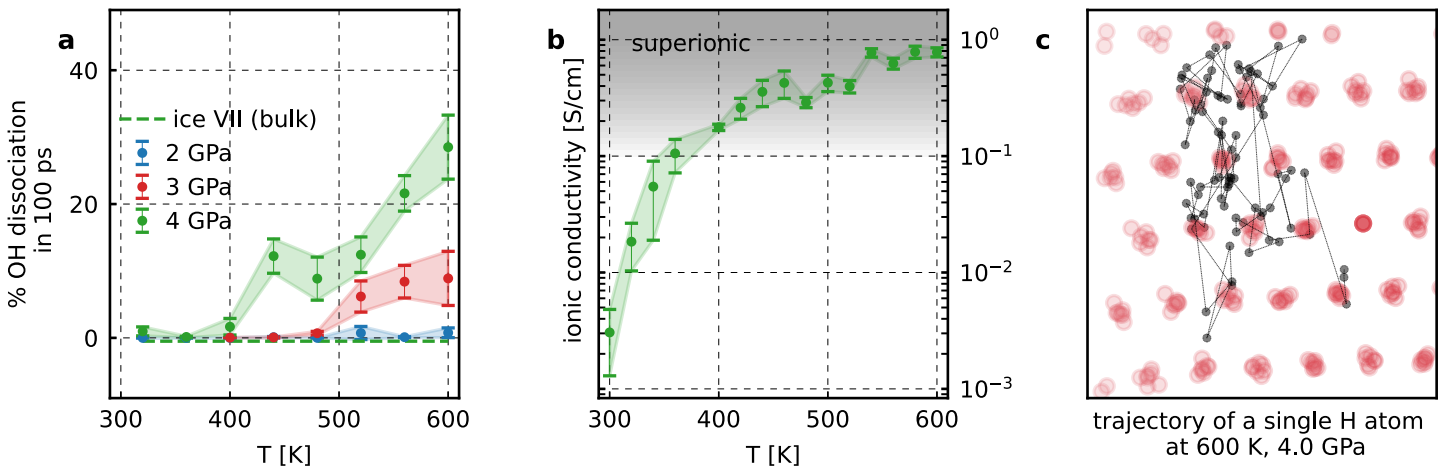
[1] Kapil, V. et al. Nature **2022**, *just accepted*.

Phase Diagram of Monolayer Confined Water
Neither liquid, nor solid

- No translational long range order
- Hexagonal orientational short range order
- Resemblance with free rotor phase of H2

[1] Kapil, V. et al. Nature **2022**, *just accepted*.

Phase Diagram of Monolayer Confined Water
Superionic phase



- Pressure increases OH dissociation significantly
- Threshold for superionic conductivity reached at 400 K for 2 GPa
- Fixed lattice of oxygen atoms, diffusing hydrogen atoms

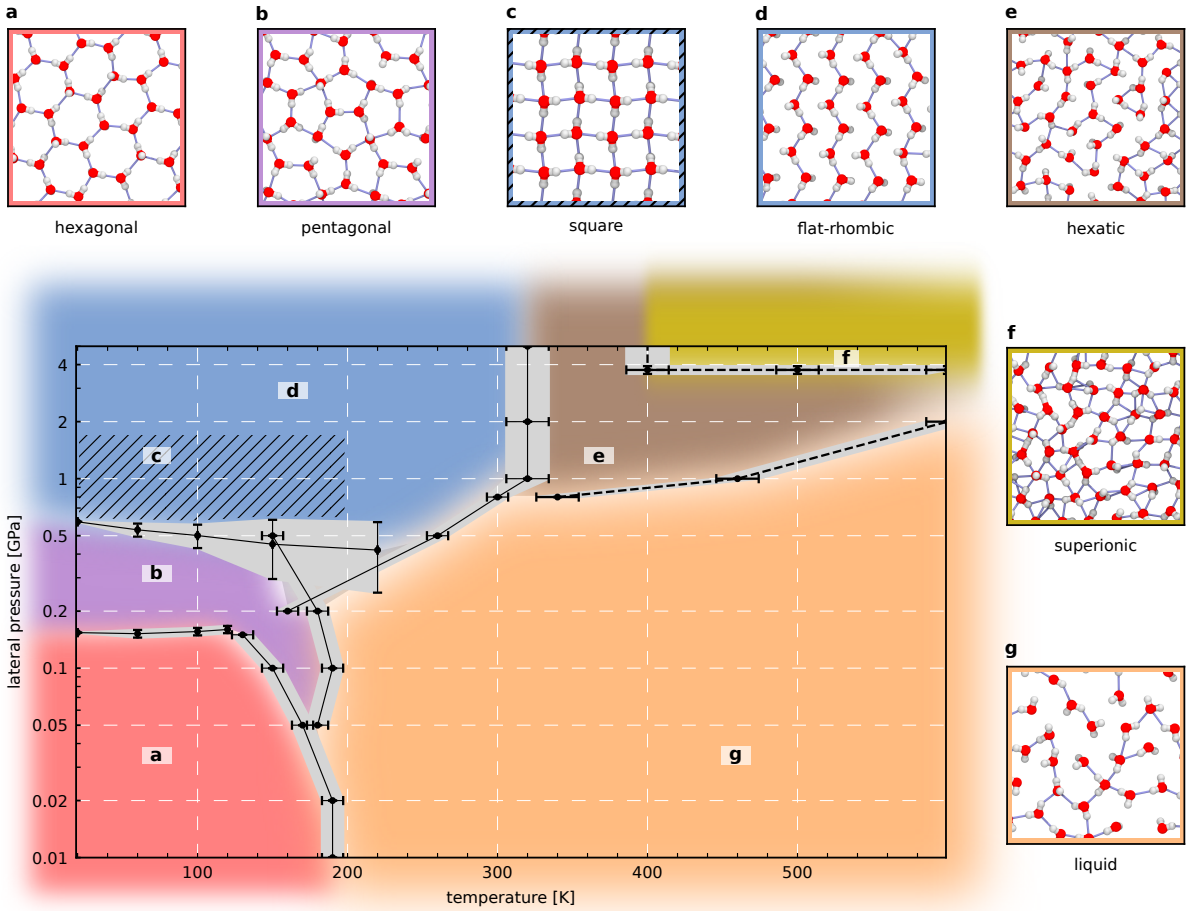
[1] Kapil, V. et al. Nature **2022**, *just accepted*.

Phase Diagram of Monolayer Confined Water
Superionic phase

- Facile proton diffusion through fixed oxygen lattice
- No adsorption of protons on explicit carbon validated via AIMD

[1] Kapil, V. et al. Nature **2022**, *just accepted*.

Summary



- Unique “hexatic” phase which is neither liquid nor solid
- Superionic behavior beyond 4 GPa and 400 K

➡ **Enabled by error control via committee NNPs**

[1] Kapil, V. et al. Nature **2022**, *just accepted*.

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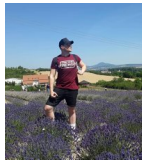

Krystof Brezina

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MATERIALS AND MOLECULAR MODELLING HUB

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