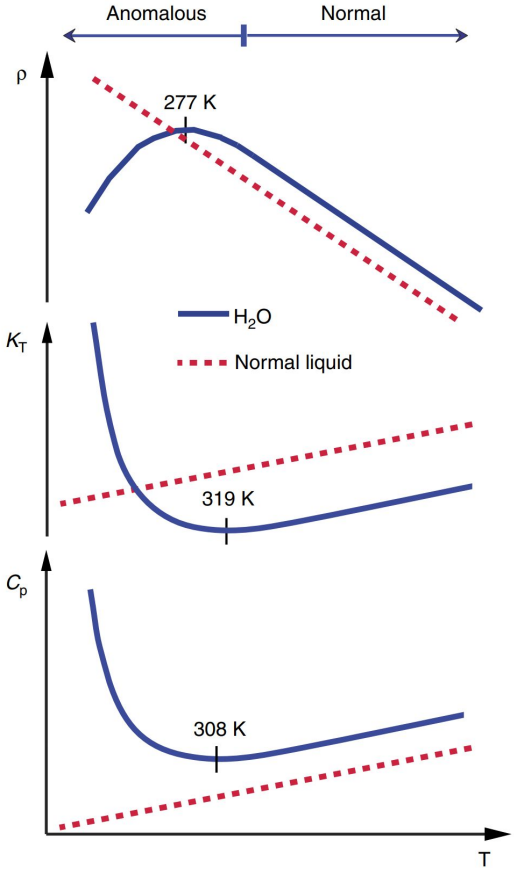
Exploring hidden structure in water using polarizable atom neural networks

HAMLET-Physics Conference, University of Copenhagen

2026-08-19

Fredrik Grote

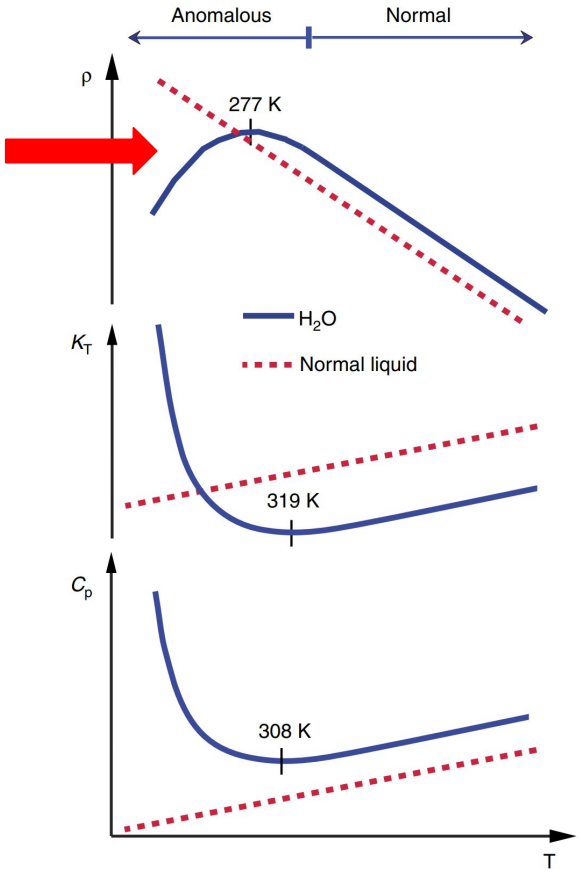
Water anomalies



R. J. Speedy and C. A. Angell, *J. Chem. Phys.*, 65, (1976)

Water anomalies

Density maximum



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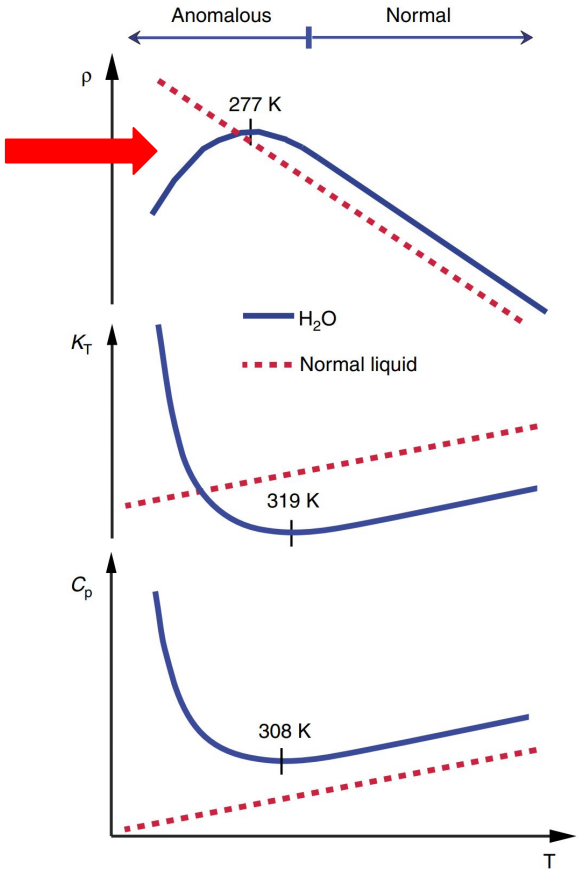

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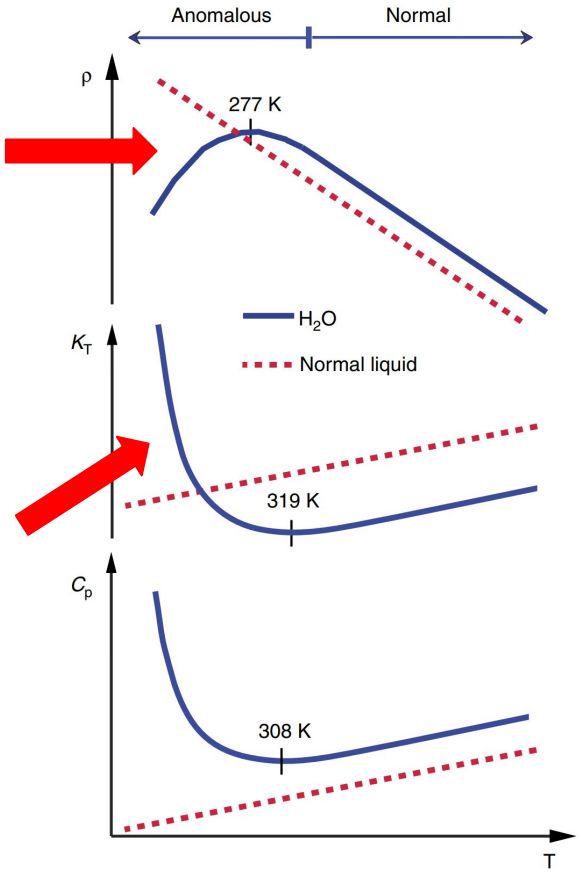

Density

Fluctuations increase as temperature decreases

Density fluctuations

$$\kappa_T \propto \langle V^2 \rangle - \langle V \rangle^2$$

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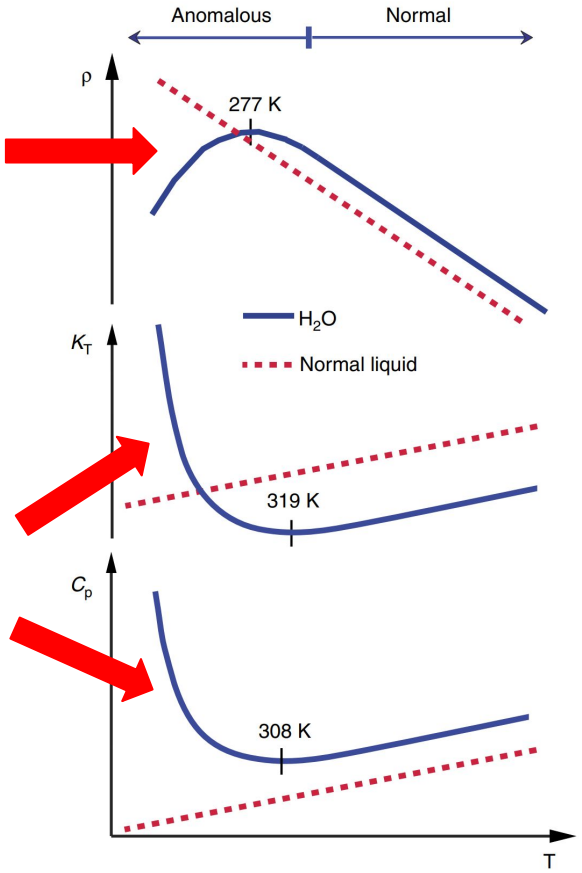


Density

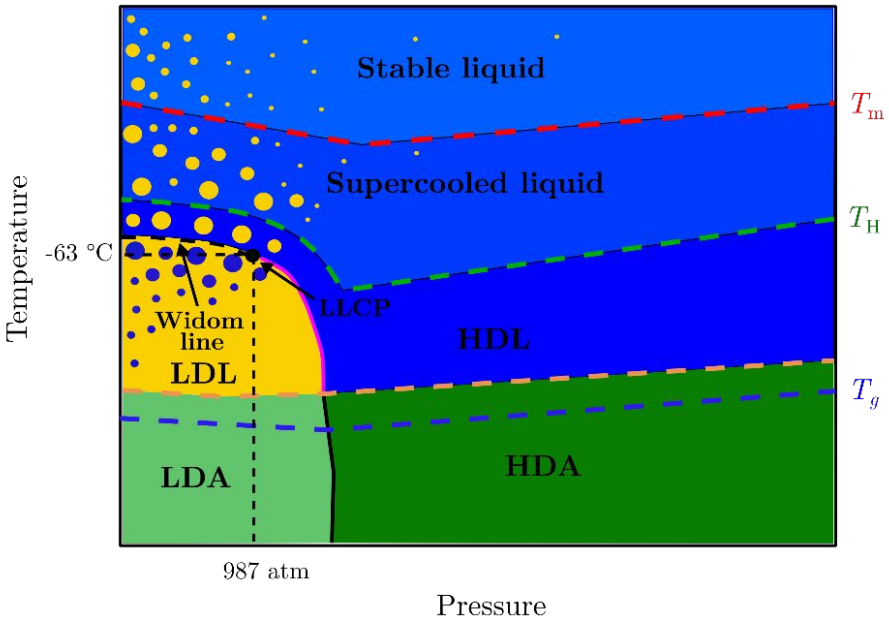
Density fluctuations $\kappa_T \propto \langle V^2 \rangle - \langle V \rangle^2$

Entropy fluctuations $C_p \propto \langle S^2 \rangle - \langle S \rangle^2$

R. J. Speedy and C. A. Angell, *J. Chem. Phys.*, 65, (1976)

What is the origin of these *non-thermal* fluctuations?

Liquid-liquid transition and liquid-liquid critical point



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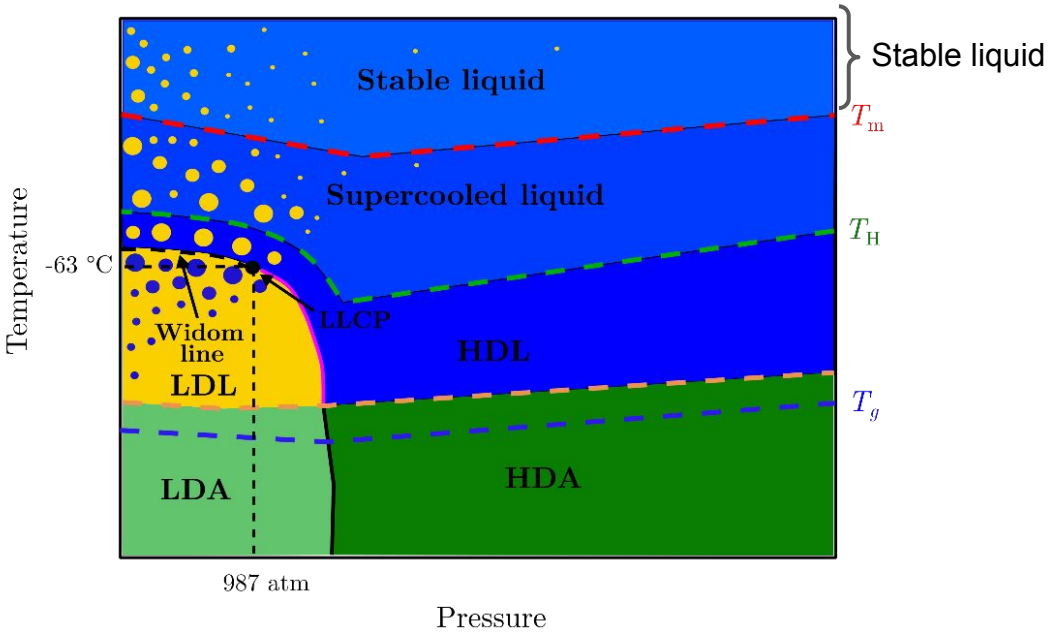

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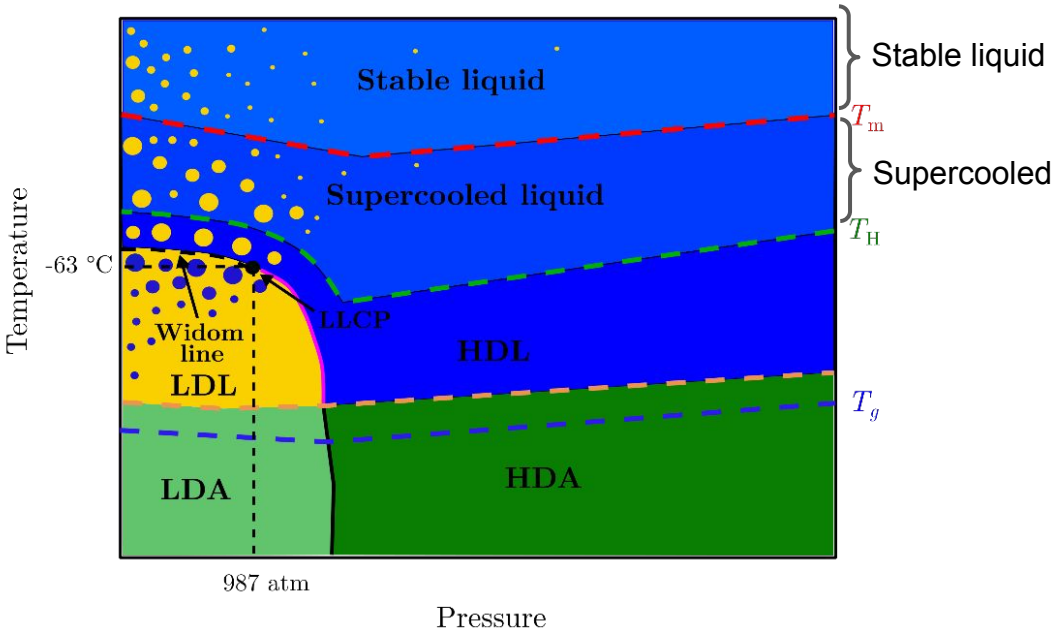

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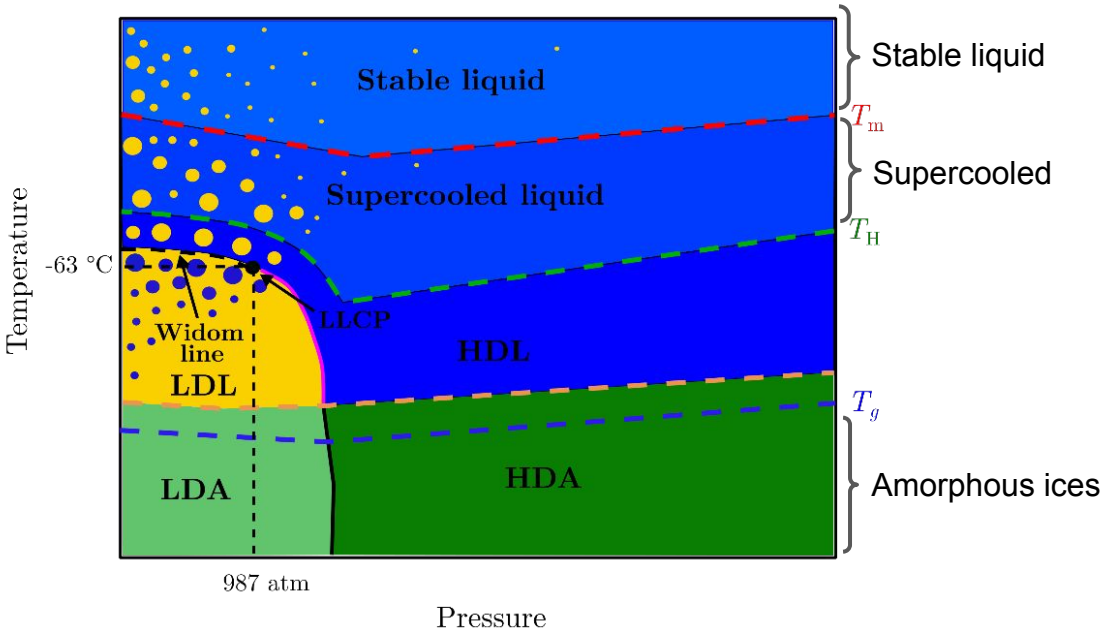

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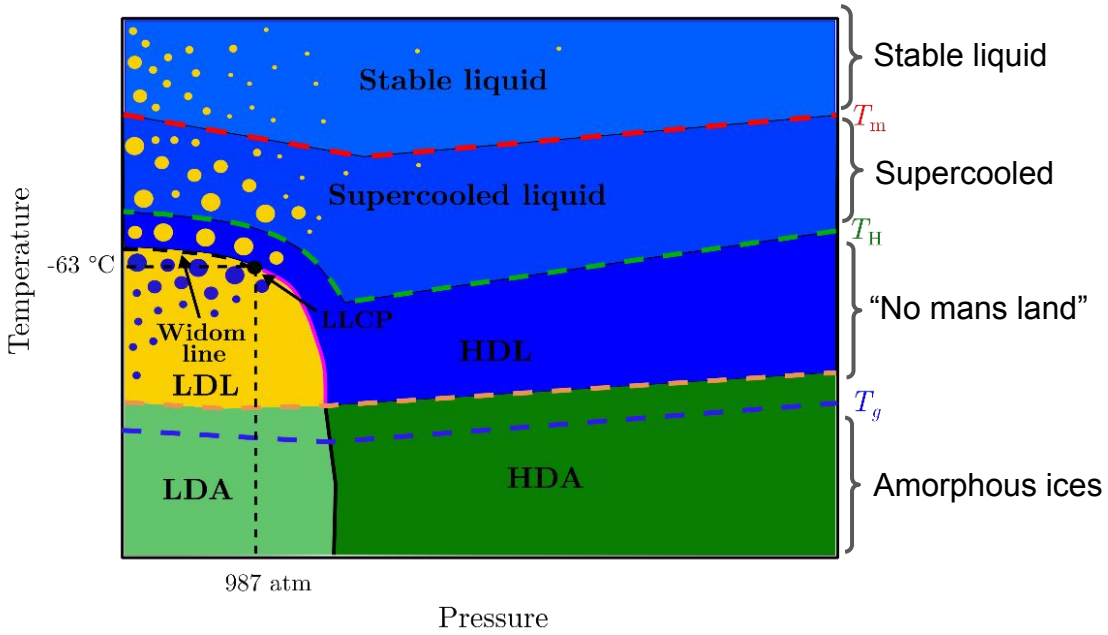

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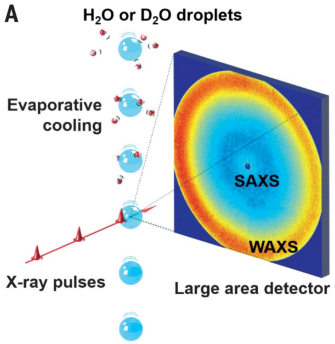

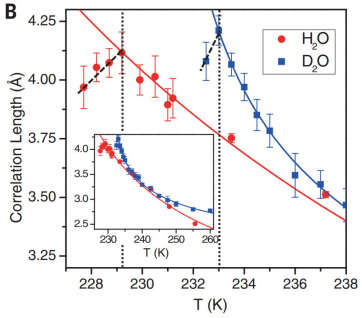

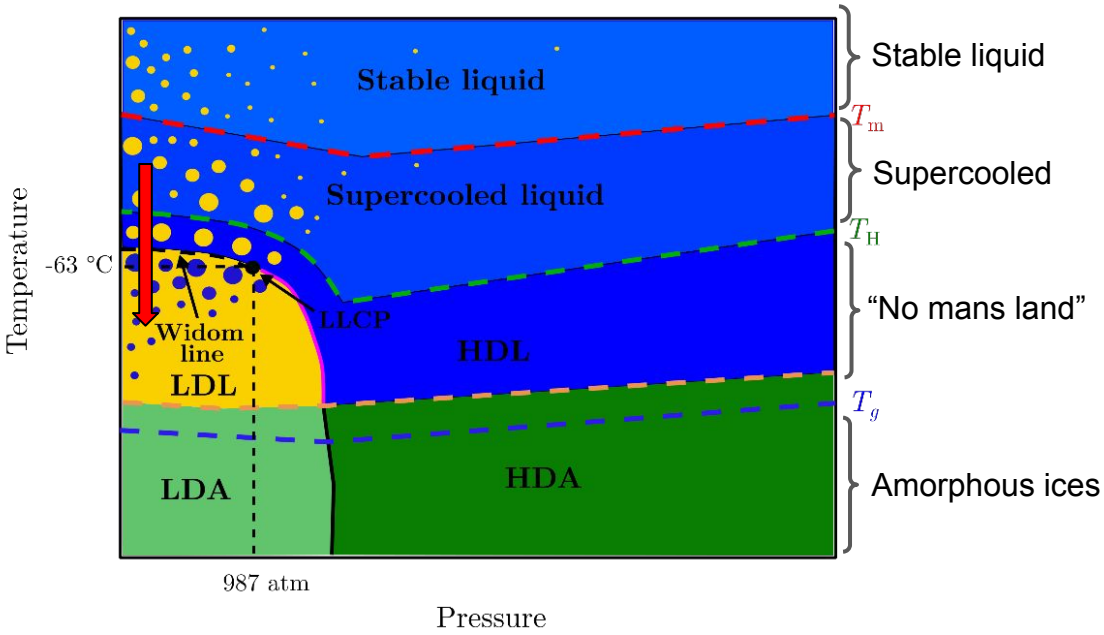

Kim et al., *Science* **358**, 1589-1593 (2017)

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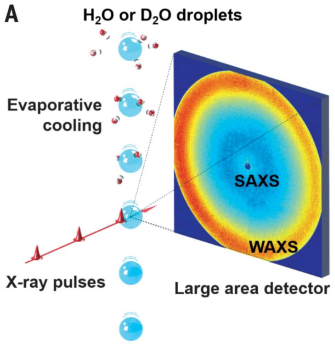

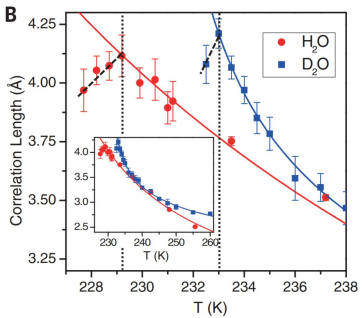

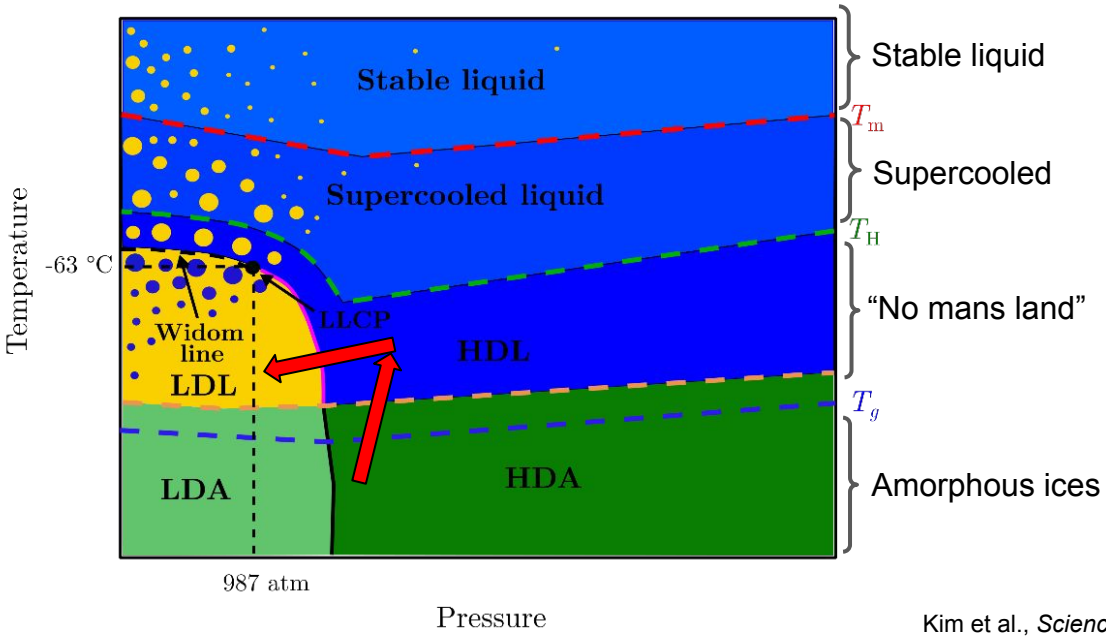

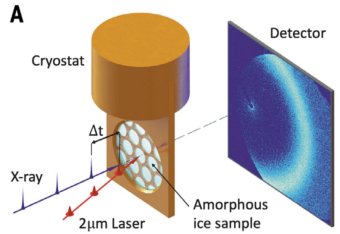

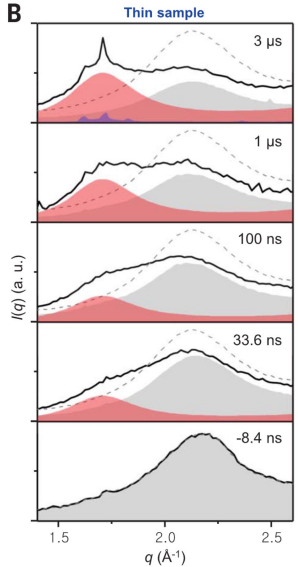

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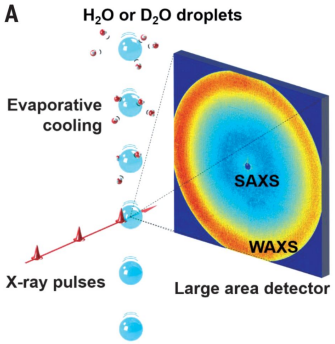

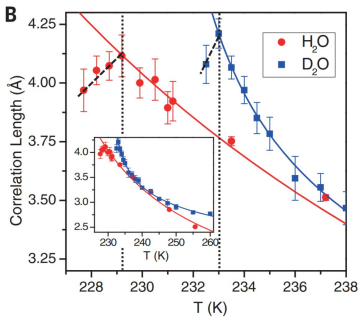

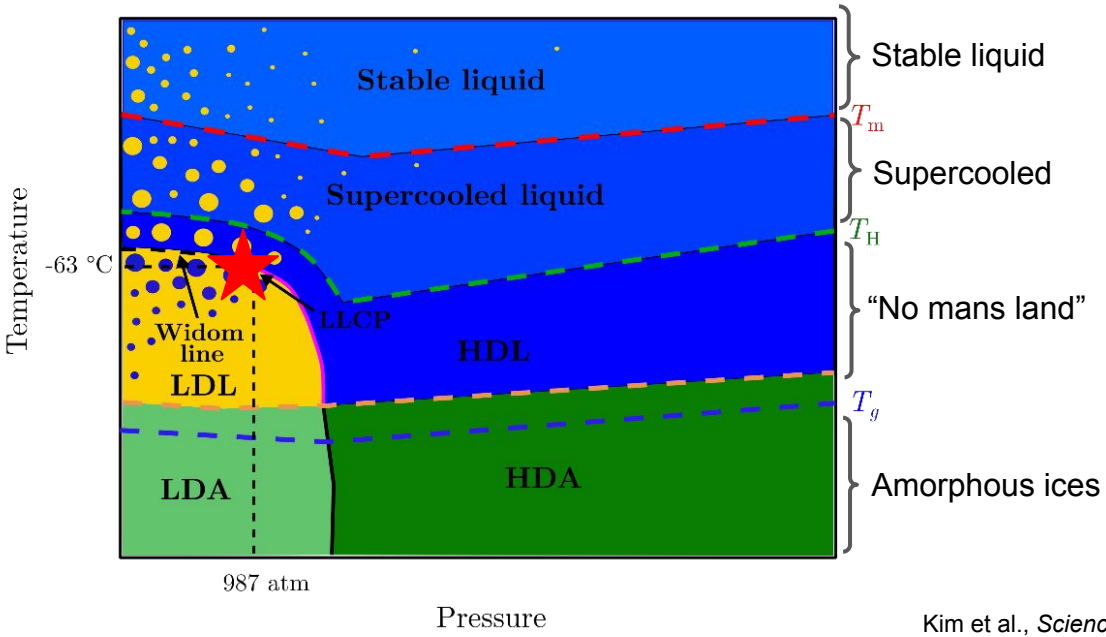

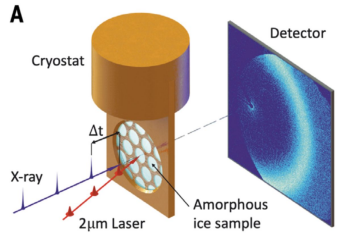

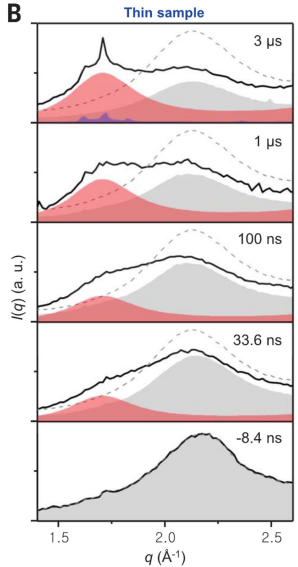

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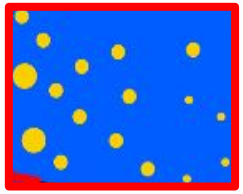
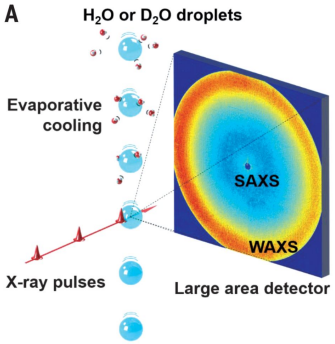
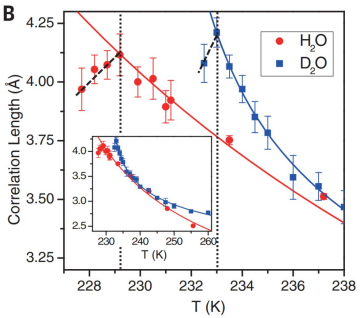
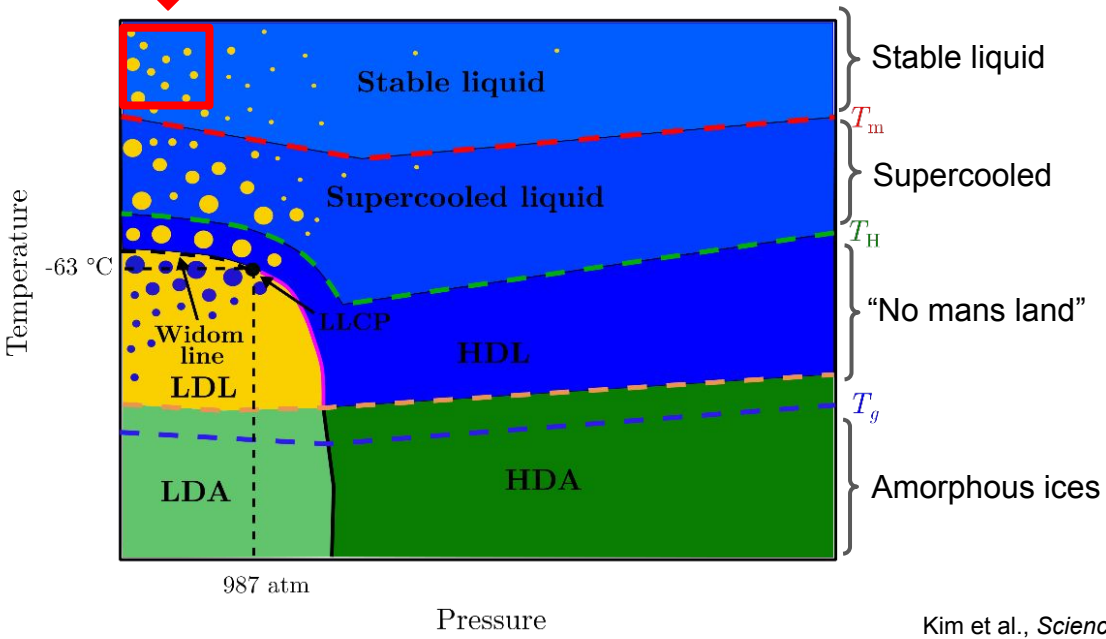


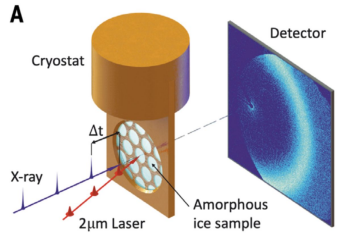
Ambient water is mainly **HDL**
with **LDL** fluctuations

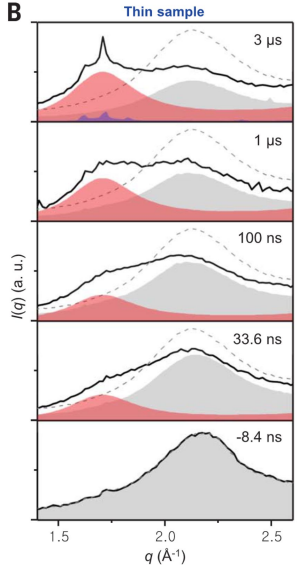
"Supercritical"











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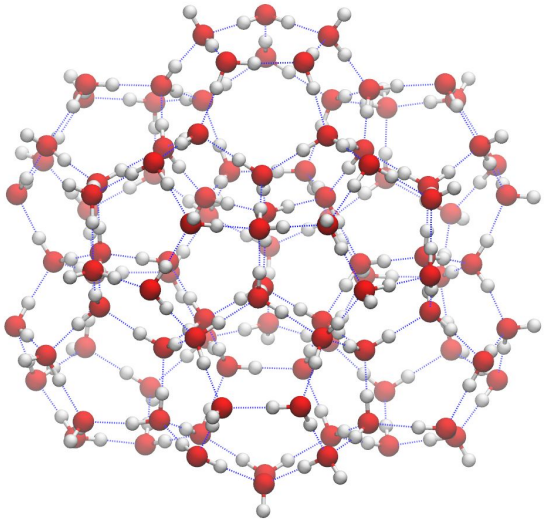
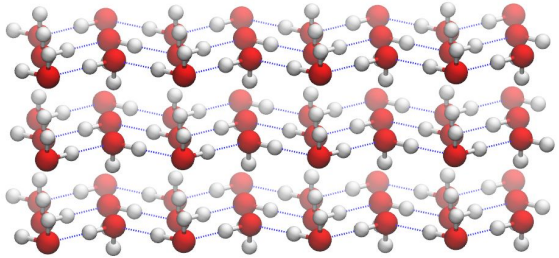
What is the structure of HDL and LDL?

A proposal for the structure of LDL and HDL

LDL - Fused dodecahedra



HDL - Chains



Camisasca et al., *J. Chem. Phys.* 151, (2019)

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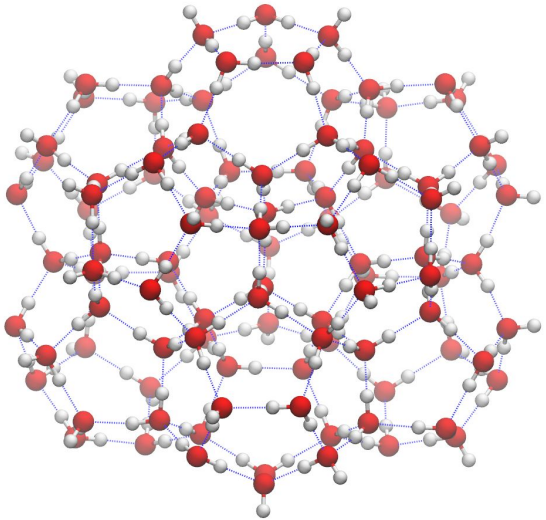
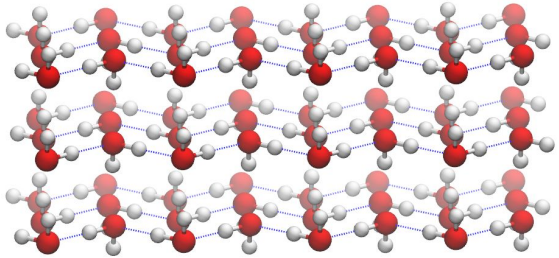


Maximize number of H-bonds

⇌

HDL - Chains



Librational motion

A competition between energy and entropy

Camisasca et al., *J. Chem. Phys.* 151, (2019)

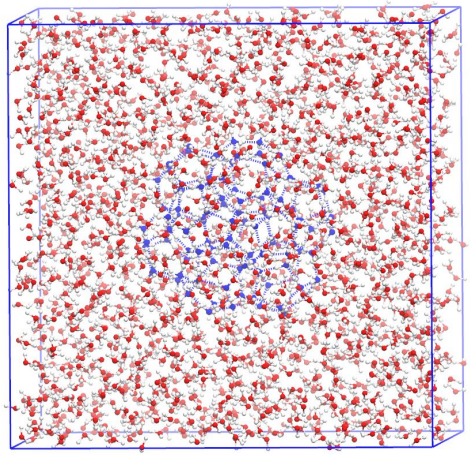
How can we study these template structures?

Molecular dynamics simulations and the FCM-GAP water model

Newtonian equation of motion

$$\mathbf{F}_i = m_i \mathbf{a}_i$$

$$\mathbf{F}_i = -\nabla_i U(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_n)$$



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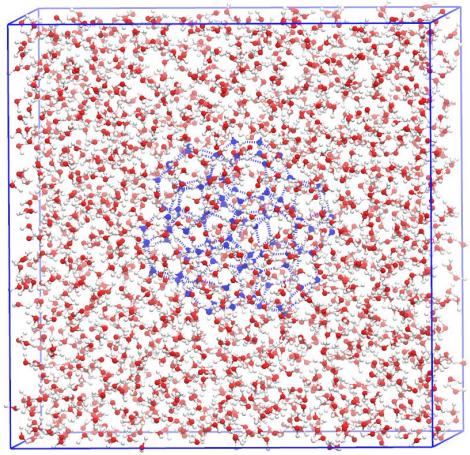
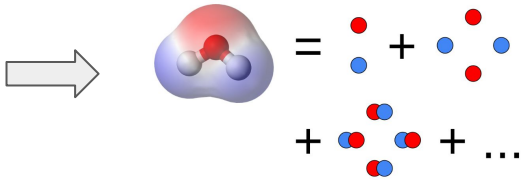
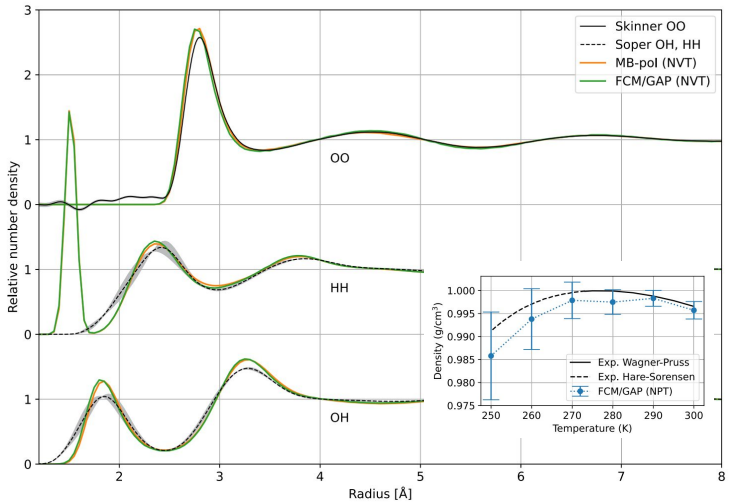


FCM-GAP water model

CCSD(T)

SAPT





J. Öström and L. G. M. Pettersson, *J. Chem. Phys.* 163, (2025)

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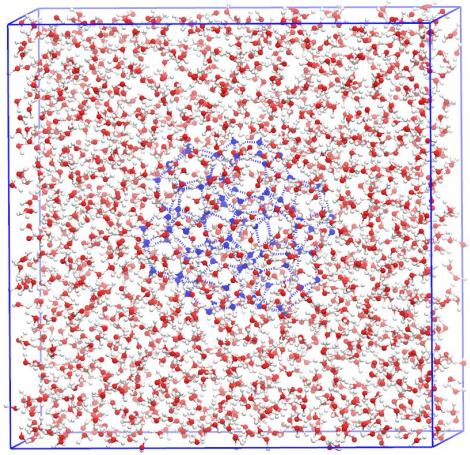

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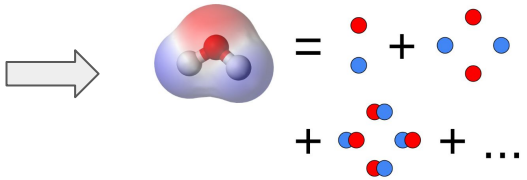
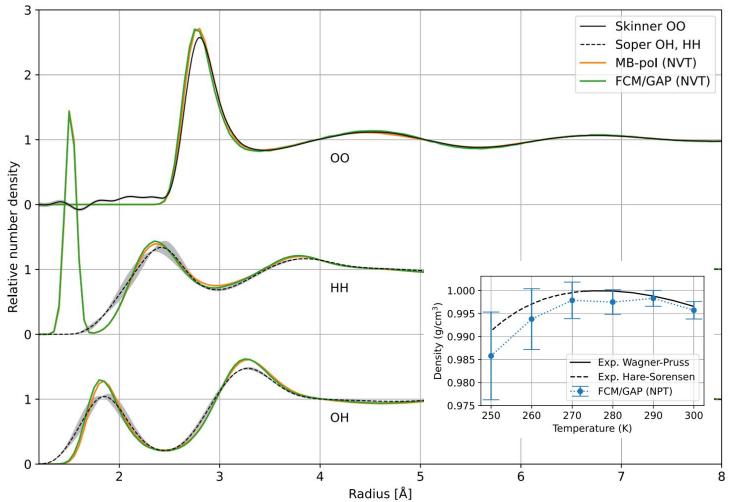




High computational cost - Limited to system size ~100 molecules

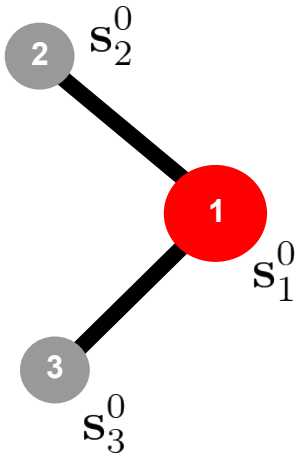
J. Öström and L. G. M. Pettersson, *J. Chem. Phys.* 163, (2025)

How can we extend the limits of the FCM-GAP water model?

Polarizable atom interaction neural network (PAINN)

Initialization

$$\mathbf{s}_i^0 \in \mathbb{R}^d$$



K. T. Schütt, O. T. Unke, M, Gastegger, *Proceedings of the 38 th International Conference on Machine Learning, PMLR,* 139, (2021).

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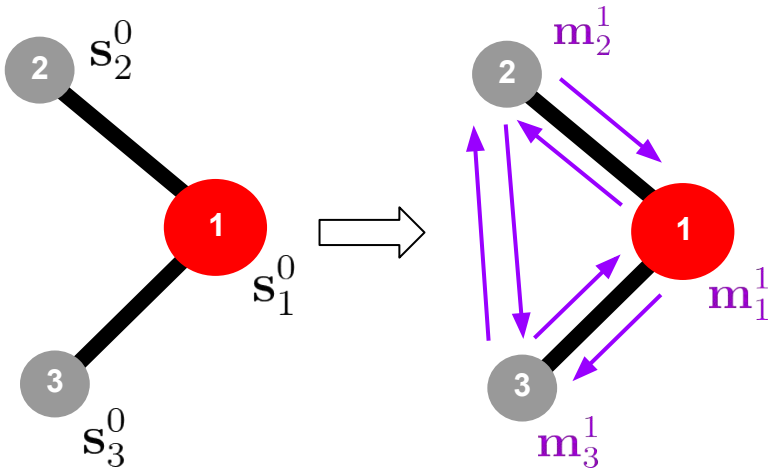
$$\mathbf{m}_i^{t+1} = \sum_{j \in N(i)} \mathbf{M}_t(\mathbf{s}_i^t, \mathbf{s}_j^t, \vec{r}_{ij})$$



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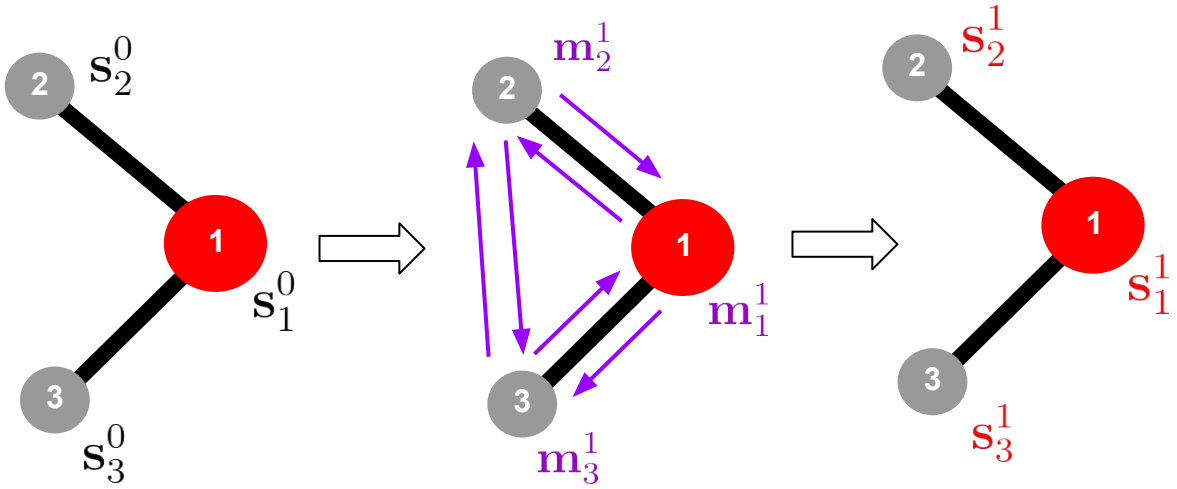

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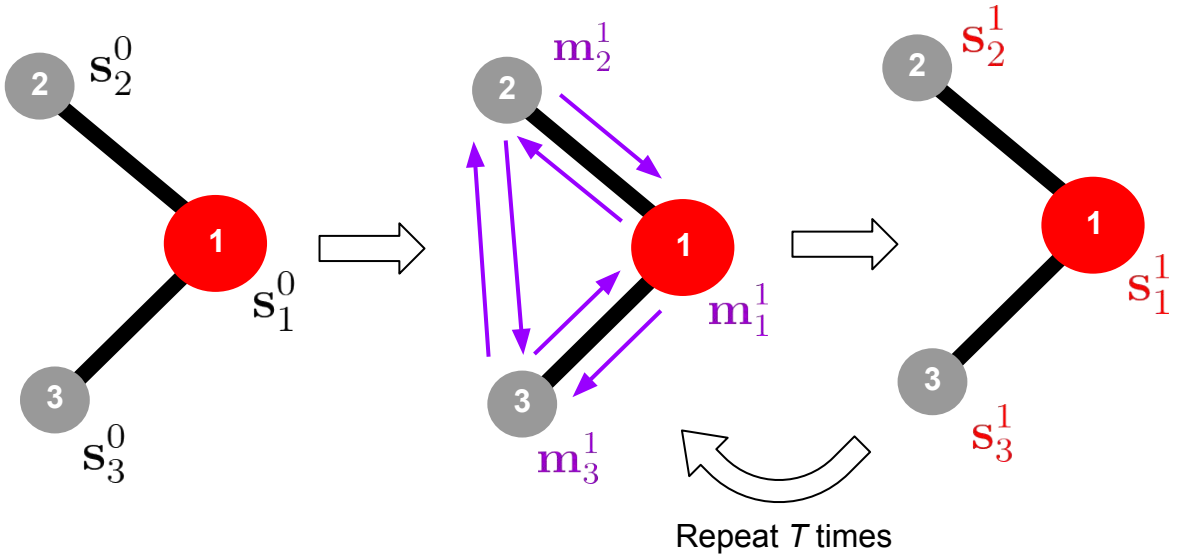

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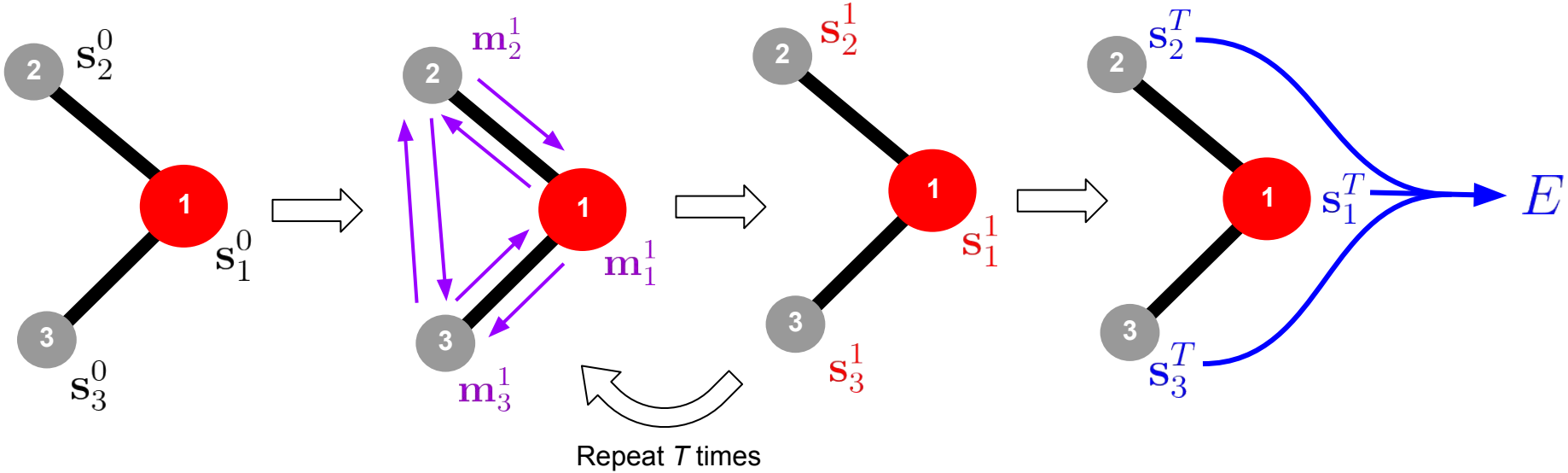
$$E = \sum_i \epsilon(\mathbf{s}_i^T)$$



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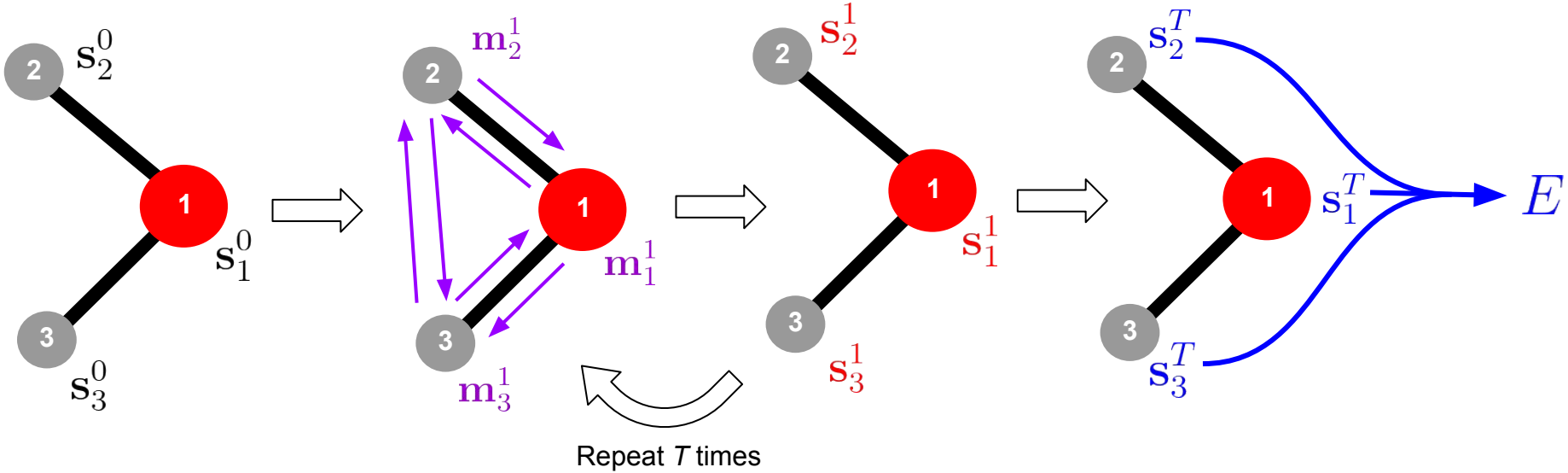
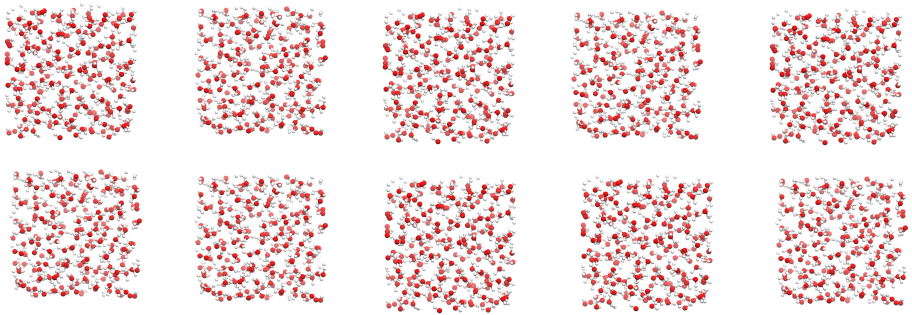


PAINN uses both *invariant* and *equivariant* features

K. T. Schütt, O. T. Unke, M, Gastegger, *Proceedings of the 38 th International Conference on Machine Learning, PMLR,* 139, (2021).

Data set

FCM-GAP: Potential energy, force and stress



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- Bulk MD frames
- Fused dodecahedra
- Distorted geometries

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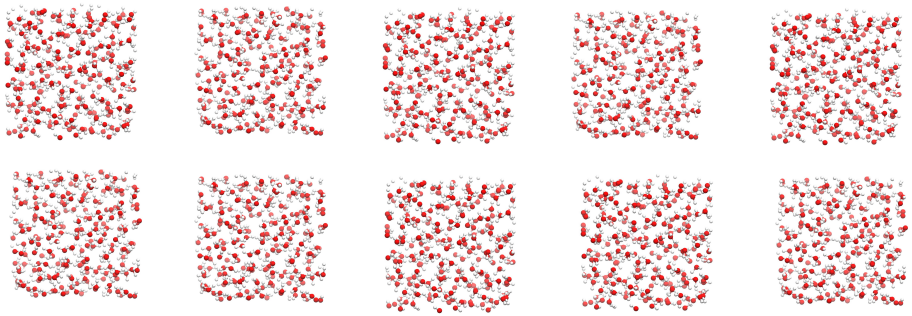

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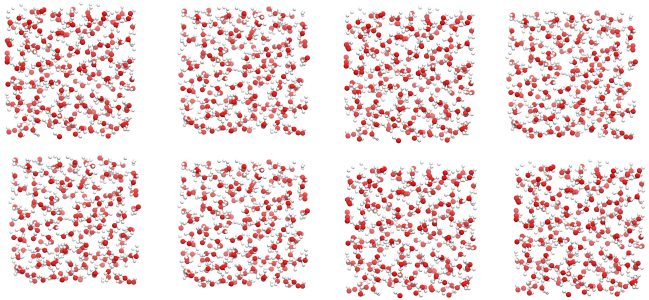
Training set: 80 %



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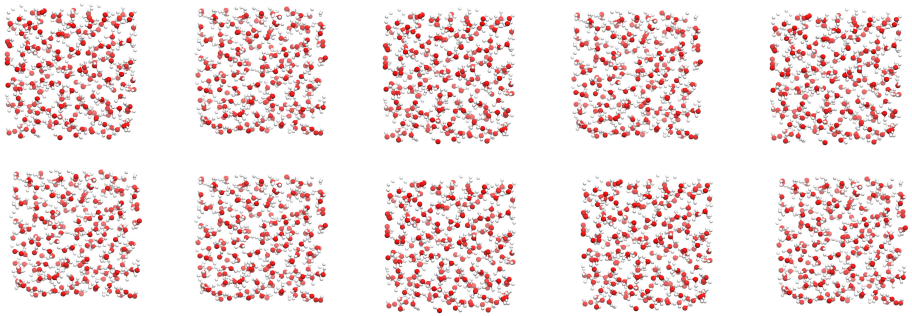

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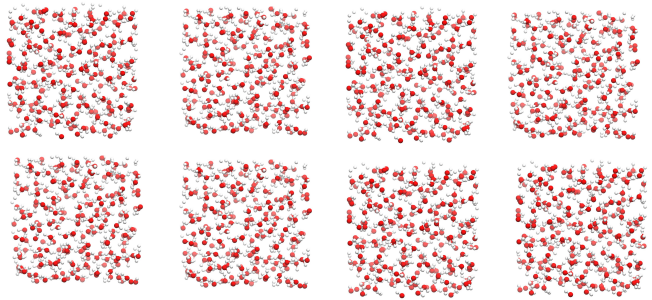
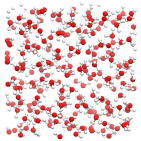


Validation set: 10 %



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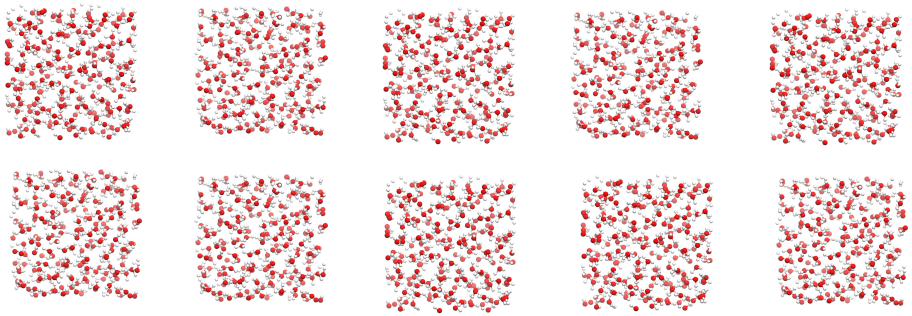

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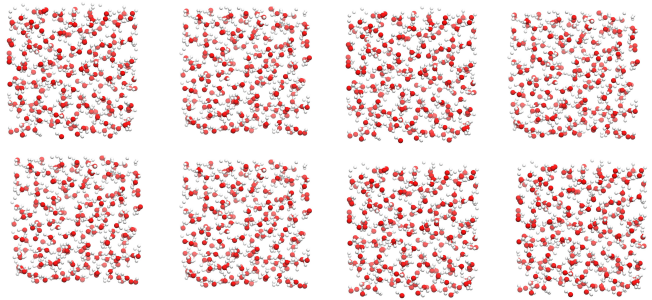

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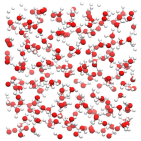
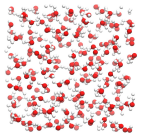


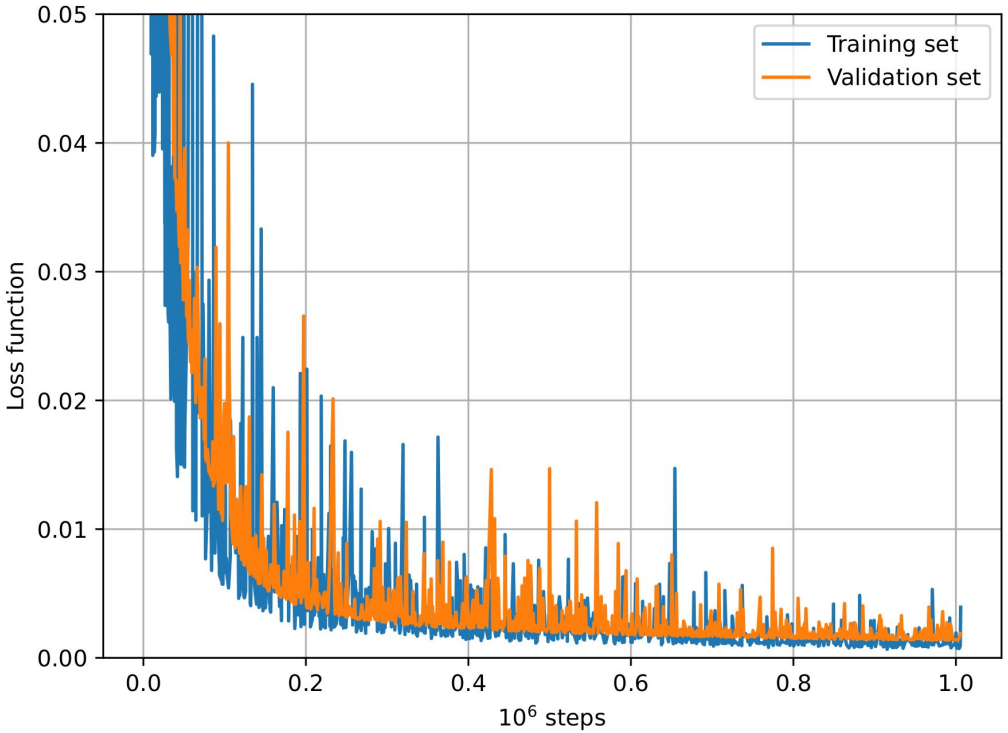
Test set: 10 %



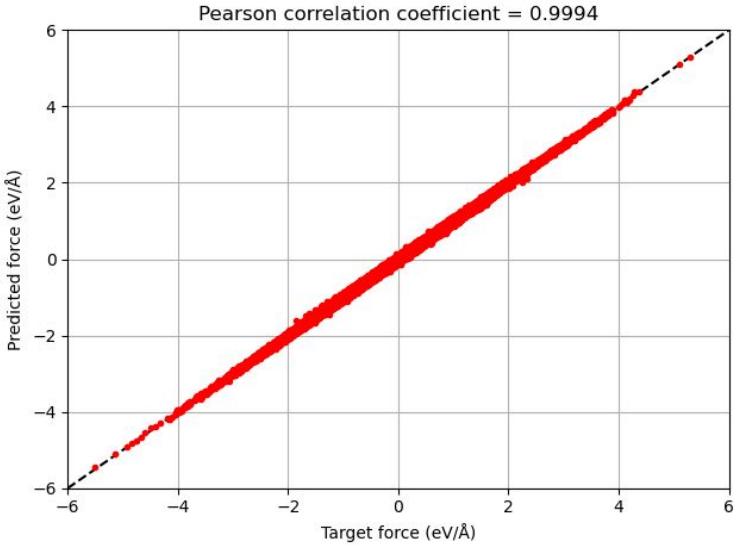
Training

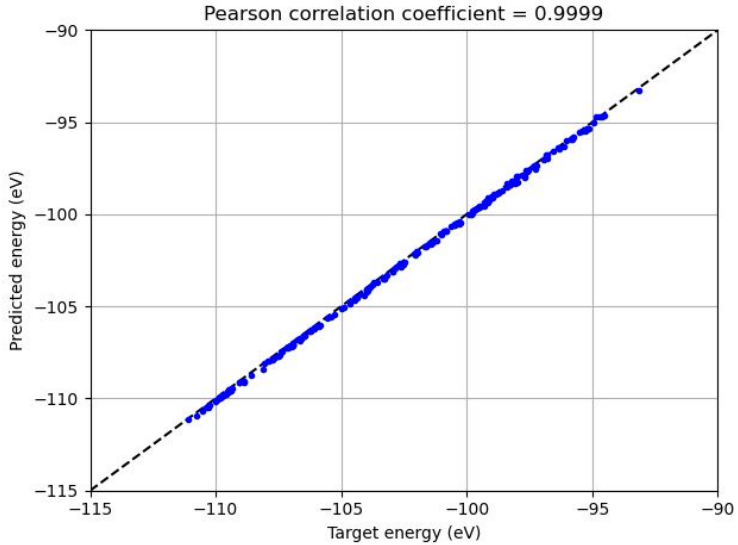
$$L = c_1 MSE_{\text{Force}} + c_2 MSE_{\text{Energy}} + c_3 MSE_{\text{Stress}}$$

$$c_1 = 0.90 \qquad c_2 = 0.01 \qquad c_3 = 0.09$$



Accuracy of ML potential





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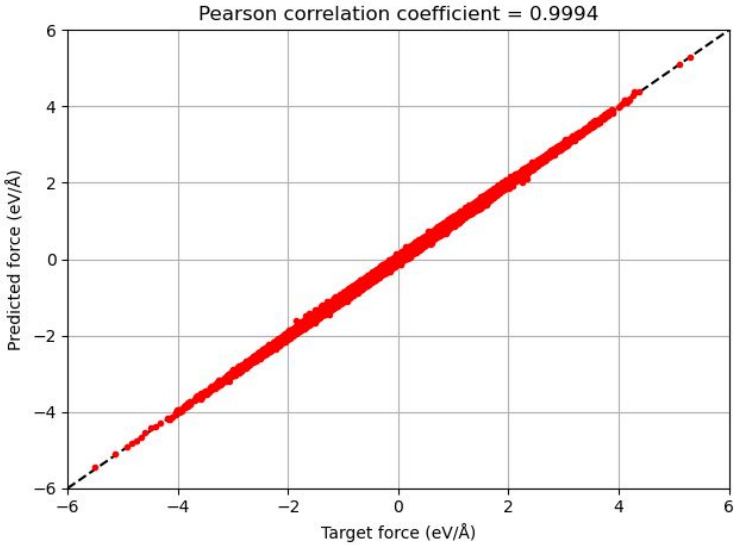

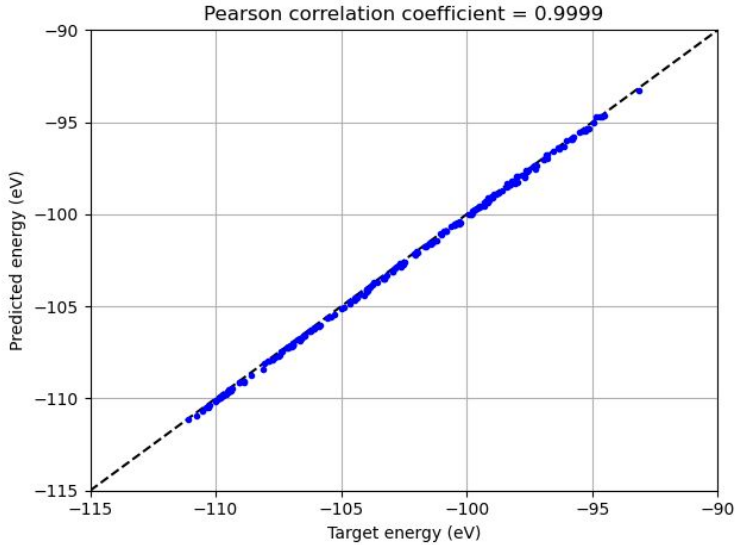

Metric	Train	Validation	Test
Energy MAE (eV)	0.116 ± 0.069	0.122 ± 0.066	0.121 ± 0.066
Energy ME (eV)	0.396	0.304	0.314
Force MAE (scalar) (eV/Å)	0.019 ± 0.016	0.019 ± 0.016	0.019 ± 0.016
Force ME (scalar) (eV/Å)	0.458	0.296	0.259
Force MAE (vector) (eV/Å)	0.038 ± 0.020	0.038 ± 0.020	0.038 ± 0.020
Force ME (vector) (eV/Å)	0.476	0.366	0.346

Are these errors small enough?

Force error analysis

$$\mathbf{F}_i = \mathbf{F}_i^{\text{FCM-GAP}} + \lambda \hat{\mathbf{R}}_i$$ ⟵ Random unit vector

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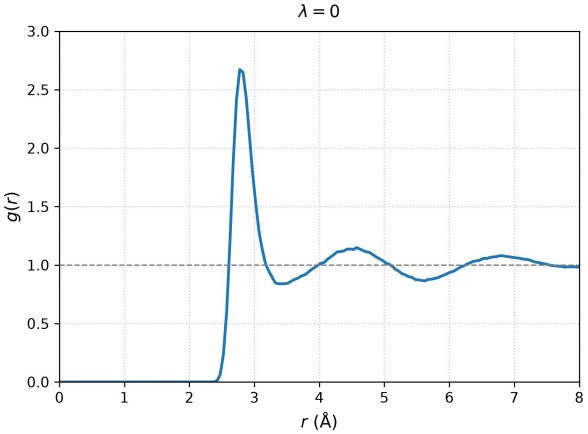

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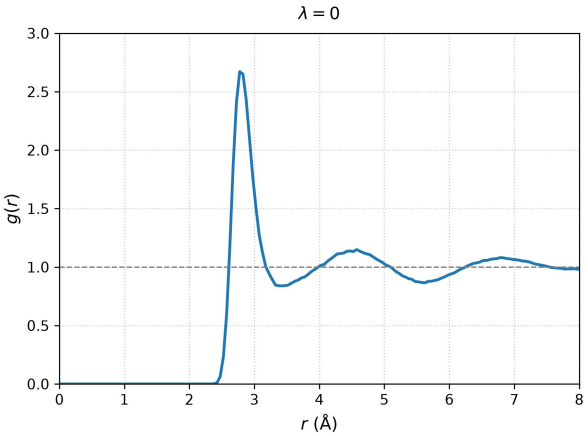

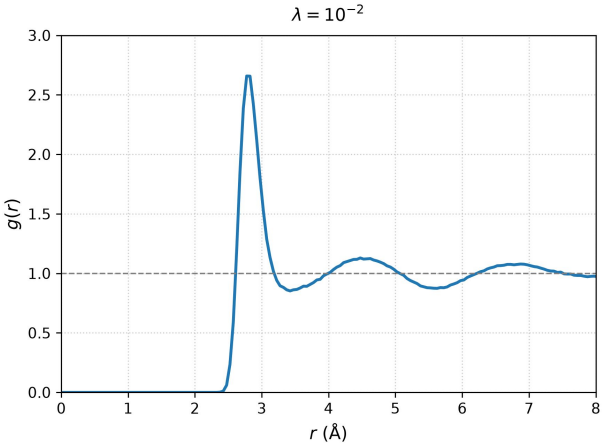

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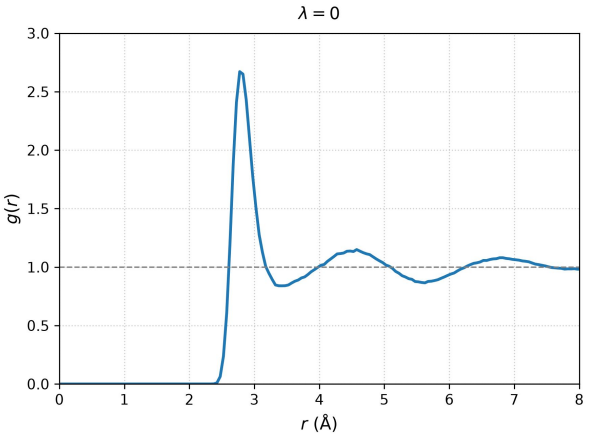

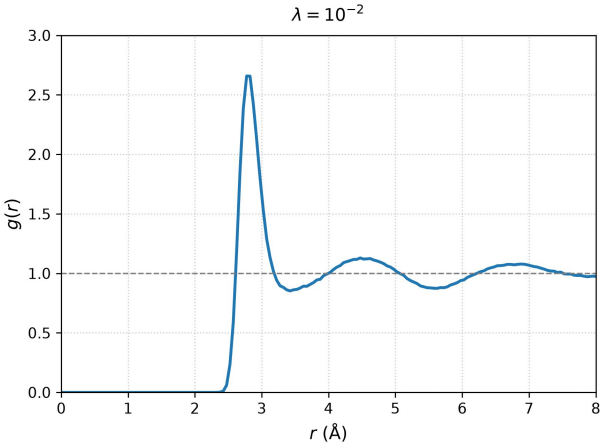

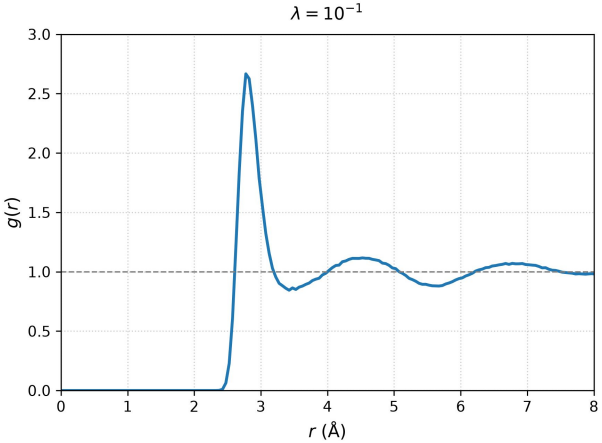

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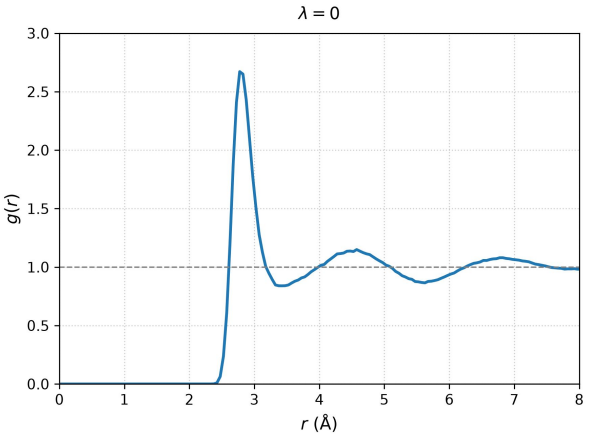
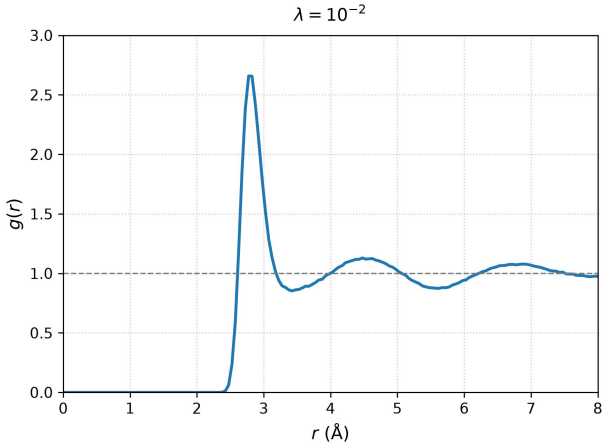
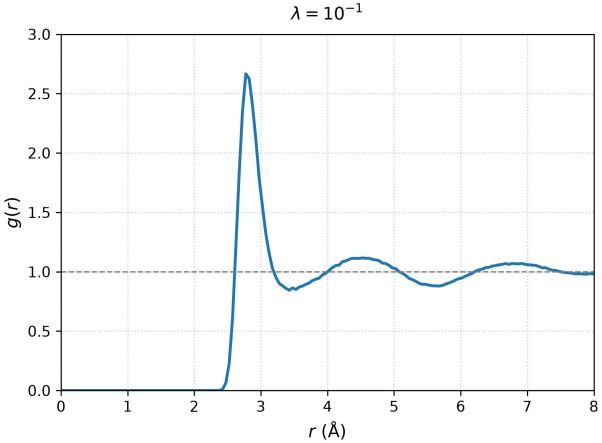
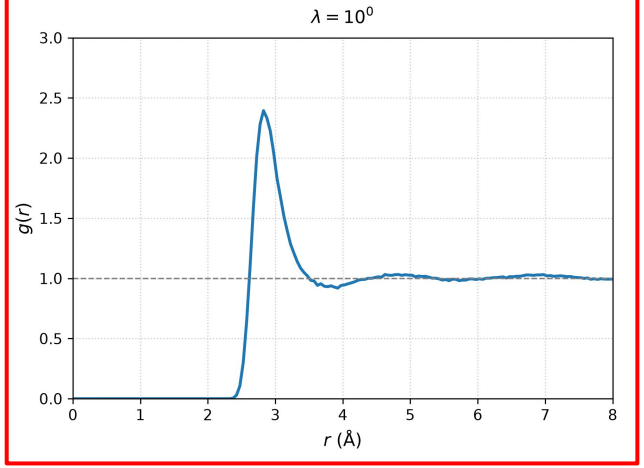


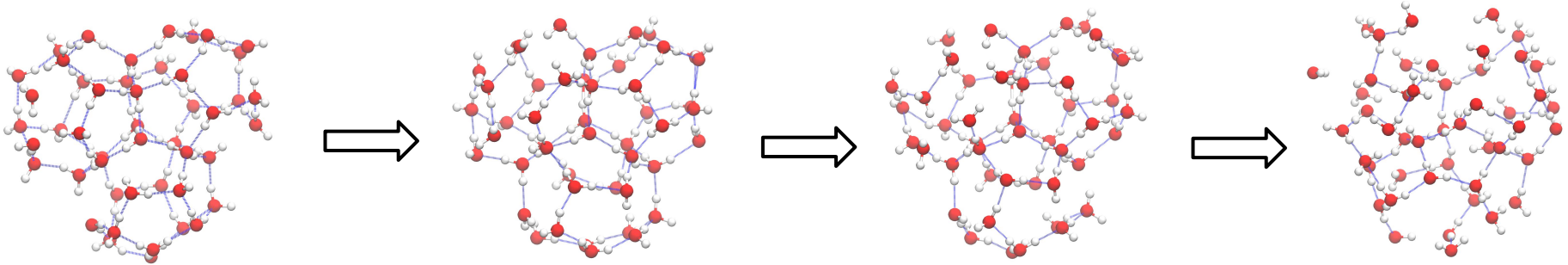






MD simulations of LDL motifs

Life-time of LDL motifs in ambient liquid



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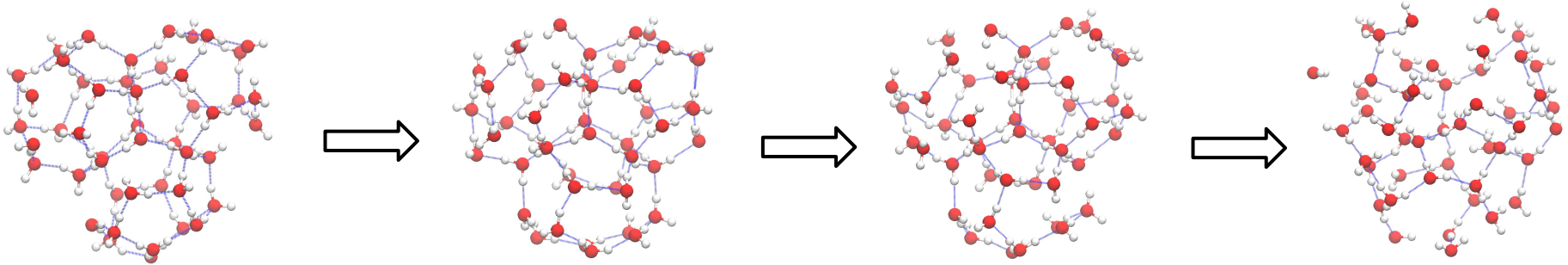

~ 10 picosecond time scale

Soft equilibration is needed

Conclusions

- The origin of water’s anomalies is a HDL-LDL transition and a liquid-liquid critical point

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- The model allows us to perform accurate simulations of LDL motifs in bulk water
- Fused dodecahedra have a life-time of ~10 ps
- Future work will provide estimates for the abundance of different LDL motifs in ambient water

Acknowledgement

Principal investigator

Prof. Lars G. M. Pettersson

Machine learning expert

Dr. Mathias Ljungberg

Developer of FCM-GAP

Dr. Jonatan Öström

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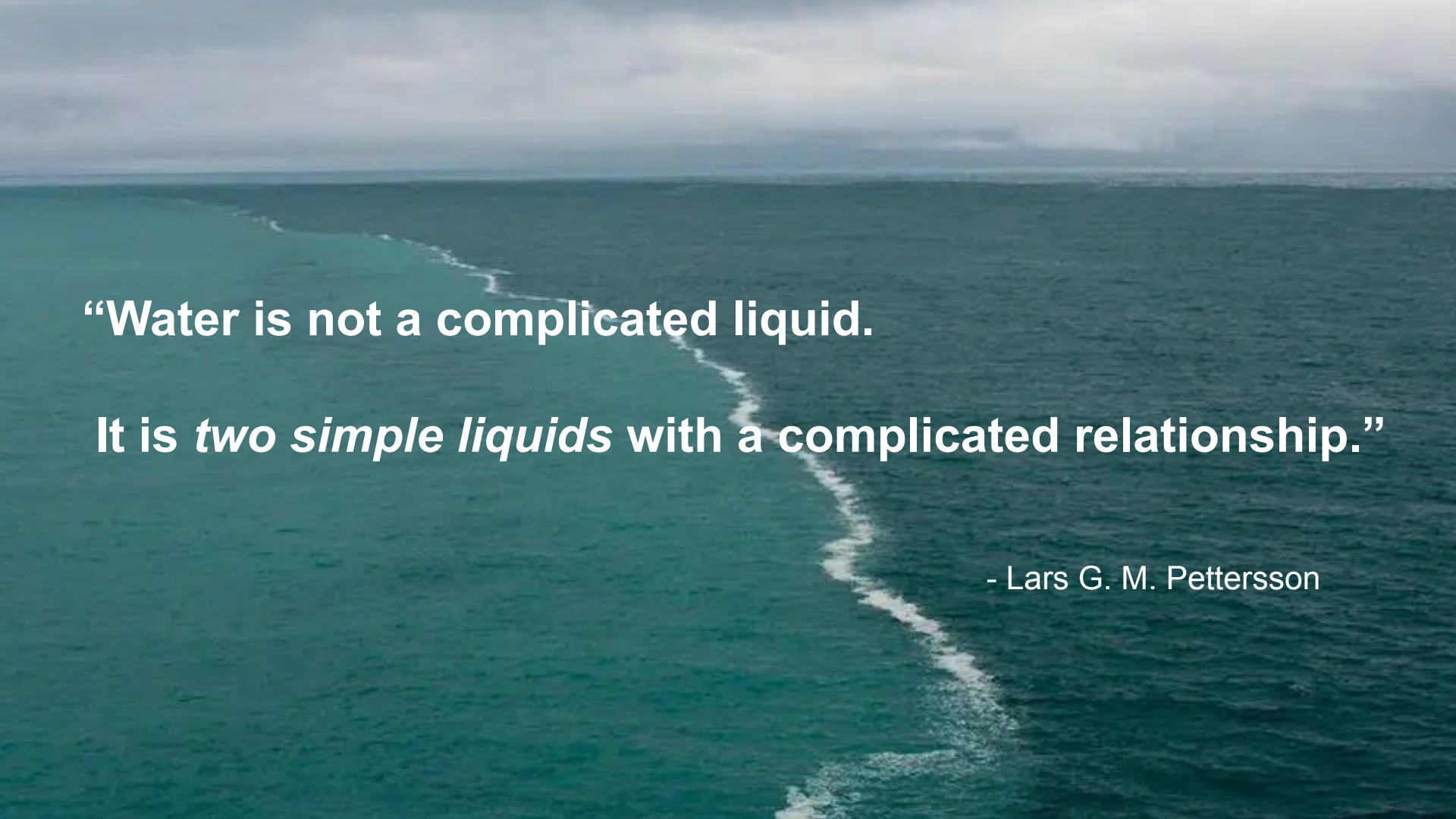
“Water is not a complicated liquid.
It is *two simple liquids* with a complicated relationship.”
- Lars G. M. Pettersson