The liquid-vapour interface of QDO water

Flaviu Cipcigan Andrew Jones Jason Crain
Vlad Sokhan Glenn Martyna

The liquid-vapour interface of QDO water

1. Molecular models
2. The Quantum Drude Oscillator (QDO)
3. Introducing QDO water
4. Liquid-vapour interface of QDO water


ARCHITECTURE: 1950

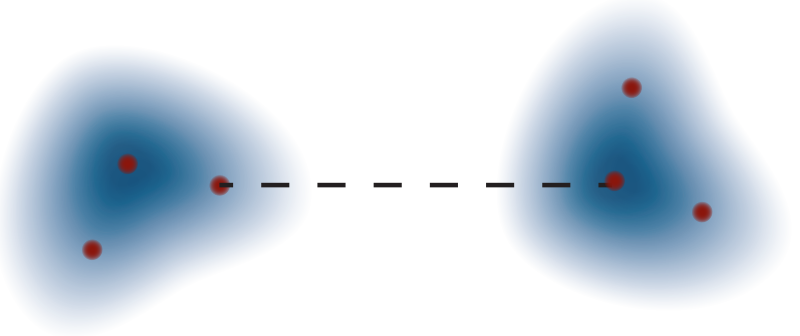

ARCHITECTURE: NOW

The liquid-vapour interface of QDO water

1. **Molecular models**
2. The Quantum Drude Oscillator (QDO)
3. Introducing QDO water
4. Liquid-vapour interface of QDO water

Challenge

efficiently model intermolecular interactions



Challenge

efficiently model intermolecular interactions

Solution

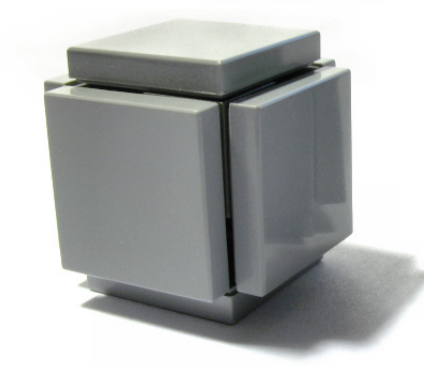
begin with simple building blocks

Challenge

efficiently model intermolecular interactions

Solution

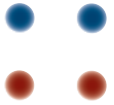
begin with simple building blocks and assemble them into molecules



Molecular building blocks

Molecular building blocks

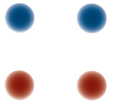
Electrostatics



Point charges

Molecular building blocks

Electrostatics



Point charges

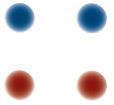
Constraints

Translational

Rotational

Molecular building blocks

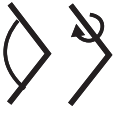
Electrostatics



Point charges

Constraints

Translational



Rotational

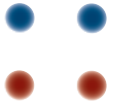
Non-Coulomb forces

van der Waals

repulsion

Molecular building blocks

Electrostatics



Point charges

Constraints

Translational

Rotational

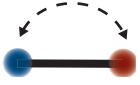
Non-Coulomb forces

van der Waals

repulsion

Response (limited)

Fluctuating dipole



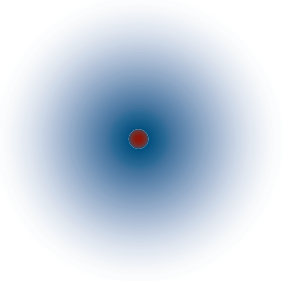
Charge transfer

The liquid-vapour interface of QDO water

1. Molecular models
2. **The Quantum Drude Oscillator (QDO)**
3. Introducing QDO water
4. Liquid-vapour interface of QDO water

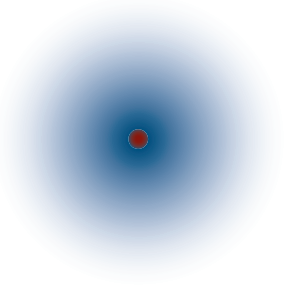
Quantum Drude Oscillator (QDO)

Light negative particle tethered harmonically
to a heavy positive, oppositely charged nucleus



Quantum Drude Oscillator (QDO)

Light negative particle tethered harmonically
to a heavy positive, oppositely charged nucleus



Free parameters

μ reduced mass

ω spring frequency

q charge

Quantum Drude Oscillator: Response

Polarisation $\alpha_l = \underbrace{\left[\frac{q^2}{\mu\omega^2}\right]}_{\text{dipole}} \left[\frac{(2l-1)!!}{l}\right] \left[\frac{\hbar}{2\mu\omega}\right]^{l-1}$

Quantum Drude Oscillator: Response

Polarisation

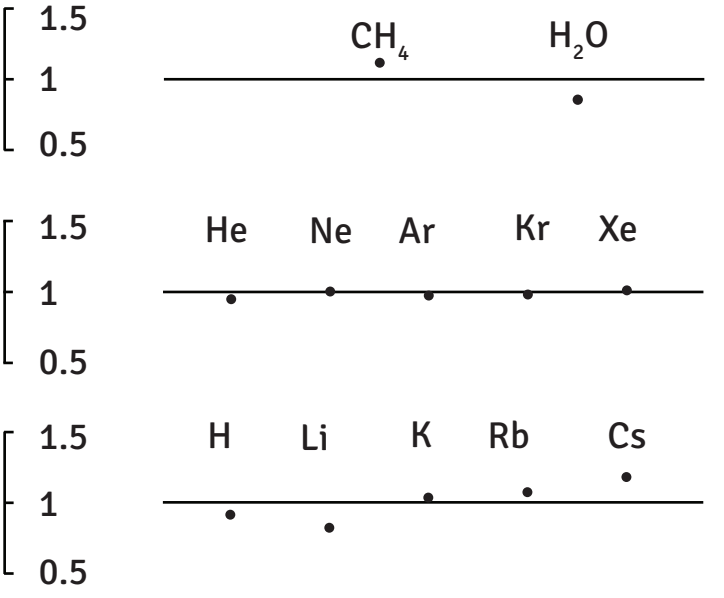
$$\alpha_l = \underbrace{\left[\frac{q^2}{\mu\omega^2}\right]}_{\text{dipole}} \left[\frac{(2l-1)!!}{l}\right] \left[\frac{\hbar}{2\mu\omega}\right]^{l-1}$$

Dispersion

$$C_6 = \frac{3}{4}\alpha_1\alpha_1\hbar\omega \quad \text{dipole-dipole}$$

$$C_8 = 5\alpha_1\alpha_2\hbar\omega \quad \text{dipole-quadrupole}$$

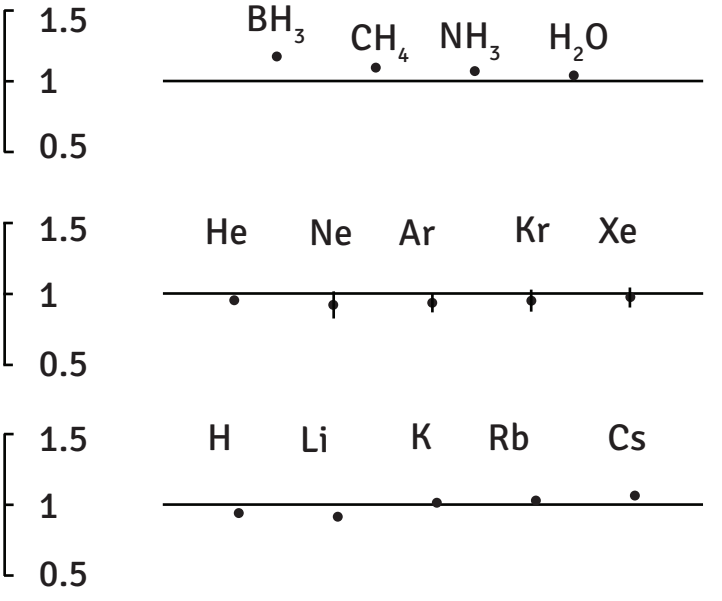
Quantum Drude Oscillator: Invariants



Polarisation

$$\sqrt{\frac{20}{9}}\frac{\alpha_2}{\sqrt{\alpha_1\alpha_3}} = 1$$

Quantum Drude Oscillator: Invariants

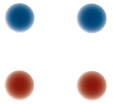


Dispersion

$$\sqrt{\frac{49}{40}}\frac{C_8}{\sqrt{C_6 C_{10}}} = 1$$

Molecular building blocks

Electrostatics



Point charges

Constraints

Translational

Rotational

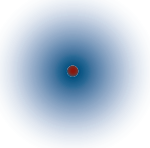
Non-Coulomb forces

van der Waals

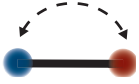
repulsion

Response

Fluctuating dipole



Quantum Drude Oscillator



Charge transfer

The liquid-vapour interface of QDO water

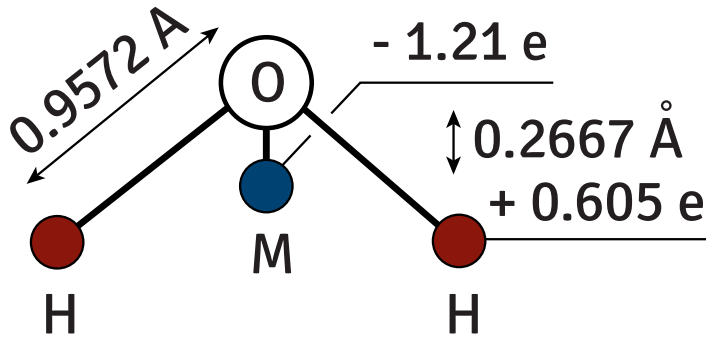
1. Molecular models
2. The Quantum Drude Oscillator (QDO)
3. **Introducing QDO water**
4. Liquid-vapour interface of QDO water

The liquid-vapour interface of QDO water

1. Molecular models
2. The Quantum Drude Oscillator (QDO)
3. **Introducing QDO water**
   - Frame
   - QDO
   - Repulsion
   - Damping
   - Sampling
4. Liquid-vapour interface of QDO water

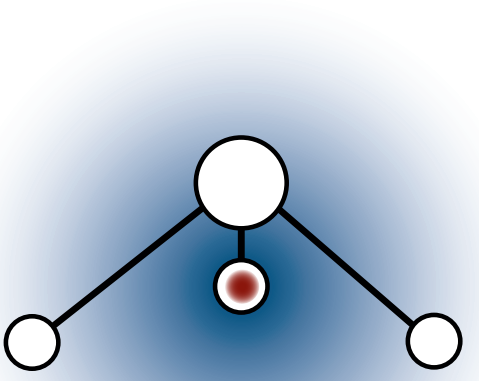
1. Frame

ground state moments



2. QDO

molecular response



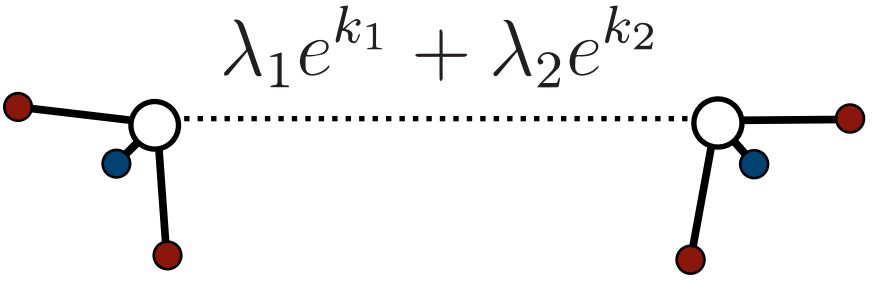
μ = 0.3656 amu

ω = 0.6287 ω_h

q =-1.1973 e

3. Repulsion

Short range correction



4. Electrostatic Damping

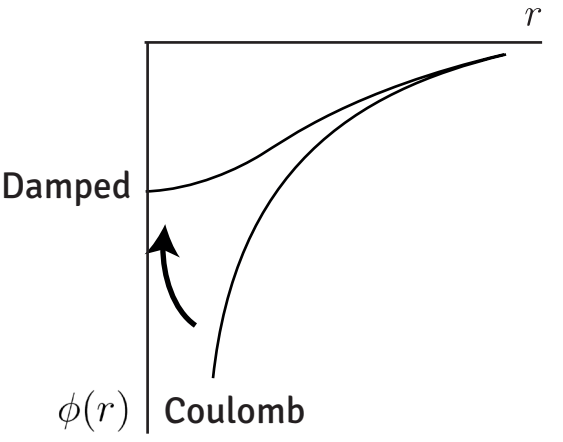
Short range correction

Gaussian charges

$$-\frac{\mathrm{erf}(\gamma r)}{r}$$

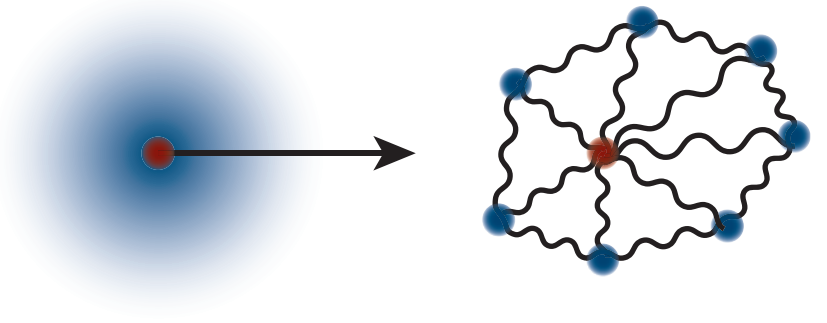
4. Electrostatic Damping

Short range correction



5. Efficient Sampling

Path Integral Molecular Dynamics

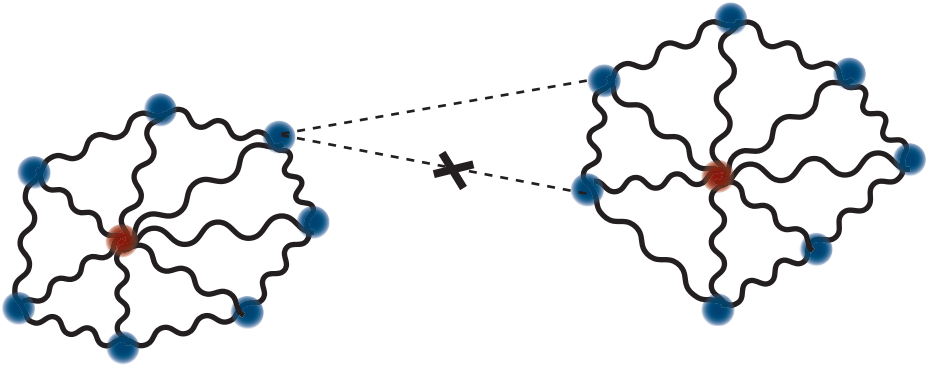


replace electron

with chain of **beads**

5. Efficient Sampling

Path Integral Molecular Dynamics



no cross interactions between beads

The liquid-vapour interface of QDO water

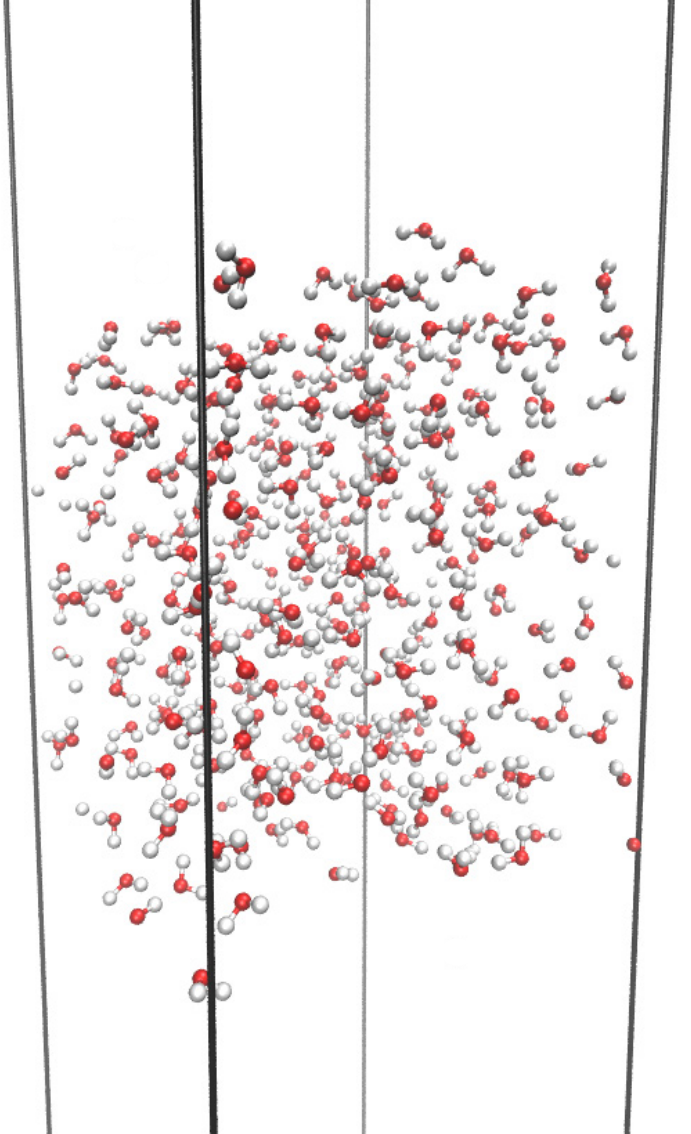
1. Molecular models
2. The Quantum Drude Oscillator (QDO)
3. Introducing QDO water
4. **Liquid-vapour interface of QDO water**

1. Setup

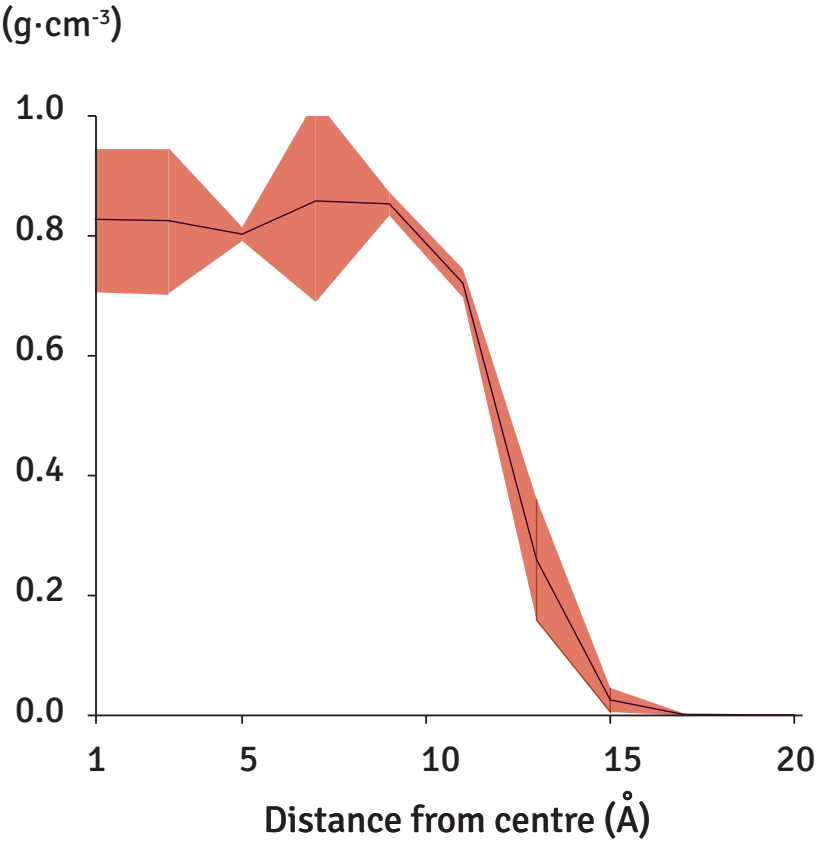
300 QDO-water molecules

Periodic boundaries

Unit cell
20.80126 × 20.80126 × 80 $Å^3$

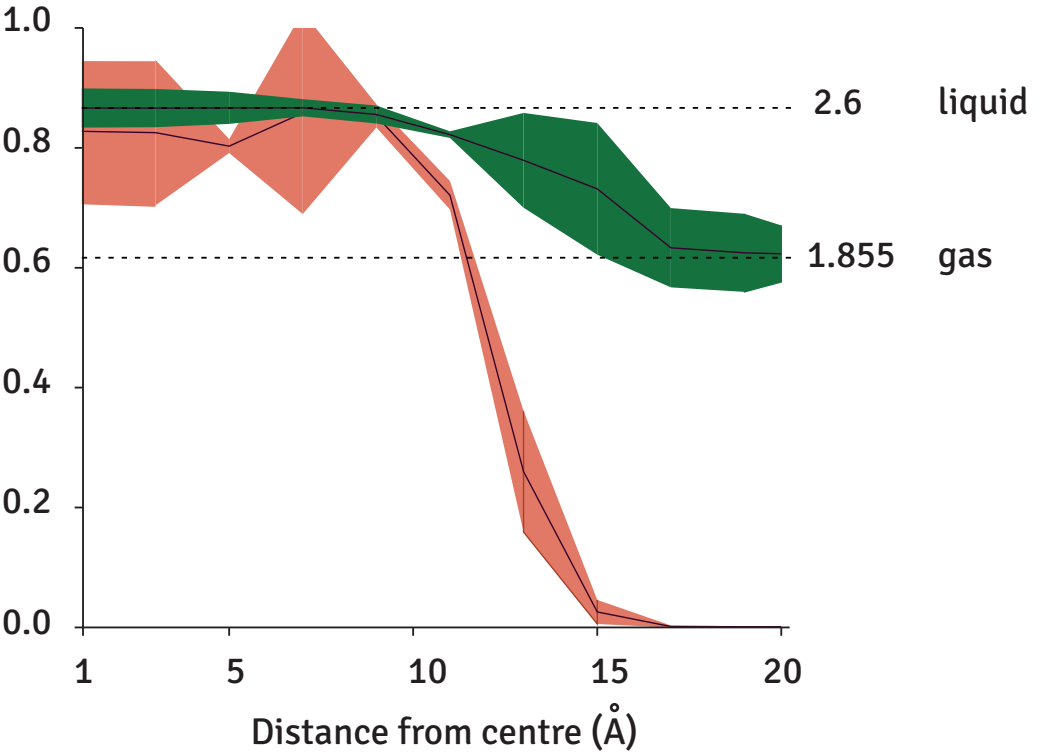


2. Density

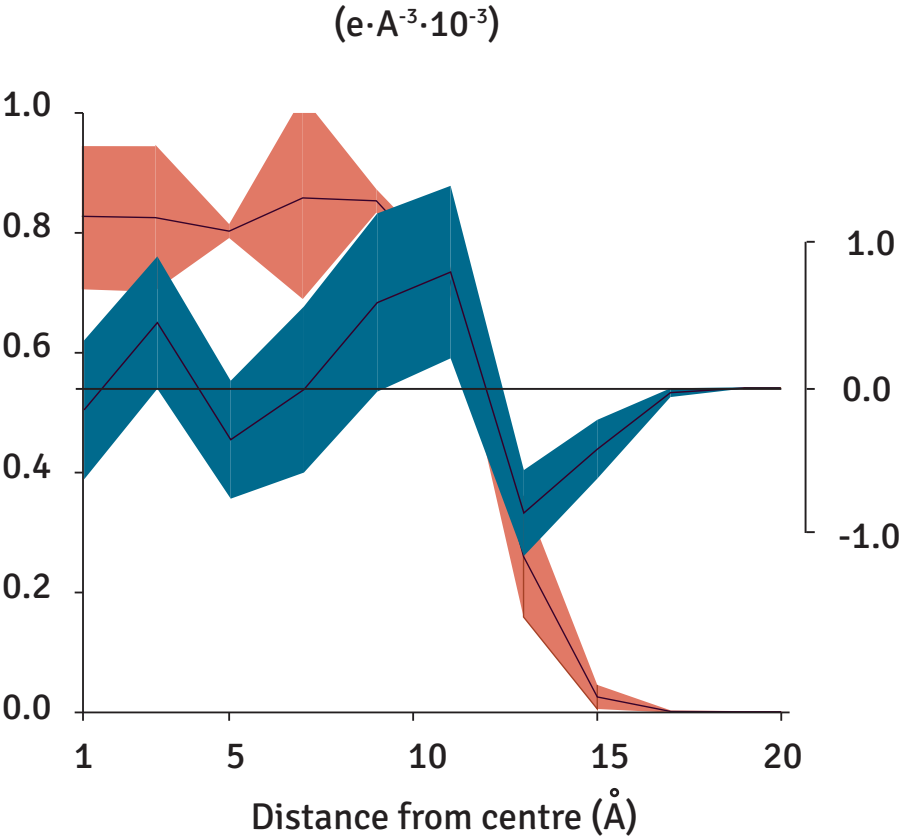


3. Dipole moment

(Debye)

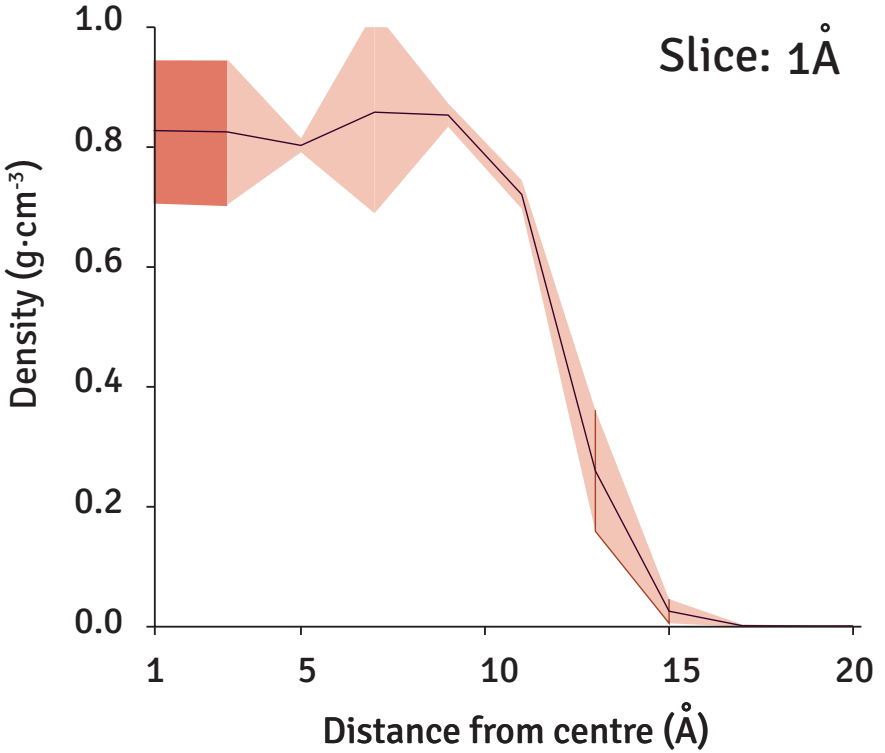


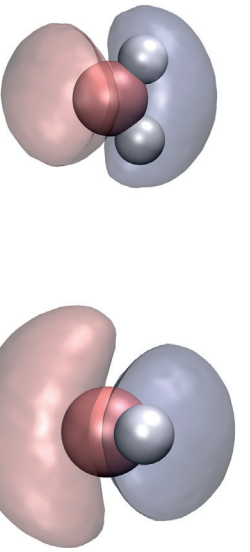
3. Surface charge density



4. Electronic distribution

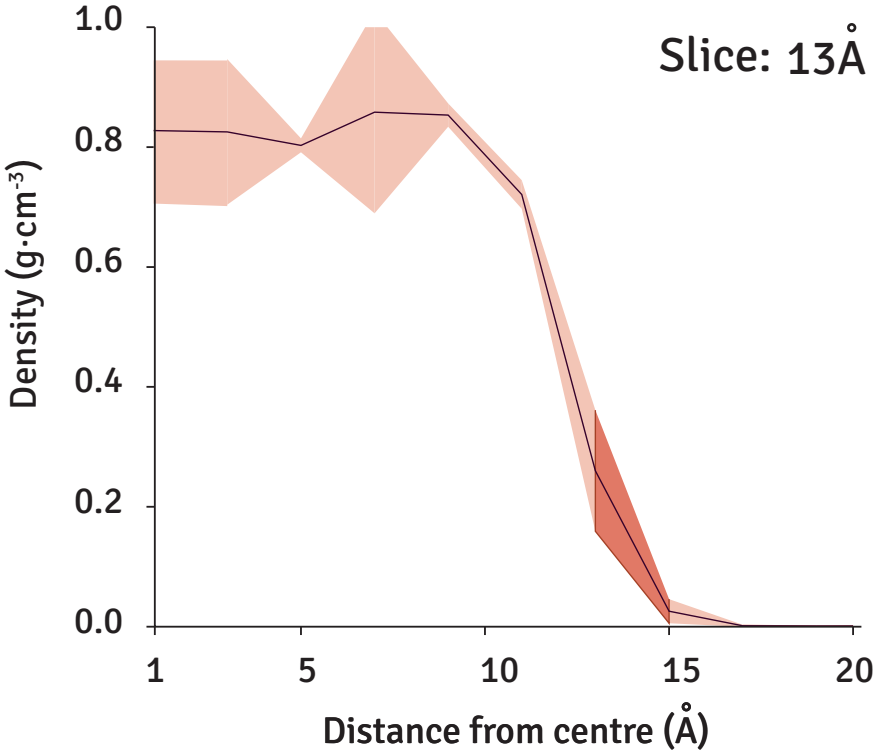
(minus gas phase ground state charge density)

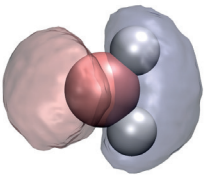


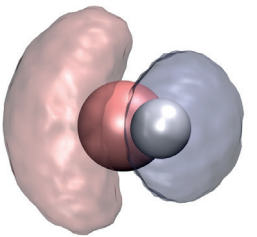


4. Electronic distribution

(minus gas phase ground state charge density)

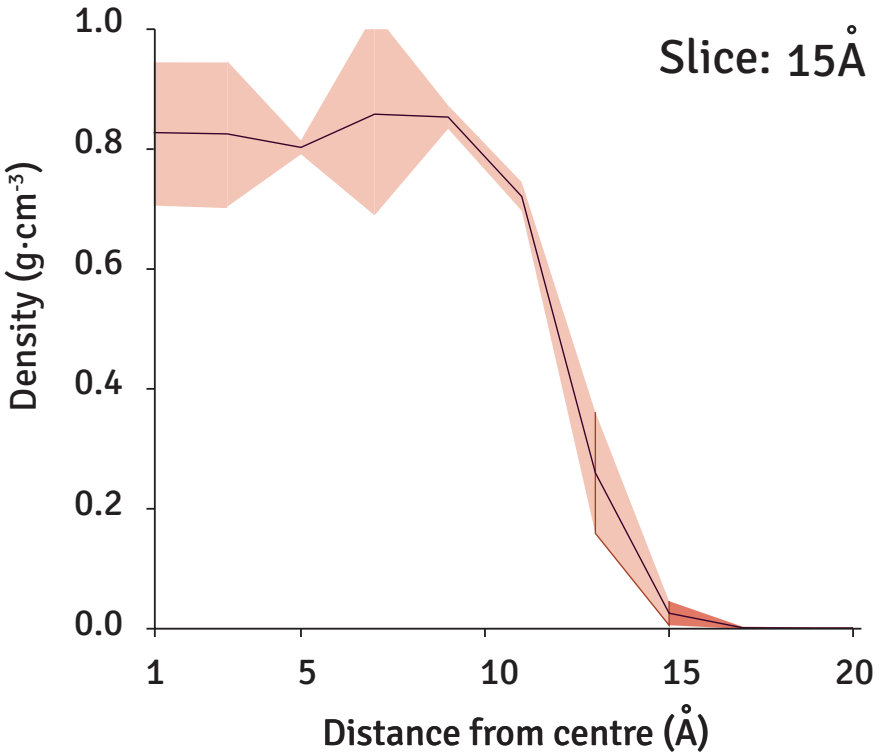


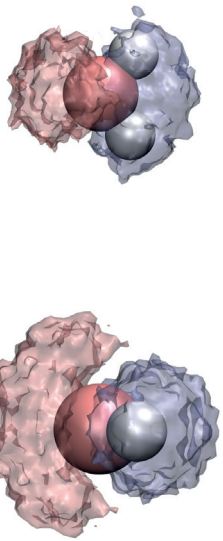




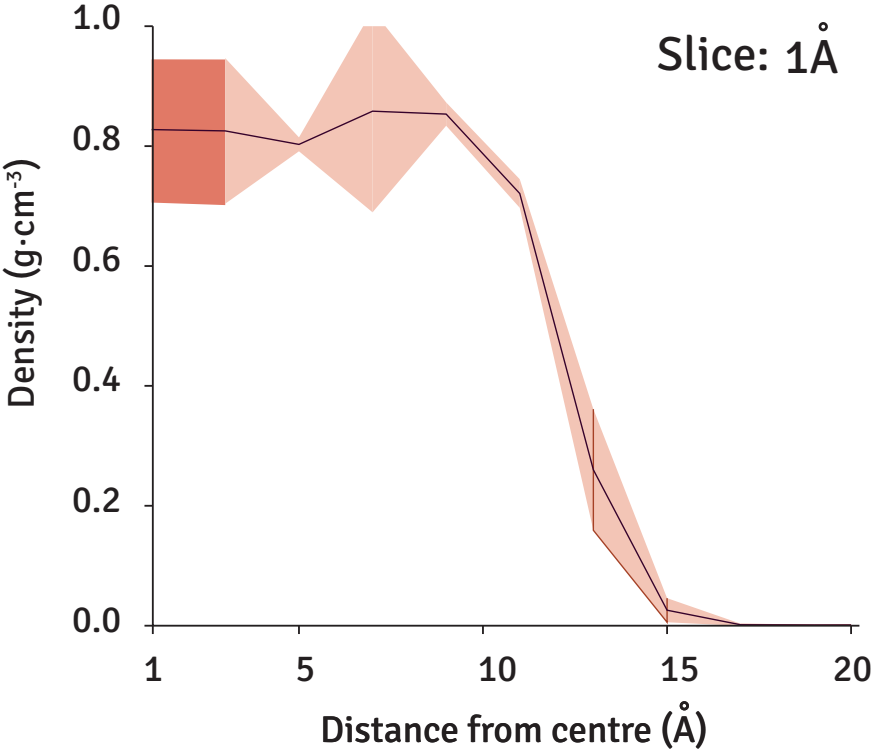
4. Electronic distribution

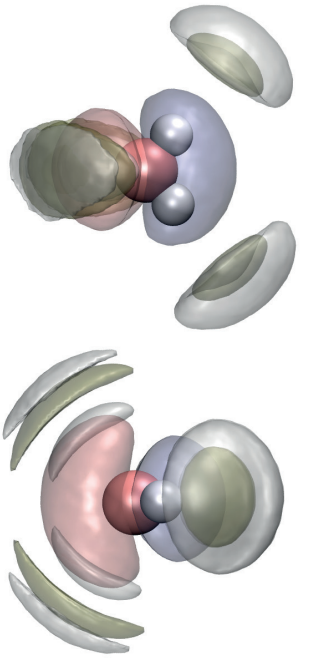
(minus gas phase ground state charge density)



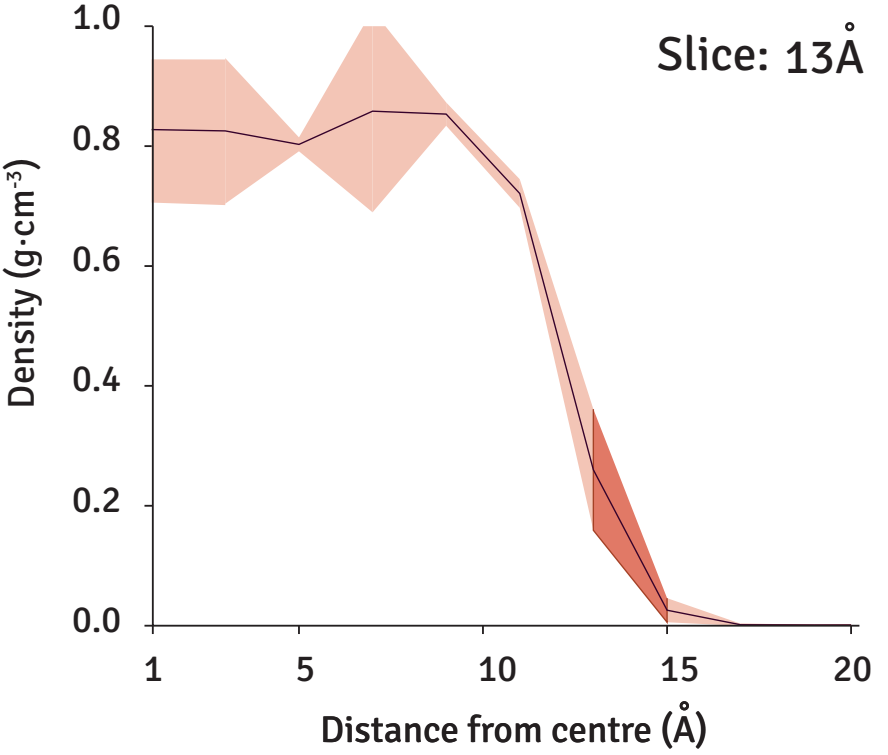


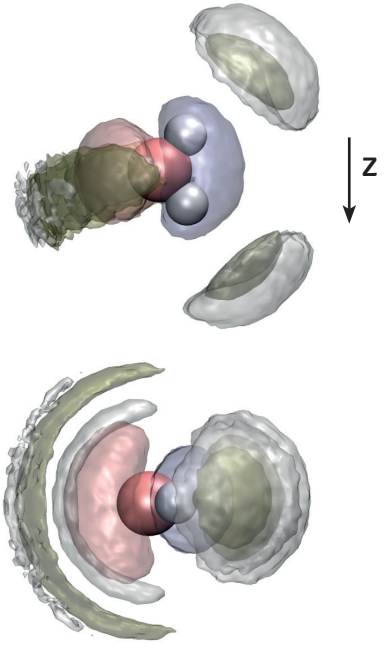
5. Nearest neighbour distribution





5. Nearest neighbour distribution





The liquid-vapour interface of QDO water

1. Molecular models
2. The Quantum Drude Oscillator (QDO)
3. Introducing QDO water
4. Liquid-vapour interface of QDO water

Conclusions

QDOs are an accurate model for long range forces

QDO water has a physical liquid-vapour interface

Next steps

Exploration of the interface's structure and the effects of dispersion and polarisation on physical properties

References

A. Jones, Quantum drude oscillators for accurate many-body intermolecular forces, PhD thesis, The University of Edinburgh

A. Jones, F. Cipcigan, V. Sokhan, J. Crain, G. Martyna, Electronically coarse grained water, PRL (under review)

THE UNIVERSITY *of* EDINBURGH

NPL

National Physical Laboratory

IBM®

Liquid radial distribution function