Electronically coarse grained water

Andrew Jones, **Flaviu Cipcigan**, Vlad Sokhan, Jason Crain, Glenn Martyna

Challenge: extending the transferability of empirical potentials
Our solution: coarse grained electronic structure

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 model for water, PRL 110, 227801 (2013)**

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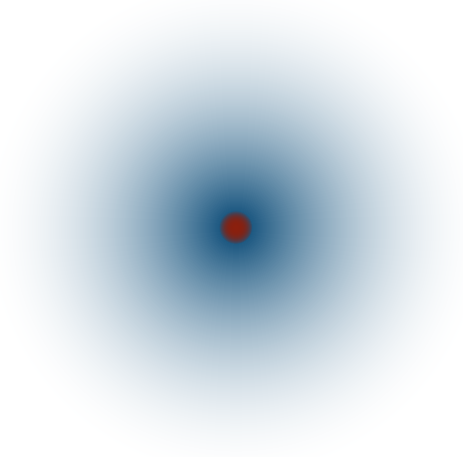
1. Quantum Drude Oscillator (QDO)

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



Free parameters

μ : reduced mass ω : spring constant q : charge

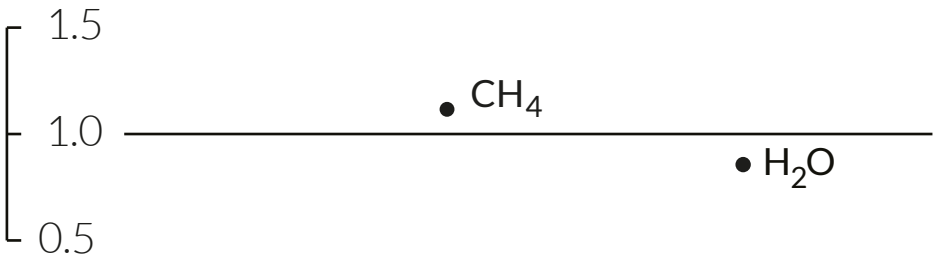
Response

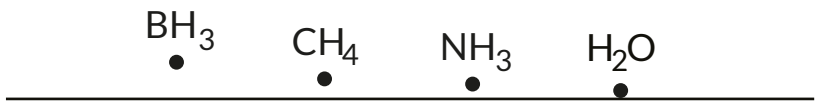
Polarisation: $$\alpha_l = \left[\frac{q^2}{\mu\omega^2}\right]\left[\frac{(2l-1)!!}{l}\right]\left[\frac{\hbar}{2\mu\omega}\right]^{l-1}$$

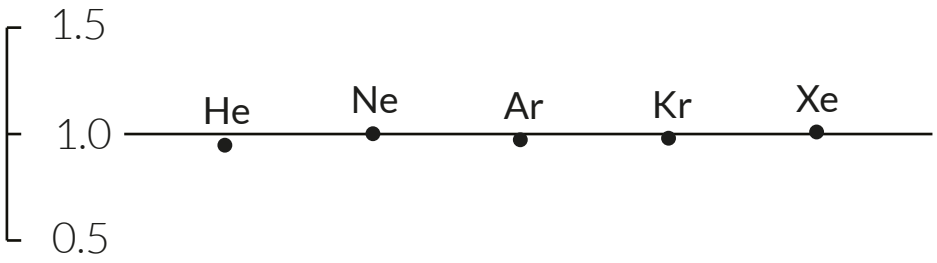
Dispersion:
$$C_6 = \tfrac{3}{4}\alpha_1\alpha_1\hbar\omega,$$
$$C_8 = 5\alpha_1\alpha_2\hbar\omega,$$
$$C_{10} = \left[\tfrac{21}{2}\alpha_1\alpha_3 + \tfrac{70}{4}\alpha_2\alpha_2\right]\hbar\omega$$
$$\ldots$$

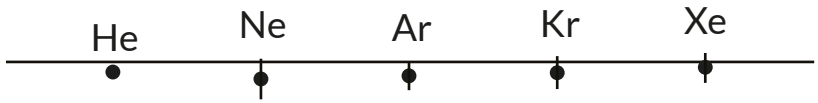
2. Invariants predicted by QDOs

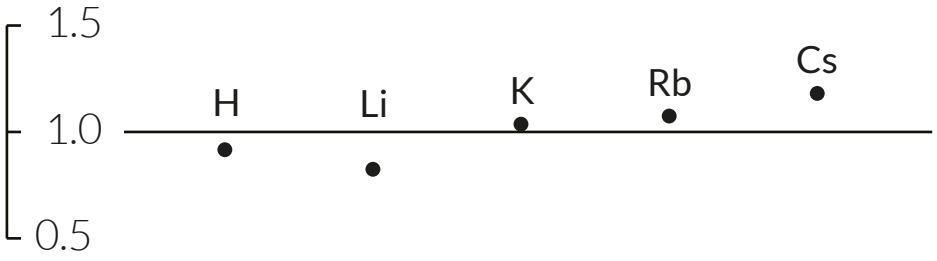
Polarisation: $\sqrt{\frac{20}{9}}\frac{\alpha_2}{\sqrt{\alpha_1\alpha_3}} = 1$ Dispersion: $\sqrt{\frac{49}{40}}\frac{C_8}{\sqrt{C_6C_{10}}} = 1$

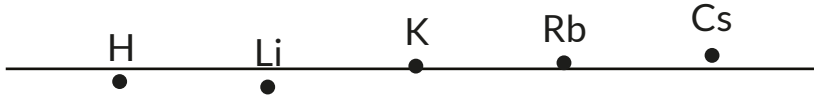






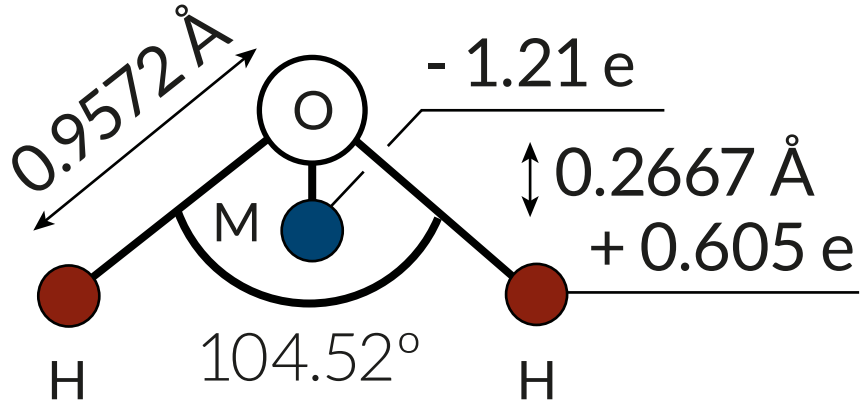




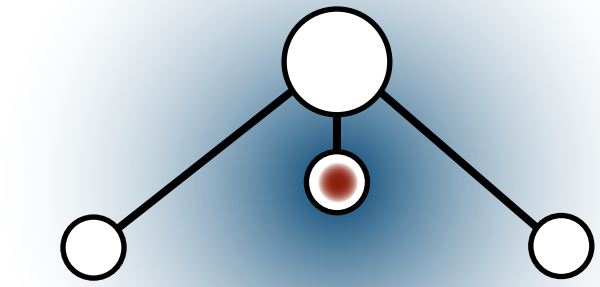


3. QDO-water model

Frame: ground state moments



QDO: molecular response



μ = 0.3656 amu

ω = 0.6287 ω_h

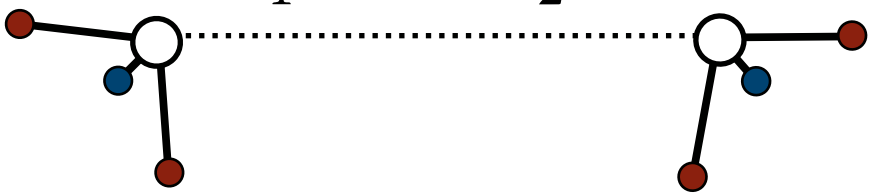
q = -1.1973 e

4. QDO-water model (continued)

Short range interactions

Repulsion

$$\lambda_1 e^{k_1} + \lambda_2 e^{k_2}$$



Electrostatic damping

Gaussian charges

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

5. Efficient sampling: APIMD-QDO

(Adiabatic Path Integral Molecular Dynamics applied to QDOs)

1. Write partition function of N particles as path integral, P slices

$$Z(\beta) = \mathrm{tr}\,\hat{\rho}(\beta) = \int \mathbf{d}^P\vec{x} \prod_{i=1}^{P} \rho(\vec{x}_i, \vec{x}_{i+1}; \tau) \qquad \tau = \beta/P$$

2. Define effective (classical) potential of N×P particles

$$Z(\beta) = \int \mathbf{d}^P\vec{x}\, \exp\left[-\beta\phi_{\mathrm{eff}}\left(\vec{x}_1, \vec{x}_2, \ldots, \vec{x}_P\right)\right]$$

$$\phi_{\mathrm{eff}}\left(\vec{x}_1, \vec{x}_2, \ldots, \vec{x}_P\right) = -\frac{1}{\beta}\sum_{i=1}^{P} \log\left[\rho\left(\vec{x}_i, \vec{x}_{i+1}; \tau\right)\right]$$

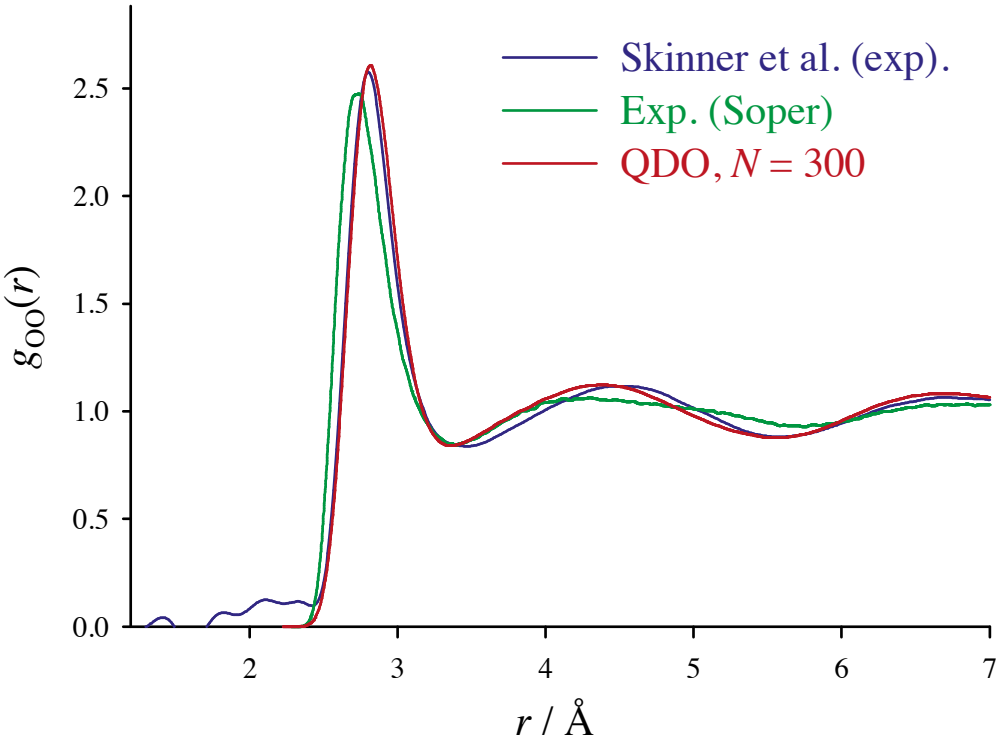
3. Approximate resulting high temperature density matrices

$$\rho(\vec{x}, \vec{x}'; \tau) \equiv \langle\vec{x}|\, e^{-\tau\left(\hat{H}_0 + \hat{V}\right)}\, |\vec{x}'\rangle$$

$$= \langle\vec{x}|\, e^{-\frac{\tau}{2}\hat{V}}\, e^{-\tau\hat{H}_0}\, e^{-\frac{\tau}{2}\hat{V}}\, |\vec{x}'\rangle + \mathcal{O}(\tau^3)$$

6 . Liquid QDO-water

Radial distribution function



Vapour pressure

46 ± 2 kJ / mol

exp: 43.91 kJ/mol

Dielectric constant

79 ± 2

exp: 78

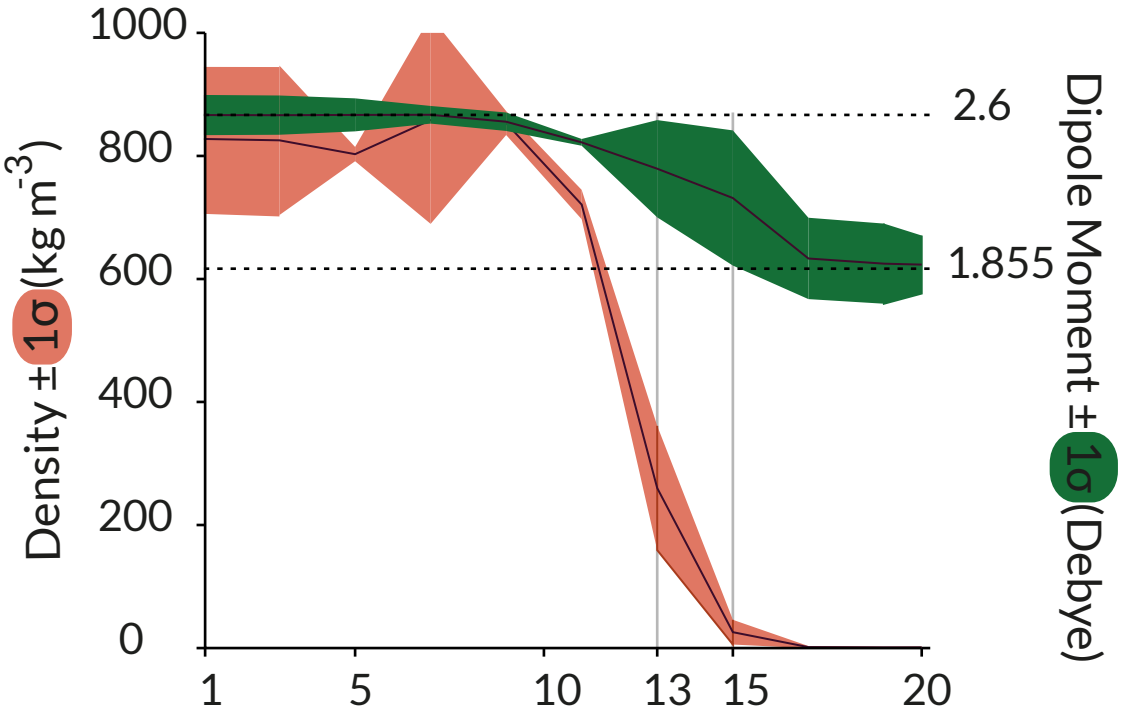
Surface tension

72.6 ± 1 mN / m

exp: 71.73 mN / m

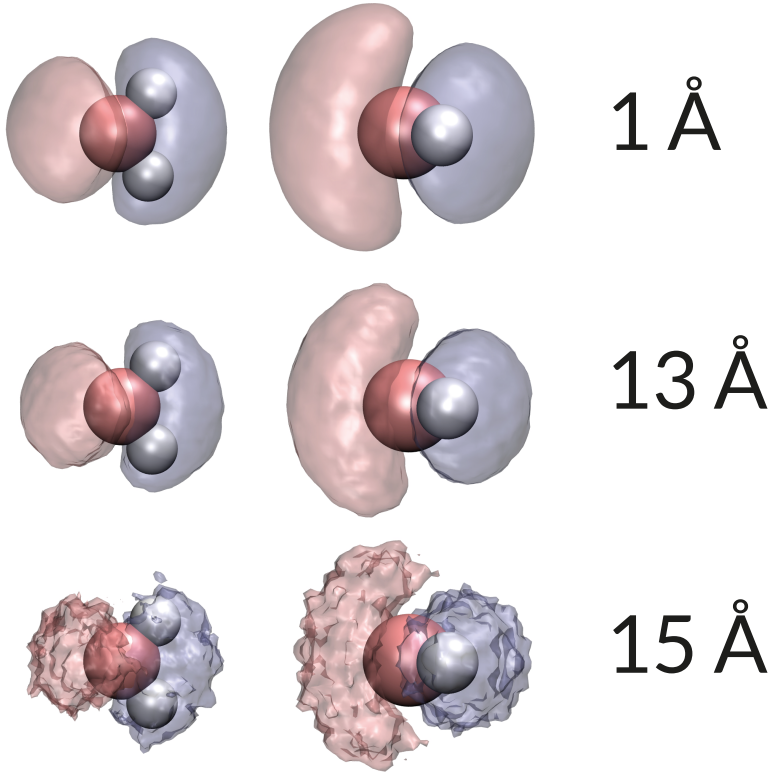
7 . Liquid–vapour interface (unoptimised model)

Density and dipole moment

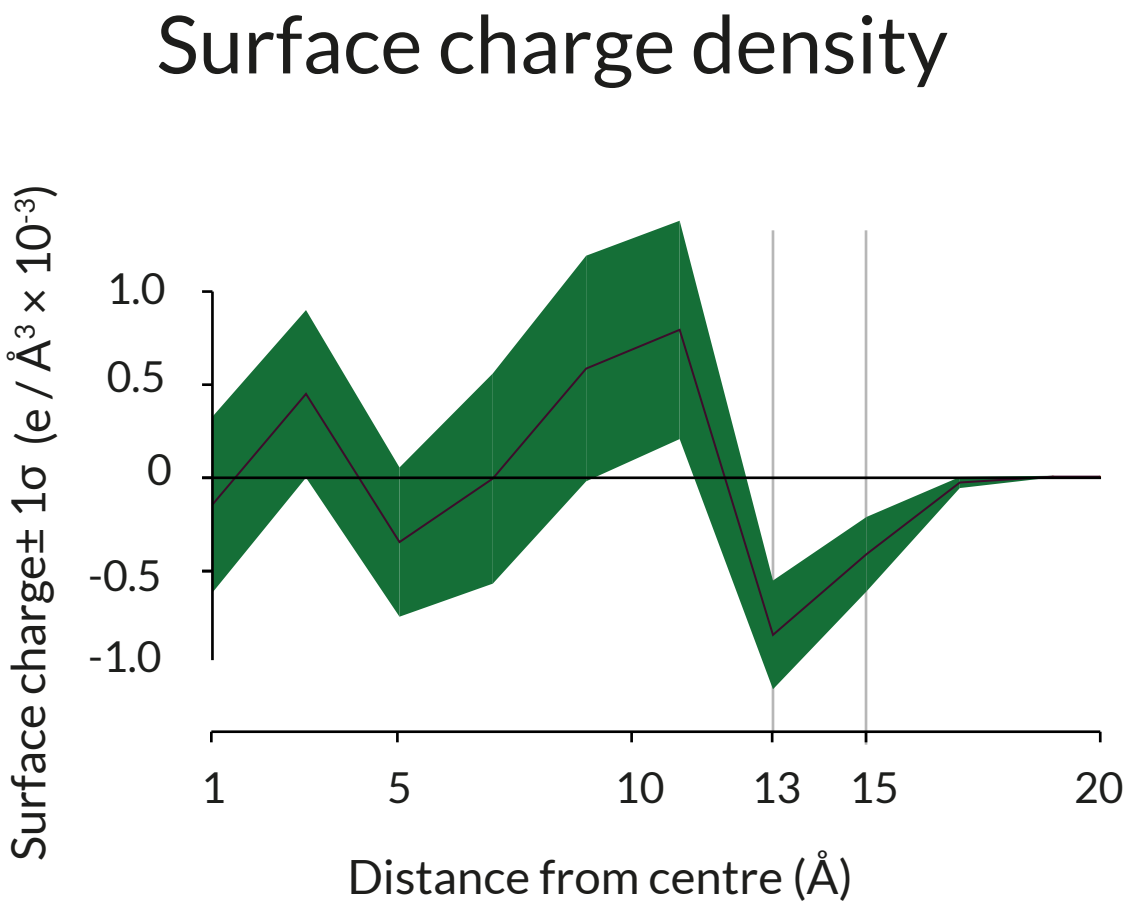


Electronic distribution

(ground state distribution substracted)



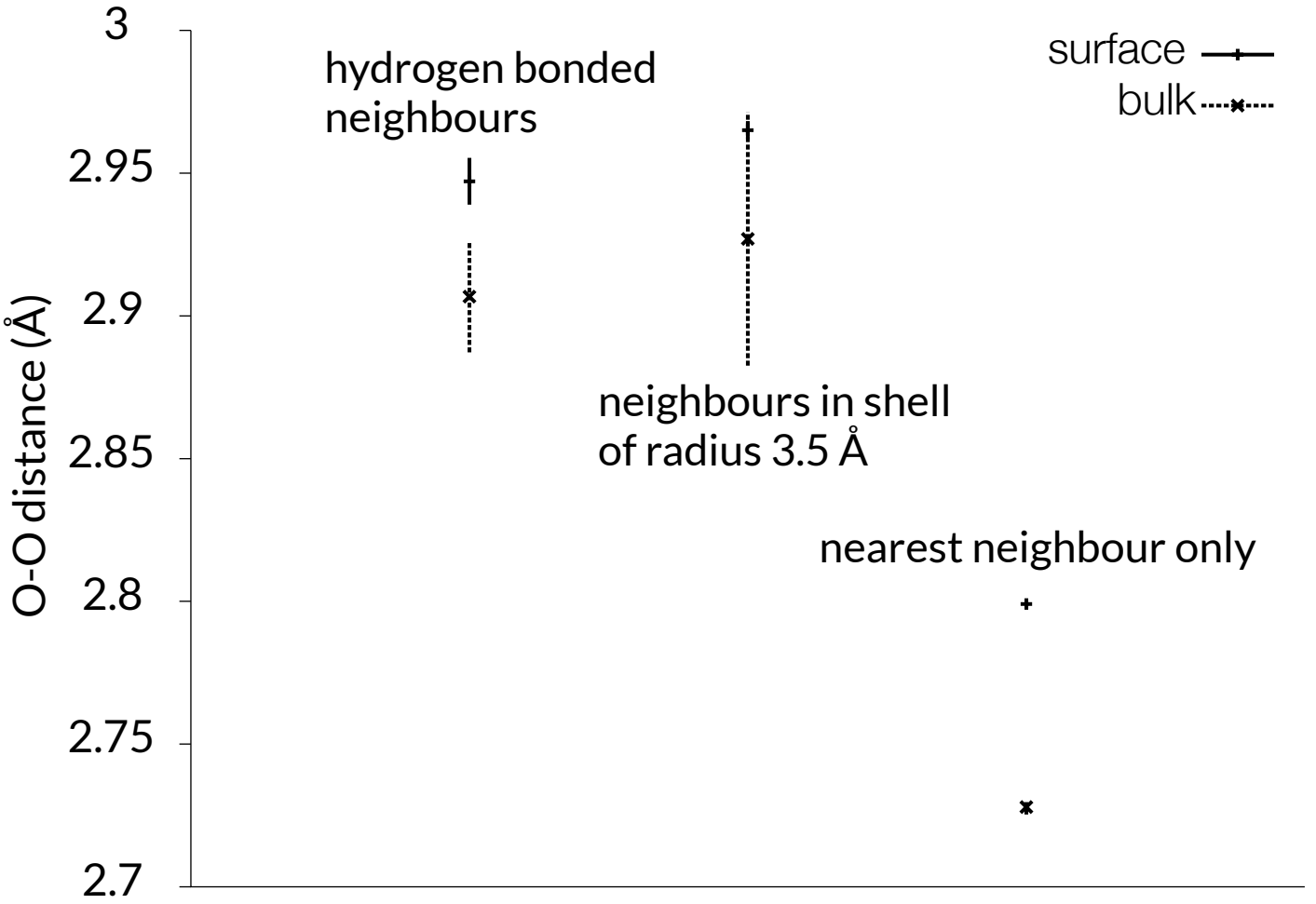
8 . Liquid–vapour interface (continued)



9 . Liquid–vapour interface (continued)

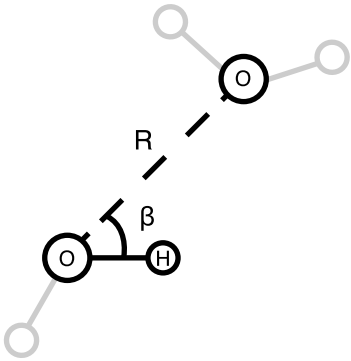
Surface expansion of nearest neighbour distance by 1–2%

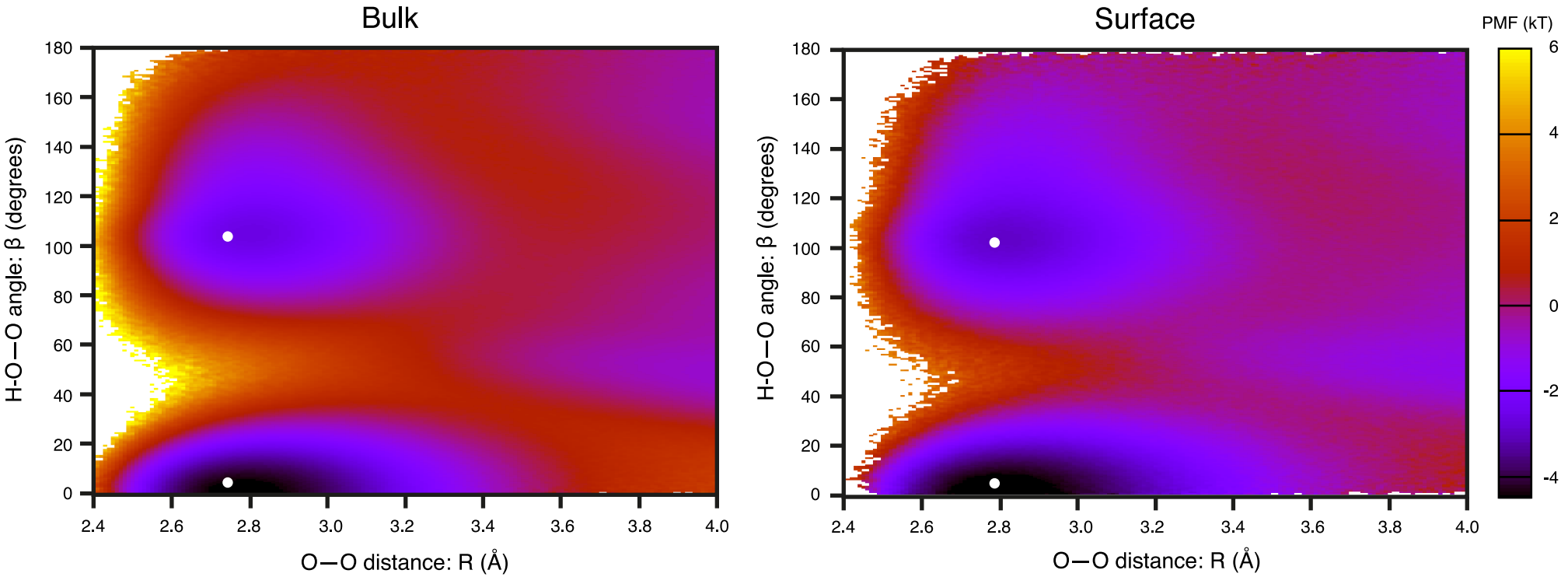
(only classical model with a surface expansion)



10 . Liquid–vapour interface (continued)

Weaker hydrogen bond at the surface



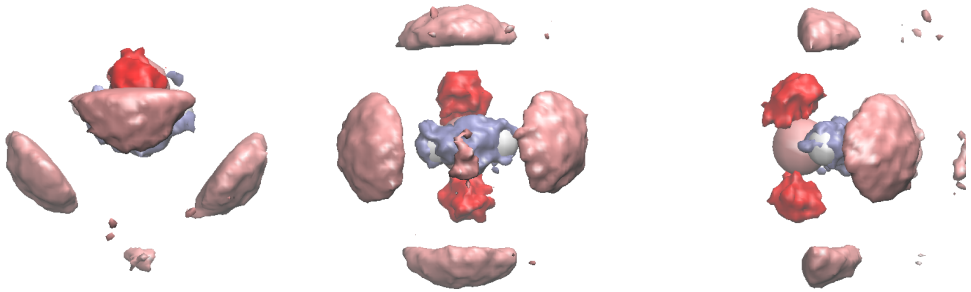


The hydrogen bond forms in the valleys of the PMF (Potential of Mean Force)

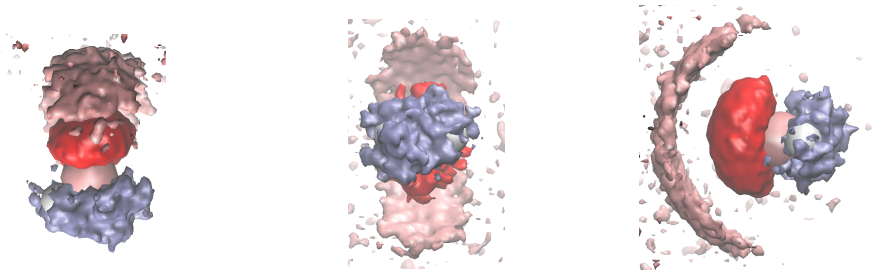
11 . Liquid–vapour interface (continued)

How are hydrogen bonds broken?

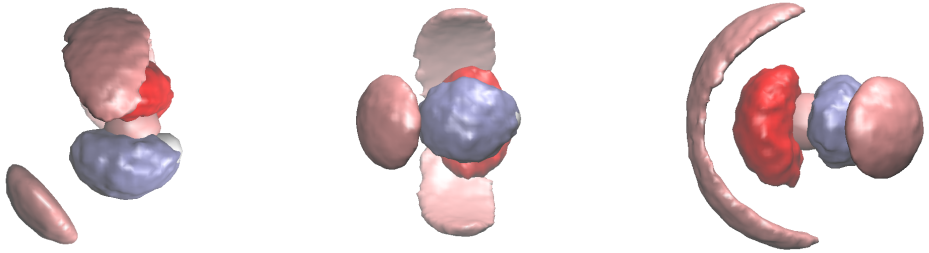
2 Acceptor: 16%



2 Donor: 4%



1 Donor: 80%



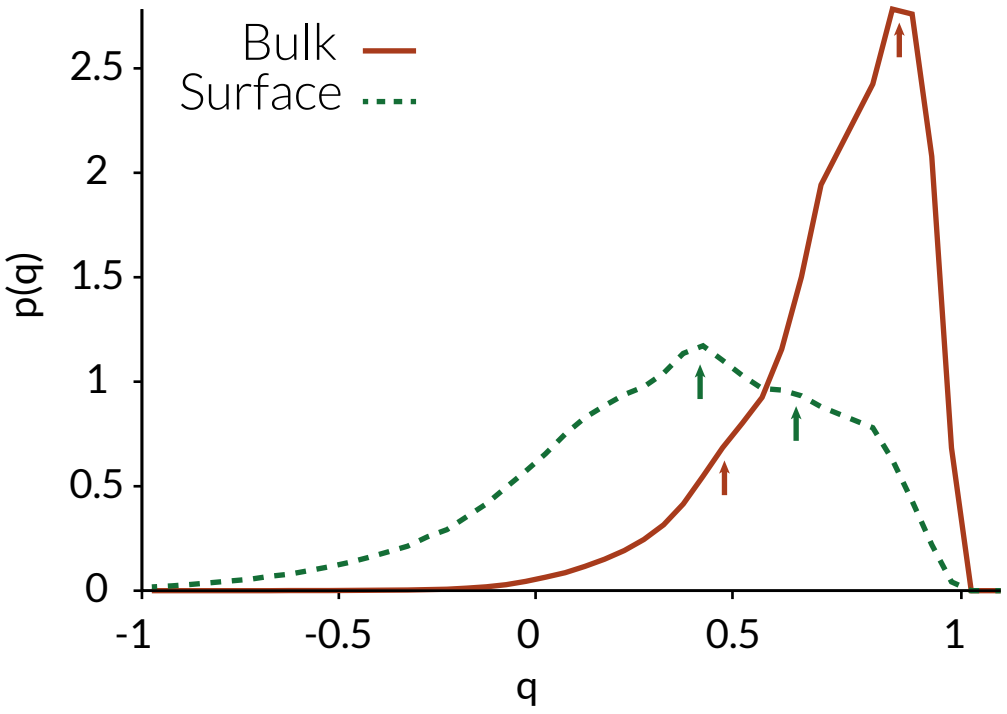
charge loss

charge gain

neighbour oxygen

12 . Liquid–vapour interface (continued)

Tetrahedrality



Number of hydrogen bonds