The hydrophobic effect at supercooled temperatures: Ab initio study

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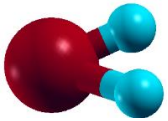
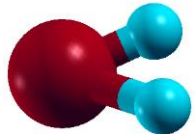




Outline

- Introduction
- Methods
- Systems
- Results
- Summary

Introduction

Water is a major ingredient for life and is the primary solvent for biological systems.

Its thermal properties are designed to enable life the way we know it.

It freezes at 273 K and current form of life will not be possible if this temperature was upset by a few degrees

(Chaplin, M. Nature Rev. Mol. Cell Biol. 2006)

Though a chemically simple molecule, the structural and dynamical nature of water is far from simple.

The complexity more crucial at supercooled temperatures (below melting point).

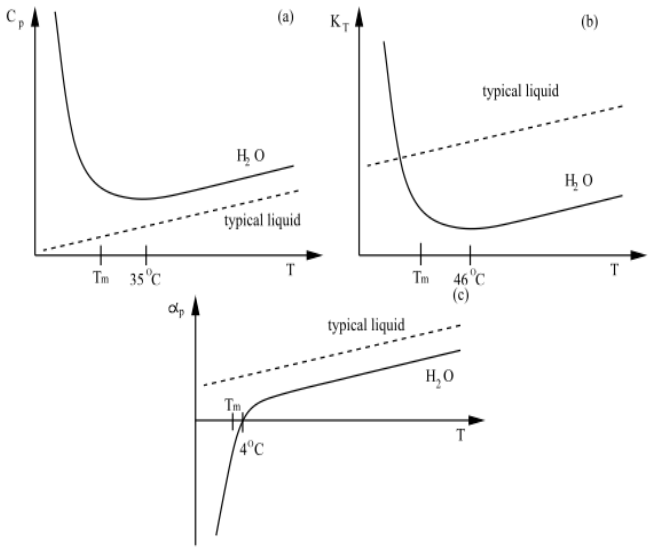
Anomalous properties of water

Water at supercooled temperatures is still hotly debated.

It is thought that the anomalous behavior of water at ambient temperature is reminiscent of non-trivial transformations in deep supercooled temperatures.

What about water in biological environment at supercooled temperatures? - Nature of hydrophobic interaction?

Anomalous properties of water



Kumar et al., J. Phys: Condens. Matter. (2008)

Density of water increases passing through a max at 4 °C as water is cooled.

Typical liquids show a monotonic decreasing trend with temperature decrease of C_p, K_T, $\langle_p$ and even C_v.

$C_p(\langle \otimes S^2 \rangle)$

$K_T(\langle \otimes V^2 \rangle)$ -compressibility

$\langle_p (\langle \otimes S \otimes V \rangle)$ - expansivity

All seem to diverge at a temperature of 220-230 K.

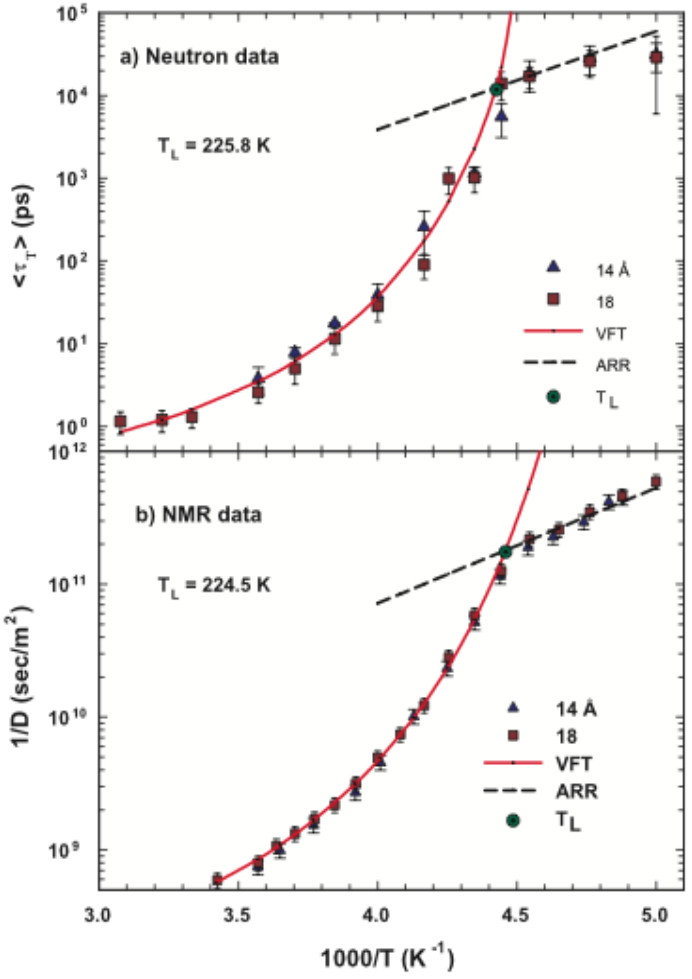
Below 235 K bulk liquid water freezes leaving no chance for low temperature studies.

Anomalous properties of water

In confined environments like silicate nano-pores and CNTs the freezing can be retarded.

Making the study of liquid water in deep supercooled temperatures possible.

The mechanism of the retardation not yet understood.



Mallamace et al. EPJ (2008)

Four hypotheses to explain apparent divergence

1. Singularity free (Sastry et al, PRE 1996) The anti-correlation of V and S explains divergence $\langle_p$ [$\langle \otimes S \otimes V \rangle$ - expansivity]

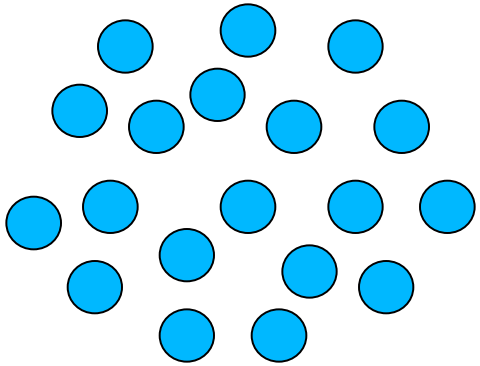
2. Stability limit (Speedy, JPC 1982): re-entrant of the liquid-gas spinodal

3. Liquid-Liquid critical point (Stanley, Nature 1992): The existence of two metastable phases of liquid water: LDL and HDL terminating in a critical point.

4. Critical point free hypothesis (Angell, Science 2008): A weakly 1st order order-disorder transition.

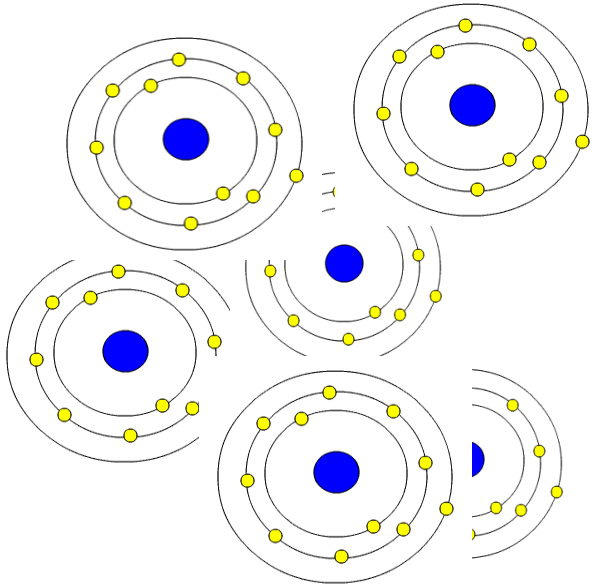
Theoretical approaches

A lot of the theoretical works on this problem use atomistic classical MD approaches that rely on model force fields that include SPC, SPC/E, TIP3P, TIP4P, TIP5P, ST2, the MB, the 2 steps Jagla potential [Hemmer and Stell, PRL 1970], etc.



We propose a quantum mechanical approach based on DFT.

Both electrons and nuclear degrees of freedom are considered
➔ small systems and short runs.



The CPMD approach

Plane-wave DFT. The Lee-Yang-Parr gradient corrected E_{xc} is used. The Grimme vdW correction [Grimme, J. Comput. Chem. 2004] used to remedy the BLYP functionals.

Core-valence electrons interactions implemented via the pseudopotential (PP). Troulier-Martin's PP (O, C and N) and Kleinman-Bylander PP (H) are used.

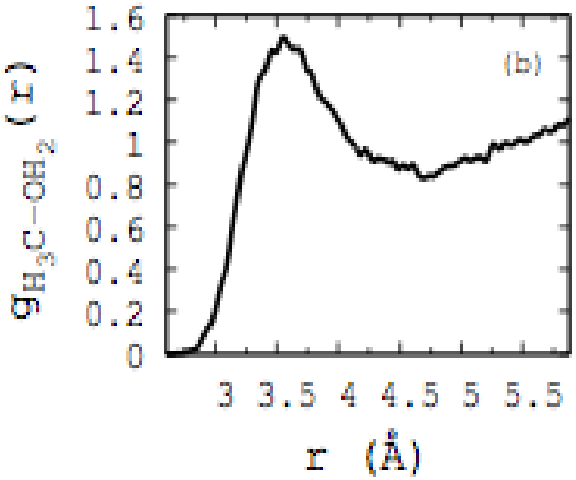
The ground state electronic density is obtained using the CG optimization approach on the Kohn-Sham equations.

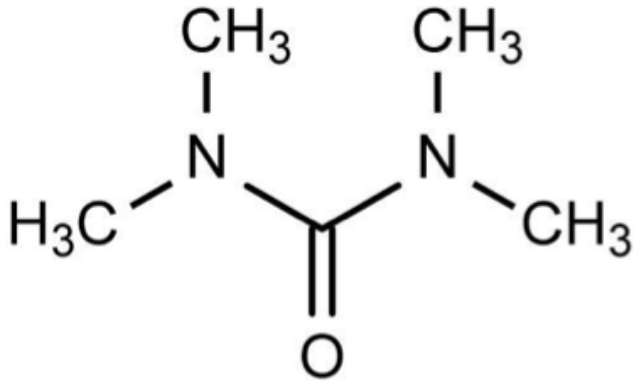
Born-Oppenheimer MD is used whereby the electronic wavefunction follows adiabatically the nuclear coordinates.

The velocity Verlet algorithm used within the Nosé-Hoover chain thermostat. Time steps of 5 a.u. (0.121 fs).

Systems of interest

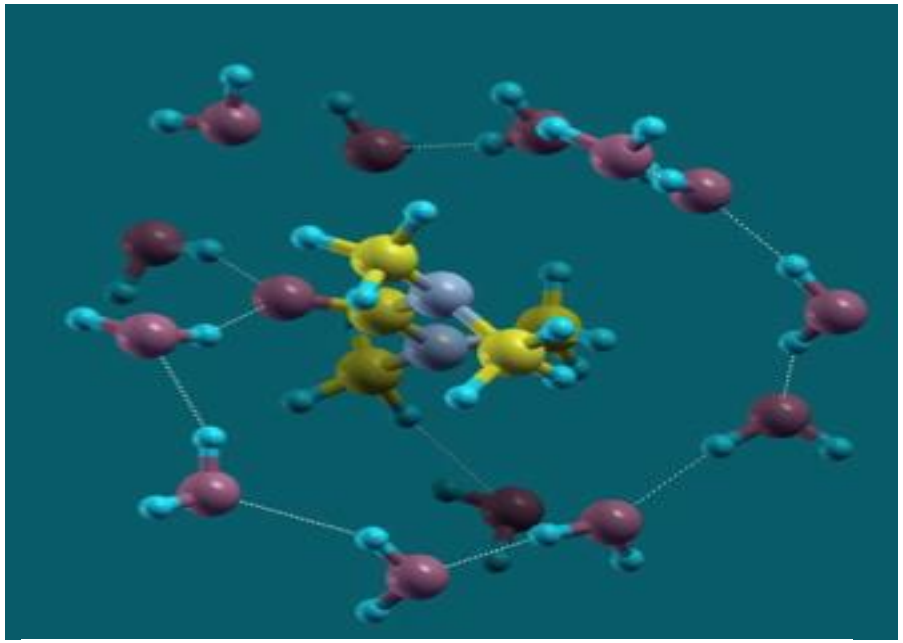
- Cubic boxes with densities fixed at 1g/cm^3.
- Neat water consists of 54 H_2O molecules
- The hydrophobic system: 50H_2O+TMU
- Test system of 105H_2O+TMU.





Tetramethylurea

Hydrophobic & hydrophilic

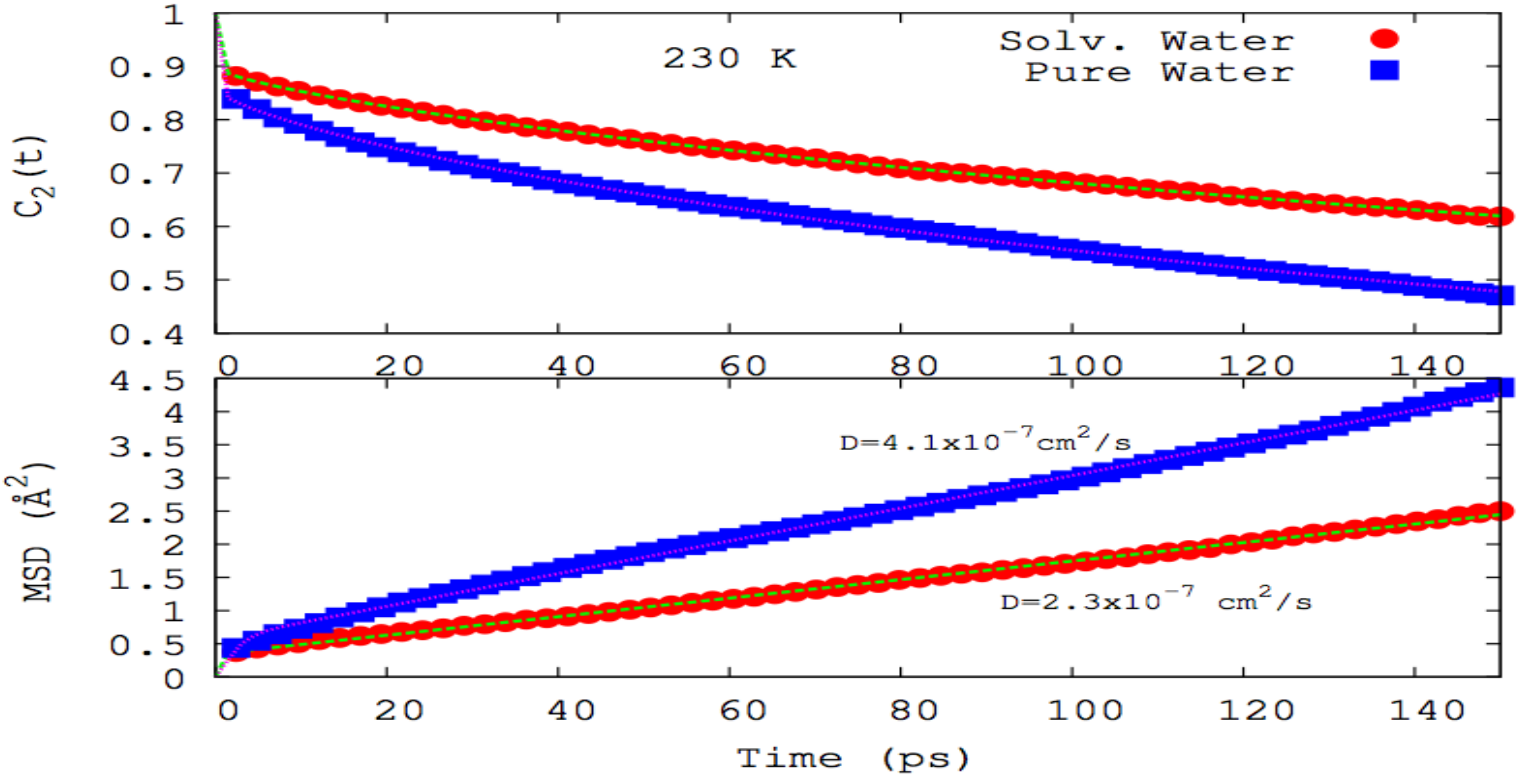


Solv. Shell of TMU

Rotational orientation and diffusion of water

$C_2(t)=\langle P_2(\cos\angle(t))\rangle$, P_2 is 2nd order Legendre polynomial. A rotational slow down in solvation shell of TMU molecule has been demonstrated for T>260K. (Titantah and Karttunen, JACS 2012)

$$MSD(t) = \frac{1}{N}\sum_{i=1}^{N}\left\langle (\mathbf{r}_i(t) - \mathbf{r}_i(0))^2 \right\rangle_0$$

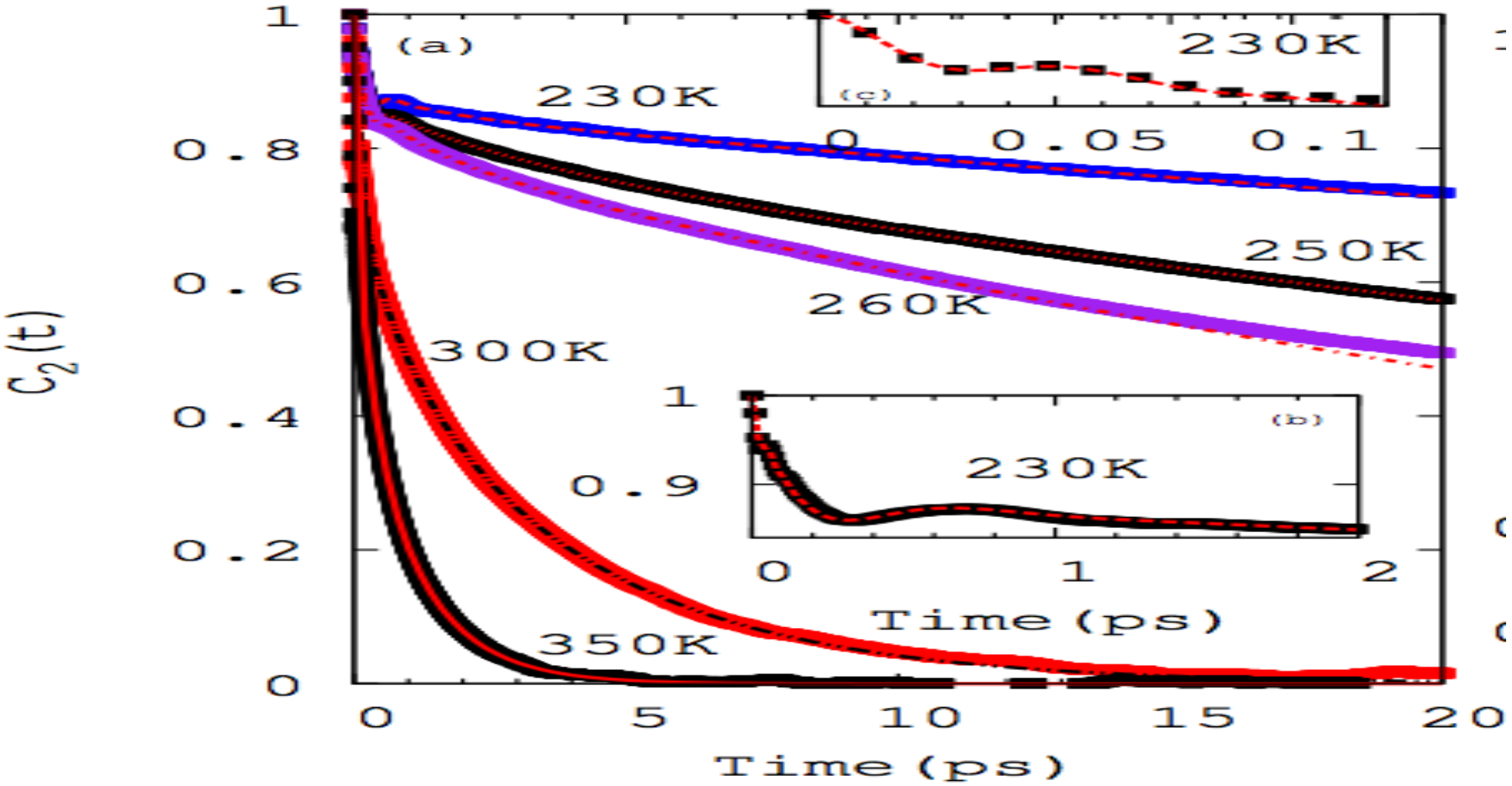


Rotational orientation and diffusion of water

Strong temperature dependence of $C_2(t)$

$$C_2(t) = \left[a_0 \exp\left(-\frac{t}{\tau_0}\right)\left(\cos\left(\frac{2\pi t}{T_{lib}}\right) + \lambda \sin\left(\frac{2\pi t}{T_{lib}}\right)\right) + a_1 \exp\left(-\frac{t}{\tau_1}\right)\right]\left(\cos\left(\frac{2\pi t}{T_{cage}}\right) + \zeta \sin\left(\frac{2\pi t}{T_{cage}}\right)\right) + a_2 \exp\left(-\frac{t}{\tau_2}\right) + (1 - a_0 - a_1 - a_2) \exp\left(-\frac{t}{\tau_\alpha}\right),$$

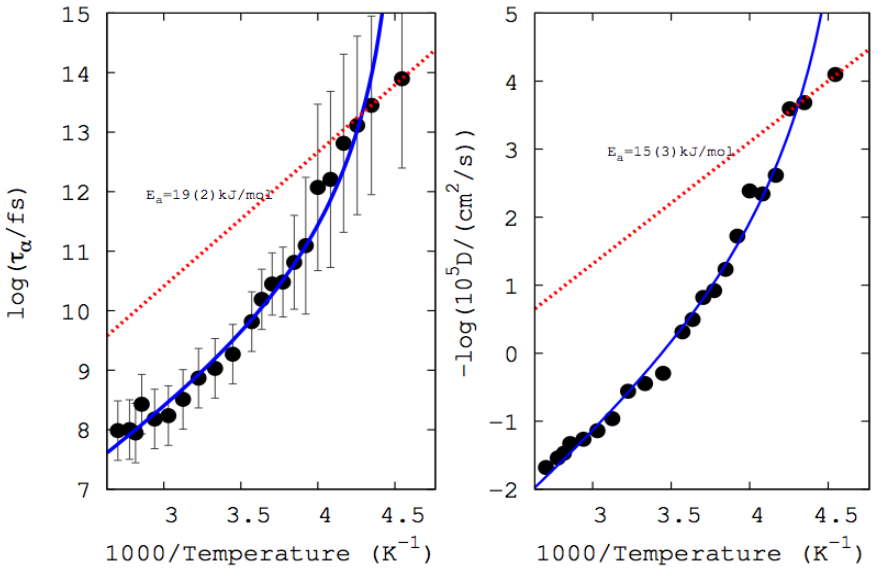
To model the fast dynamics (~50 fs), the cage dynamics (700 fs) and slow ⟨ -relaxation



Orientational correlation and Diffusion

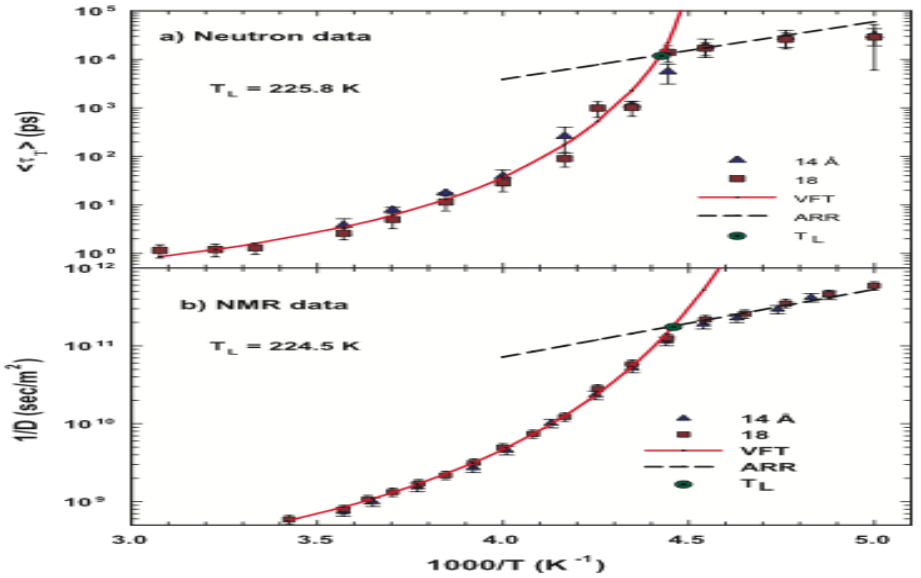
The high temperature dependences – MCT -fragile liquid

$$\tau_\alpha = \tau_0 \left(\frac{T}{T_{c\tau}} - 1 \right)^{-\gamma_\tau} \qquad \text{and} \qquad D = D_0 \left(\frac{T}{T_{cD}} - 1 \right)^{\gamma_D}$$



while Arrhenius at lower temperatures E_a=19(15)kJ/mol T_c-values range 180-220 K.

Good agreement with neutron spectroscopic and NMR measurements on nanoconfined water



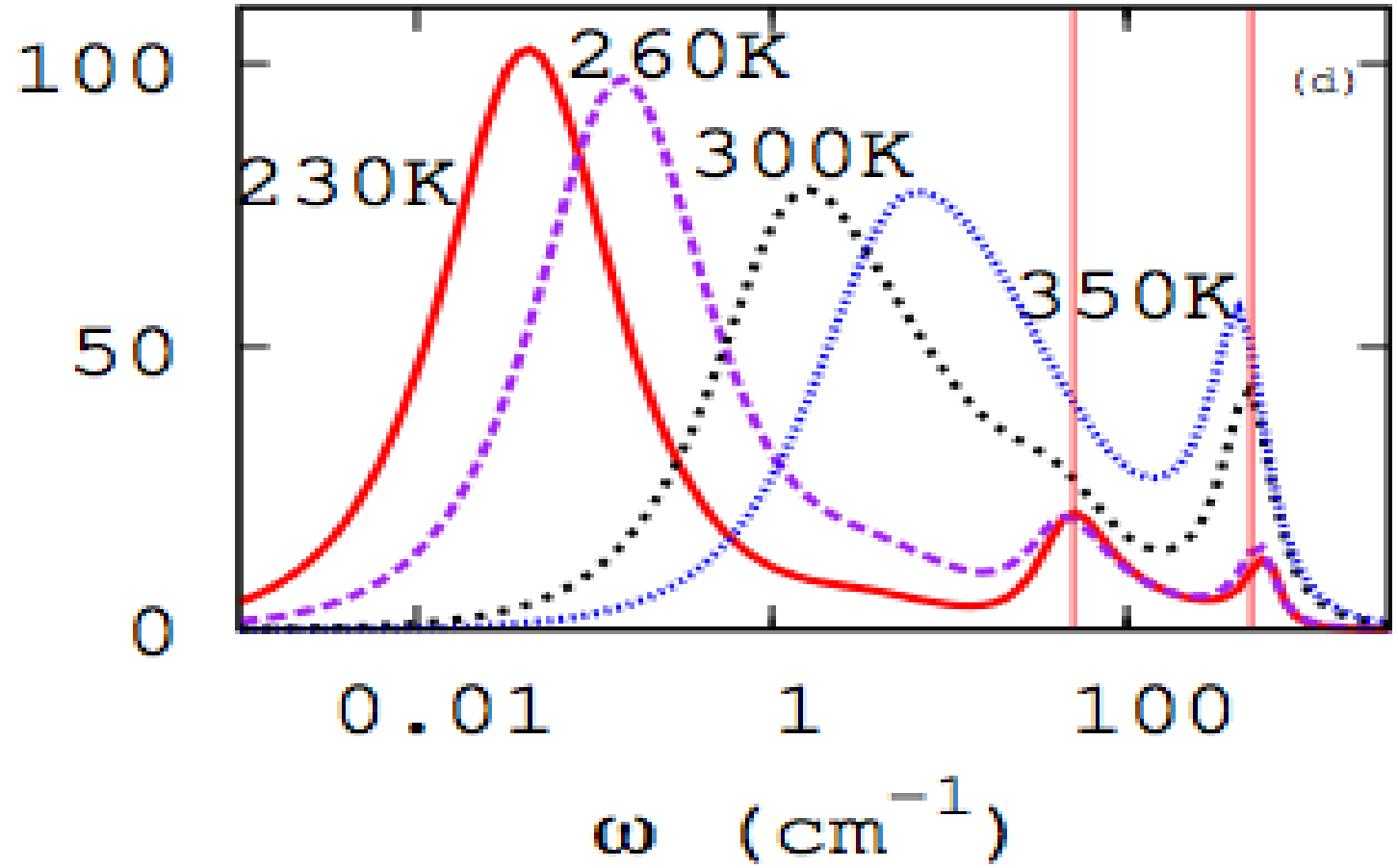
Mallamace et al. Transport properties of supercooled confined water, EPJ (2008)

Rotational orientation and diffusion of water

$$\tilde{C}_2(\omega) = \omega \tanh\left(\frac{1}{2}\beta\hbar\omega\right)\int_0^\infty C_2(t)\cos(\omega t)dt$$

Microwave (far-IR) to mid IR (500 cm^{-1})

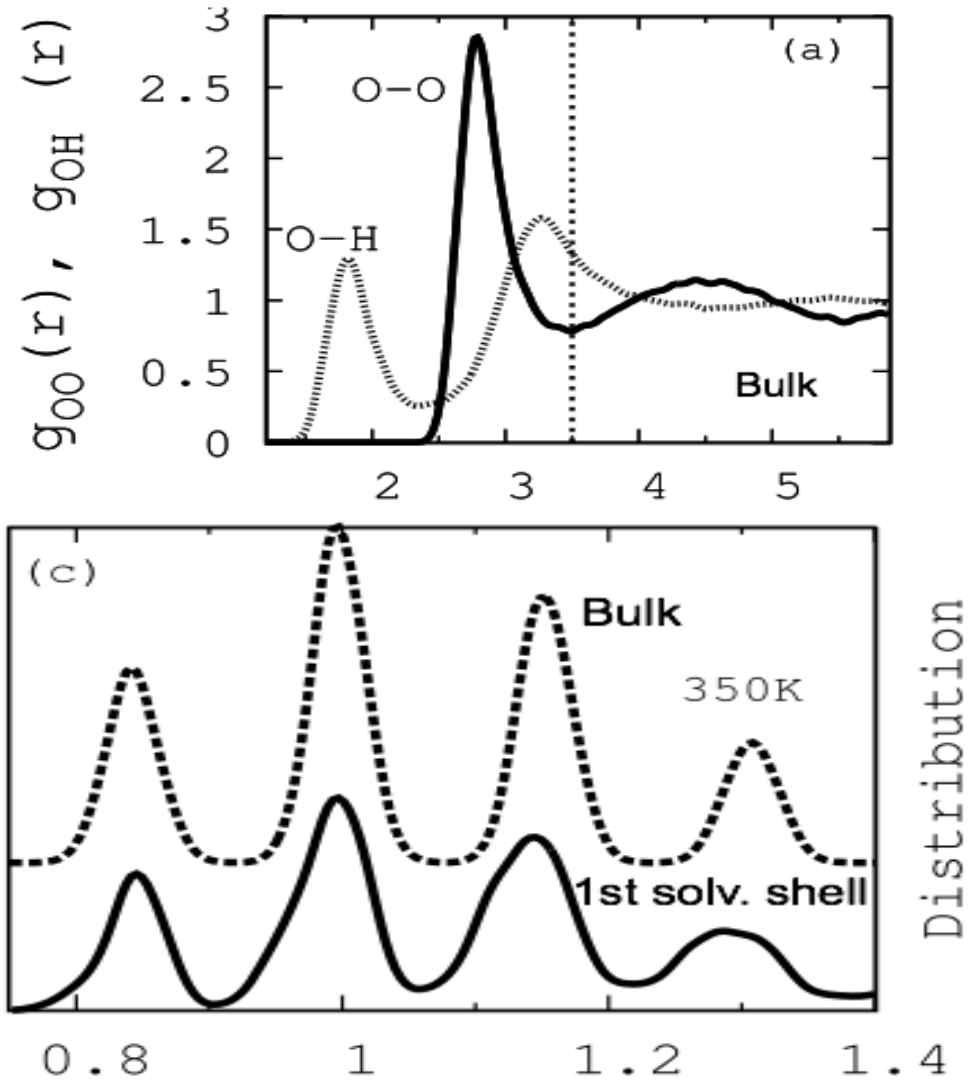
Librations (500 cm^{-1}) red shift with temperature increase



- Cage motion (40-60 cm^{-1})
- O-O-O vibration
- close to Boson peak at 37 cm^{-1}

[Kumar et al., Sci. Rep 2013]

Local water density



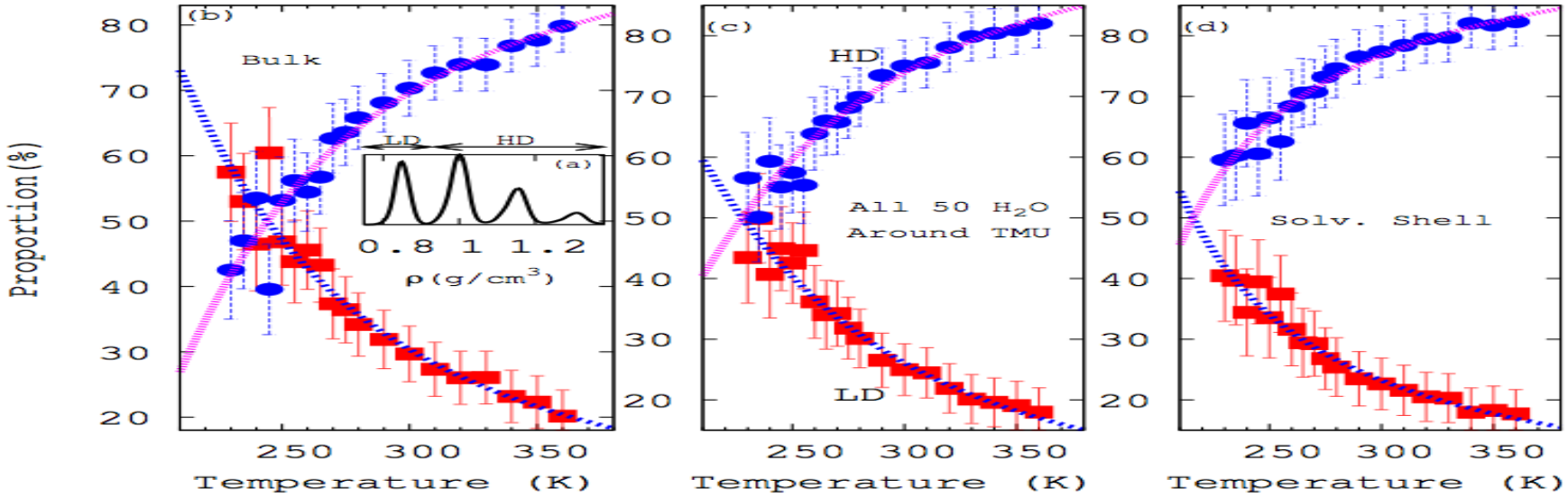
Titantah and Karttunen (sumitted)

Mass-density within sphere of radius 3.5Å, chosen to include O and H atoms in the nearest neighbor shell. Titantah and Karttunen, Sci. Rep. 2013

Four density states of water: low-density (LD), normal density (ND), high density (HD) and very high density (VHD).

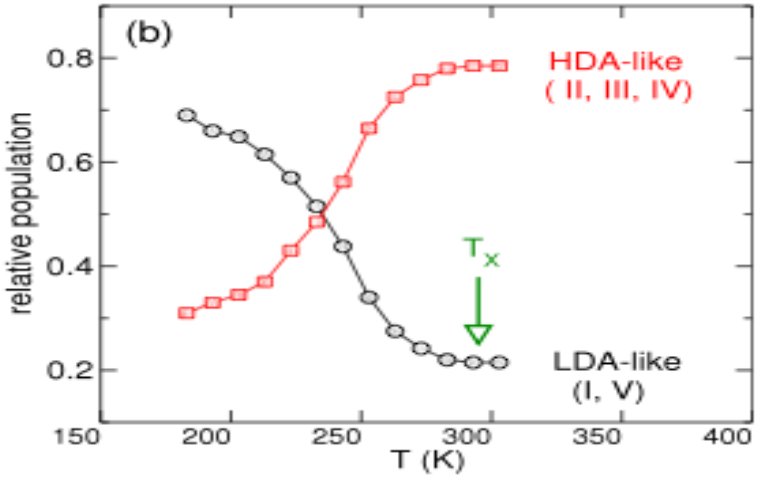
Such four density states reported for amorphous ice Soper et al., PRL 2000

Low density high density water



A crossover from dominantly HD to low density water at 245 K (-28 ° C) => similar to dynamic crossover

Neutron scattering and NMR data show similar crossover for confined water at 245 K. TIP5P water shows crossover at 255 K.



Liquid polymorphism: water in nanoconfined Environment, Stanley et al., J. Phys. Cond. (2010)

Signature of HB asymmetry in OH stretch vibration

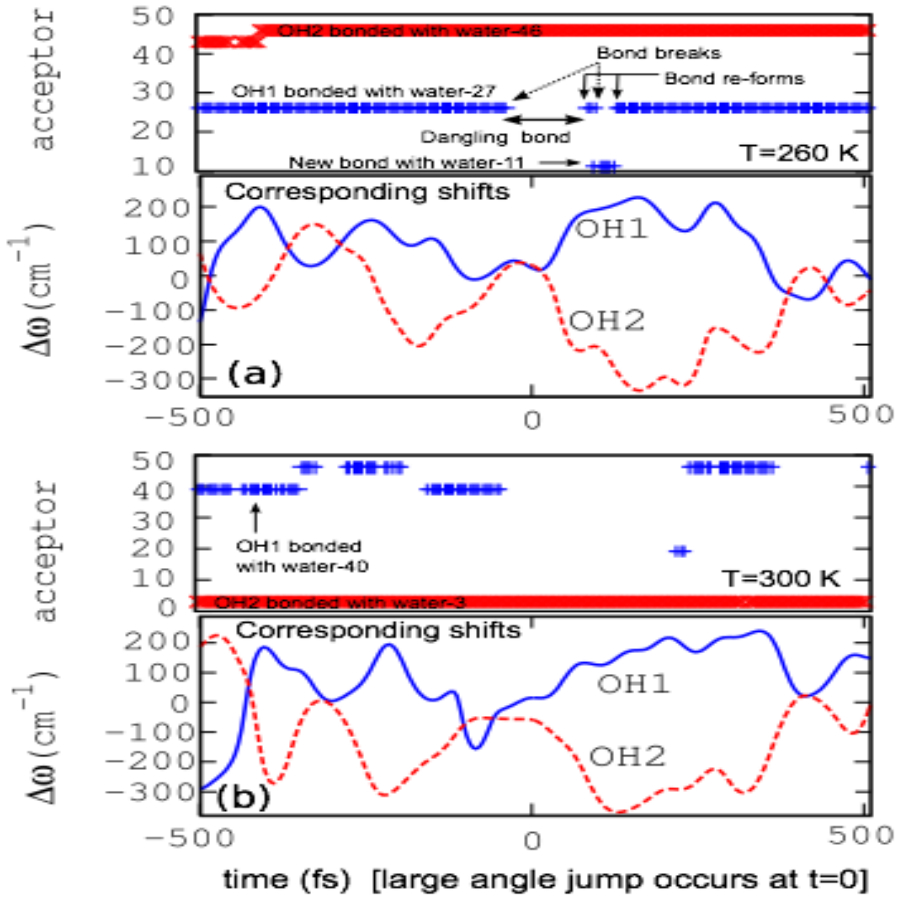
50 ps AIMD movie, Titantah and Karttunen (Sci. Rep. 2013)

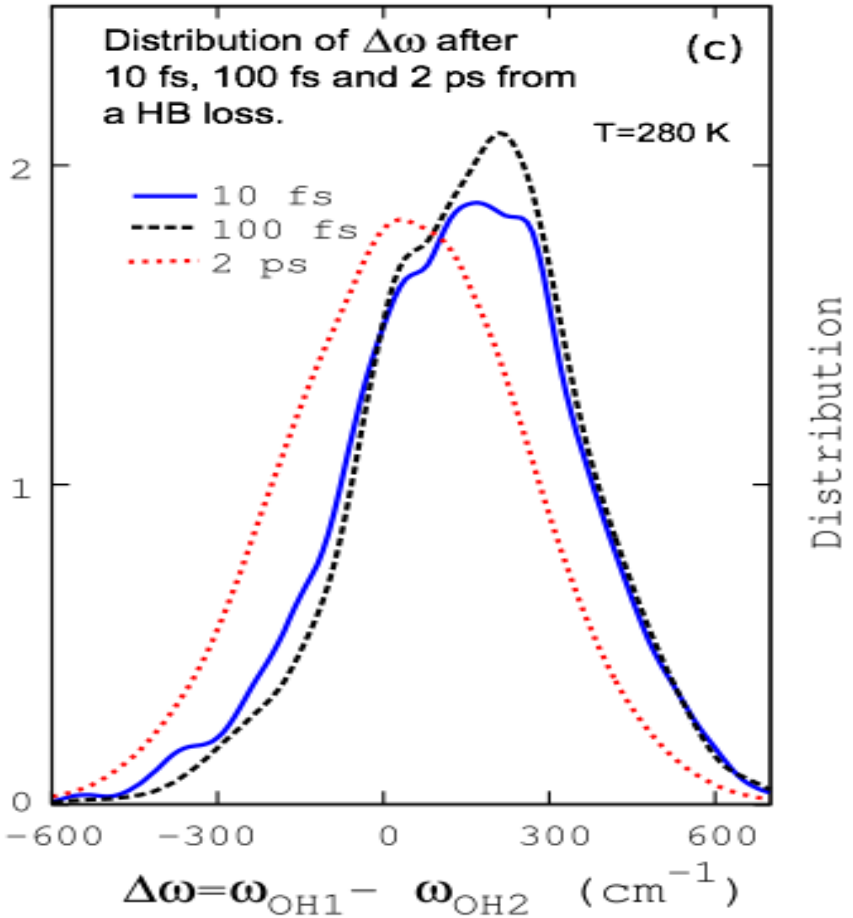
Notice the difference in stretch vibrations of the OH groups of each H_2O.

Signature of HB asymmetry in OH stretch vibration

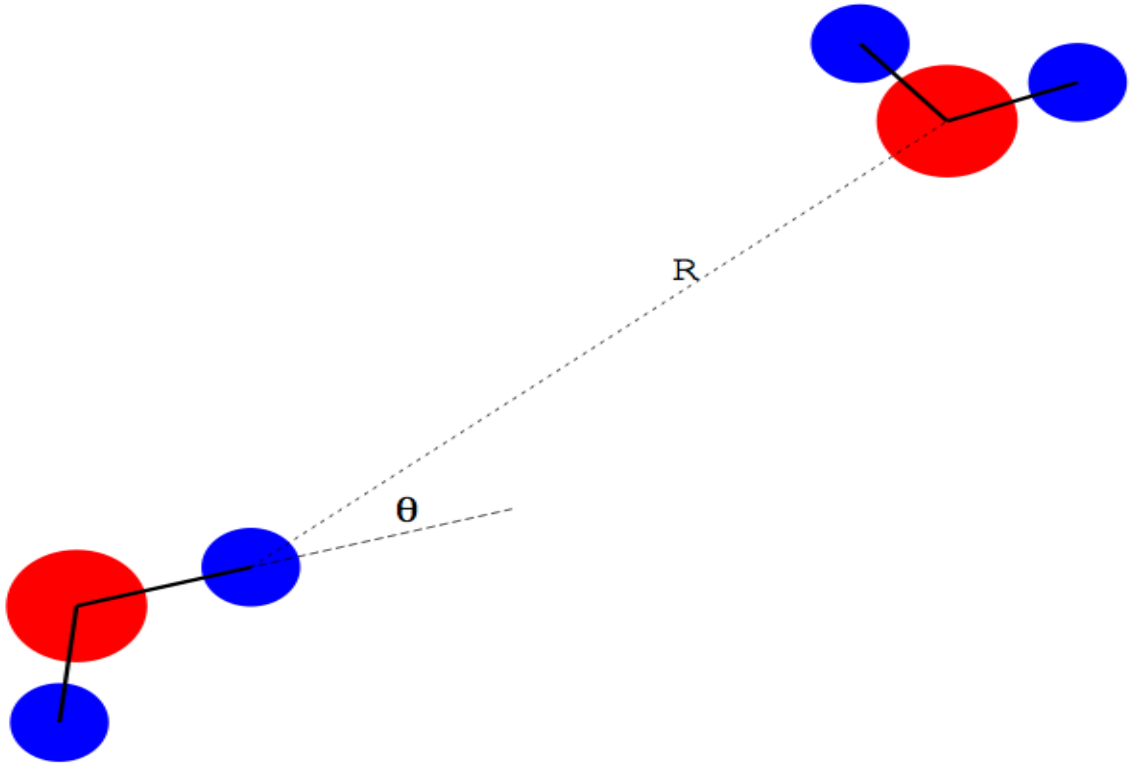
Asymmetry => HB breaking/forming, thus related to rapid (200 fs), large angle but less frequent (ps intervals) OH jumps in water

Ji et al., Science 2010, Laage and Hynes, Science 2006
Titantah and Karttunen, JACS 2012

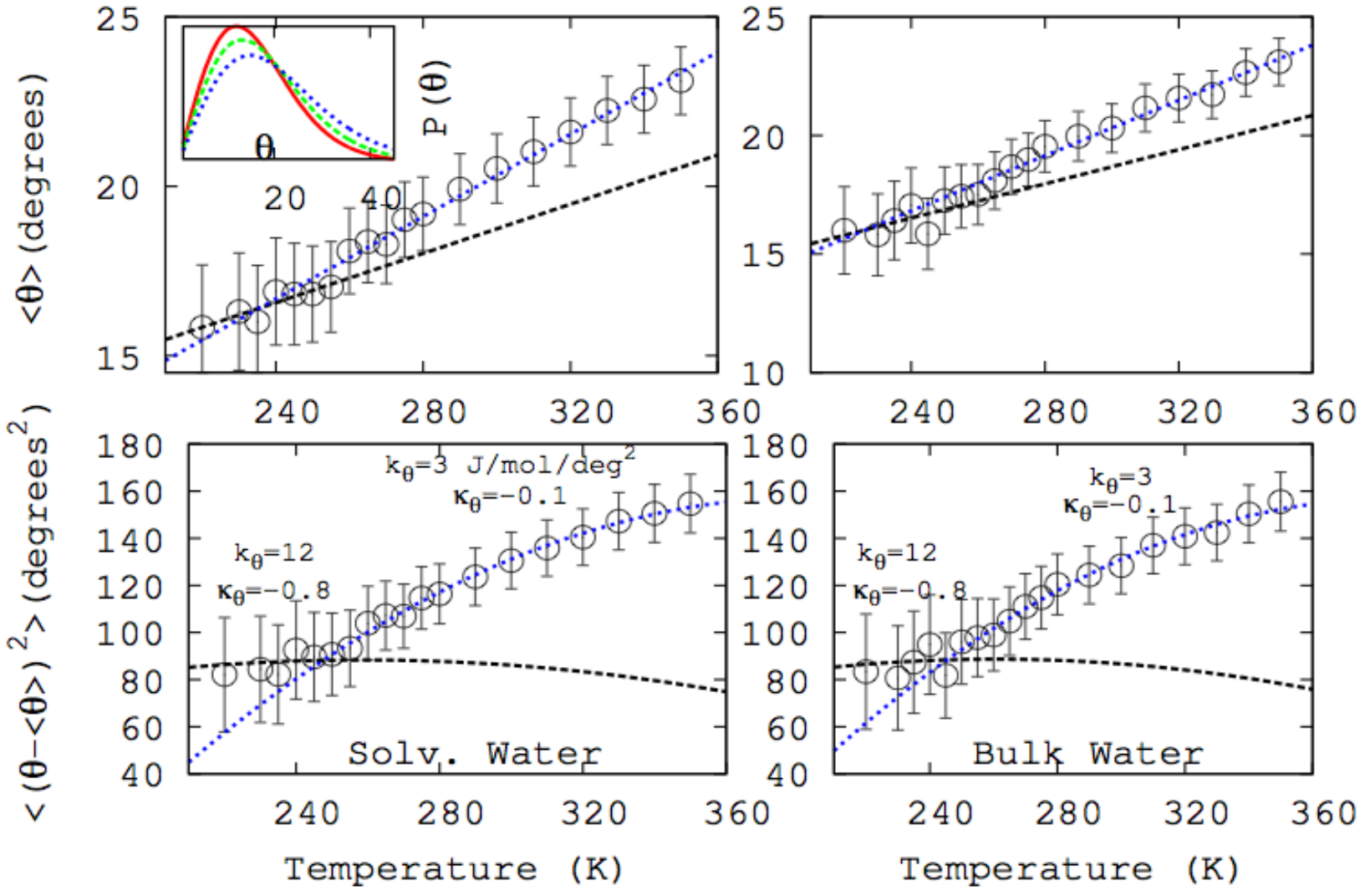




HB angular and radial potentials



HB angular and radial potentials



Almost linear T-dependence => anharmonic potential

Angular and radial potential

Model anharmonic potential

$$H(\mu) = \frac{k_\mu \mu_0^2}{2}\left[\left(\frac{\mu}{\mu_0} - 1\right)^2 + \frac{\kappa_\mu}{3}\left(\frac{\mu}{\mu_0} - 1\right)^3\right] \qquad \kappa_\mu = \frac{d \log k_\mu}{d \log \mu} \Big|_{\mu_0}$$

2 regimes: Low (<250K) and high T

Parameters:
Low T: 12 J/mol/deg^2, -0.8
High T: 3 J/mol/deg^2, -0.1

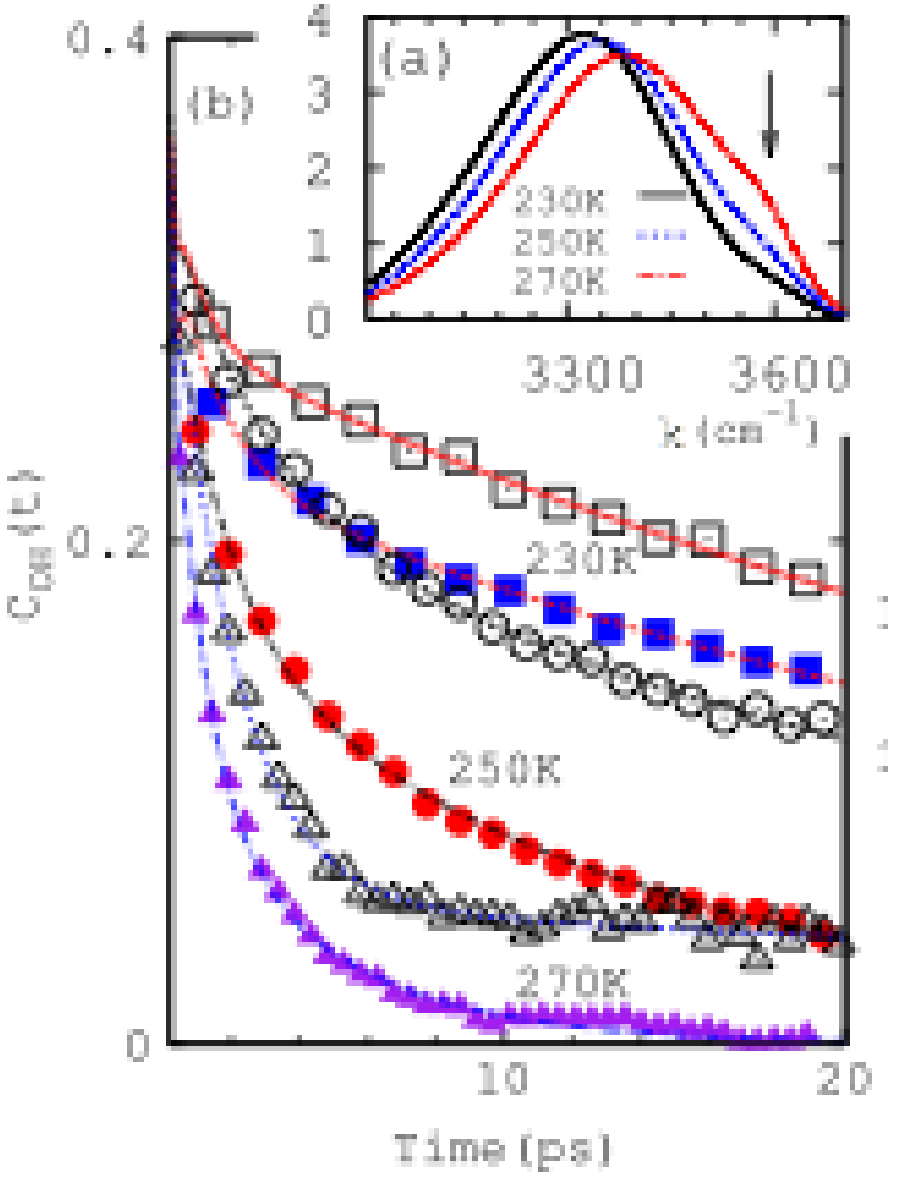
Stronger HB potential below the crossover temperature.
Qvist et al., JACS 2008, Titantah and Karttunen – submitted 2014

Stronger HBs confirmed by longer lived HBs

$$C_{HB}(t) = \frac{\sum_{ij} \langle h_{ij}(0) h_{ij}((t)) \rangle}{\sum_{ij} \langle h_{ij}(0)^2 \rangle}$$

5 ps at 300K, 30 ps at 260 K and >100ps below 250 K

Temperature effect on vibrational motions (Titantah and Karttunen – submitted 2014)



Compute OH stretch frequency and its time correlation

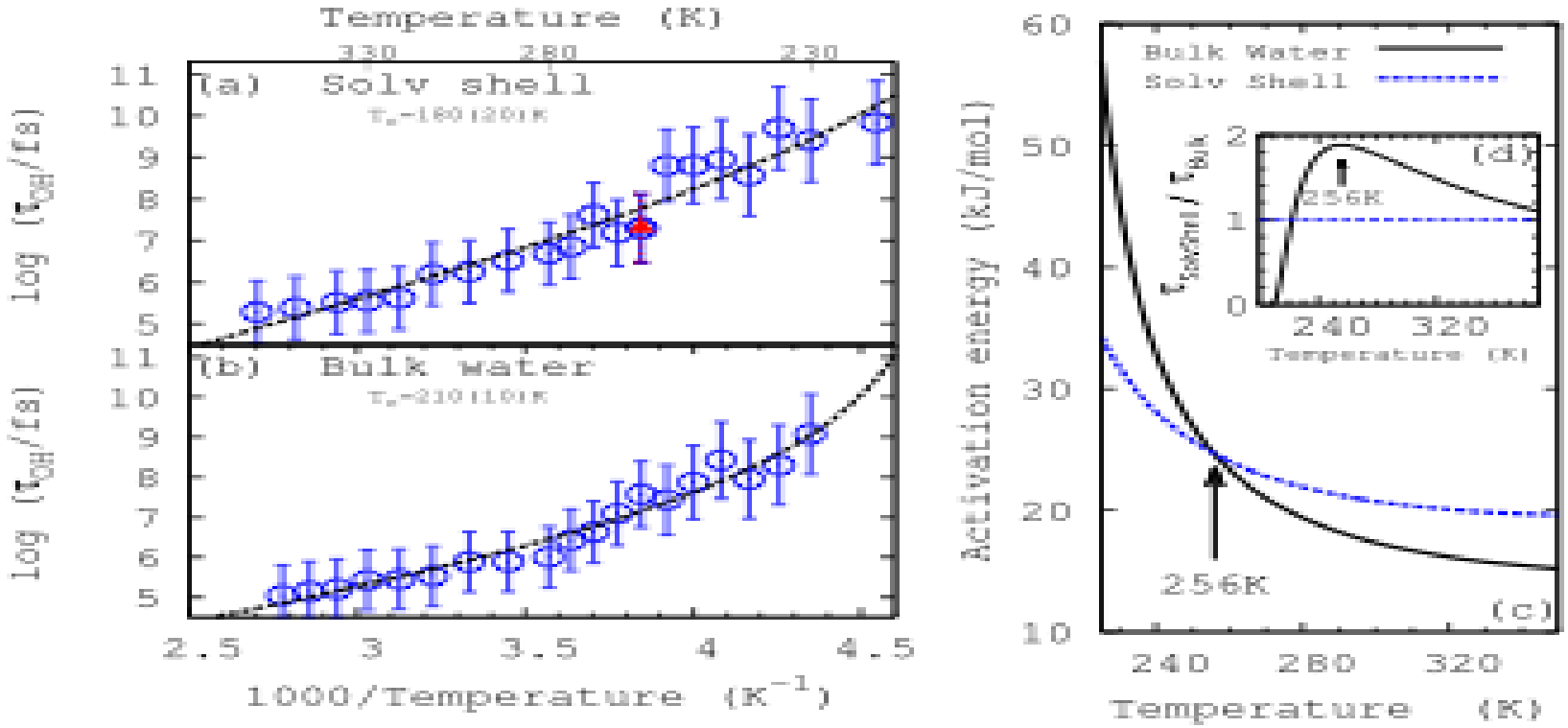
OH stretch frequency ditribution shows dangling bond mode at ~3600 cm^{-1} – that grows with temperature

Slower dynamics for solvation water (opened symbols) than bulk water (filled symbol)

Temperature effect on vibrational motions (Titantah and Karttunen – submitted 2014)

Correlation times are extracted for solv. water and bulk water

Rotational activation ene $E_a(T) = -k_B T^2 \frac{d}{dT} \log \tau(T),$



Crossover at 256 K (255K - Qvist and Halle, JACS 2008)

Summary

- A successful first attempt to use ab initio MD to probe dynamics and structure of supercooled water.
- CPMD captures essential structural/dynamical properties of supercooled water.
- We confirm a crossover from a fragile liquid composed of high density water at high temperature to a strong-low-density liquid below 245 K.
- Lending support for the LLCP hypothesis.
- The crossover is accompanied by strengthened HBs in the LD phase
- We find that the hydrophobic effect persist and intensifies at supercooled temperatures.
- We demonstrate the short-time asymmetric nature of HB
- A crossover from high activated rotational motion to weakly temperature activated rotations located at 256(4) K (255K – NMR).

Thank You!

Acknowledgements