Title: Ab initio insight in supercooled water

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Abstract: As an extension to previous ab initio studies on water [12] we present 400 psBorn-Oppenheimer ab initio Molecular dynamics study on water at deep supercooled temperatures (down to 220 K) and confirm a crossover from a fragile to strongliquid around the Widom line. This crossover is accompanied by the passage from relatively weaker hydrogen bonds in the dominantly high density liquid (HDL) at high temperatures to strong hydrogen bond in dominantly low density liquid (LDL). This crossover is accompanied by a maximum in the excess specific heat at constant volume and may lend further support to the existence of a liquid-liquid critical point (LLCP) in supercooled water as was predicted by Peter Poole and collaborators using ST2 water model[3].References[1] J. T. Titantah and M. Karttunen Long-Time Correlations and Hydrophobe-Modified Hydrogen-Bonding Dynamics in Hydrophobic Hydration. J. Am. Chem. Soc. 134 9362 (2012)[2] J. T. Titantah and M. Karttunen Water dynamics: Relation between hydrogen bond bifurcations molecular jumps local density & hydrophobicity. Sci. Rep. 3 2991 (2013)[3] Poole P. H. Sciortino F. Essmann U. & Stanley H. E. Phase behaviour of metastable water. Nature 360 324328 (1992)

An ab initio insight into supercooled water

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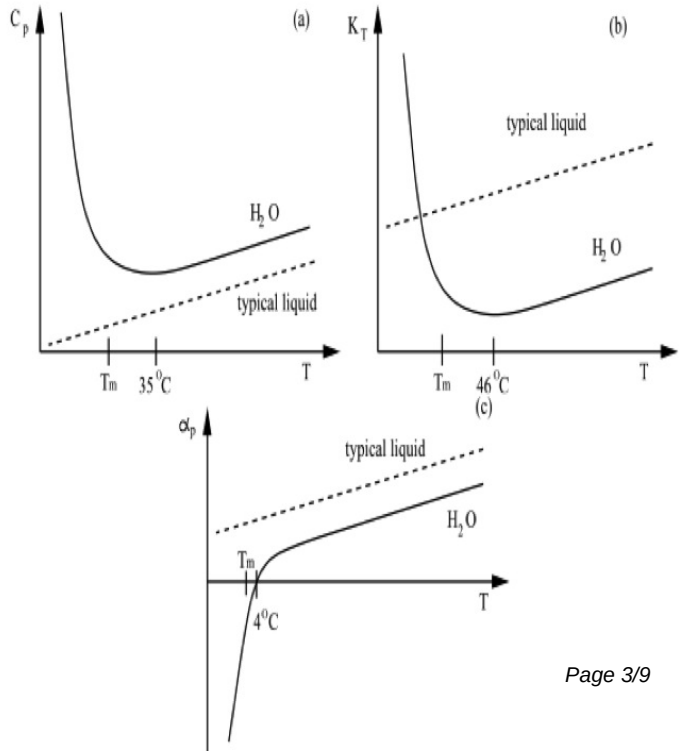
Introduction

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

Structure and dynamics of supercooled water (below freezing temperature) is complex and debated.

Liquid water freezes at 235 K, crystallizing into glassy water below 170K.

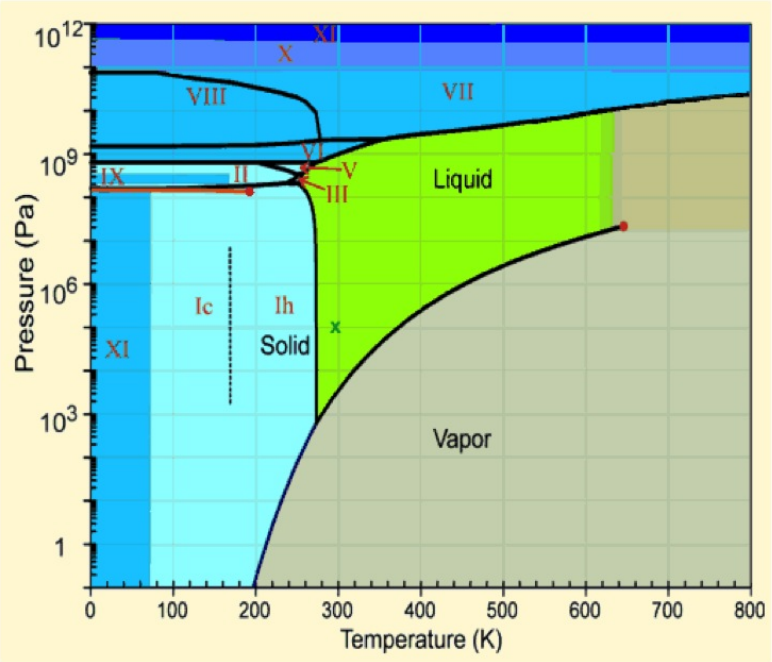
Density max at 4 °C



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

Four hypotheses to explain apparent divergence

1. Singularity free: (Sastry et al, PRE 1996)
   The anti-correlation of V and S explains divergence



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

3. Liquid-Liquid critical point: (Stanley, Nature 1992)
   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, etc.

We propose a quantum mechanical approach- CPMD -BO dynamics – DFT approach.

$C_2(t)=<P_2(\cos(t))>$

Titantah and Mikko, JACS 2012

Water's local density & HB dynamics.

Titantah and Mikko, Sci. Rep. 2013

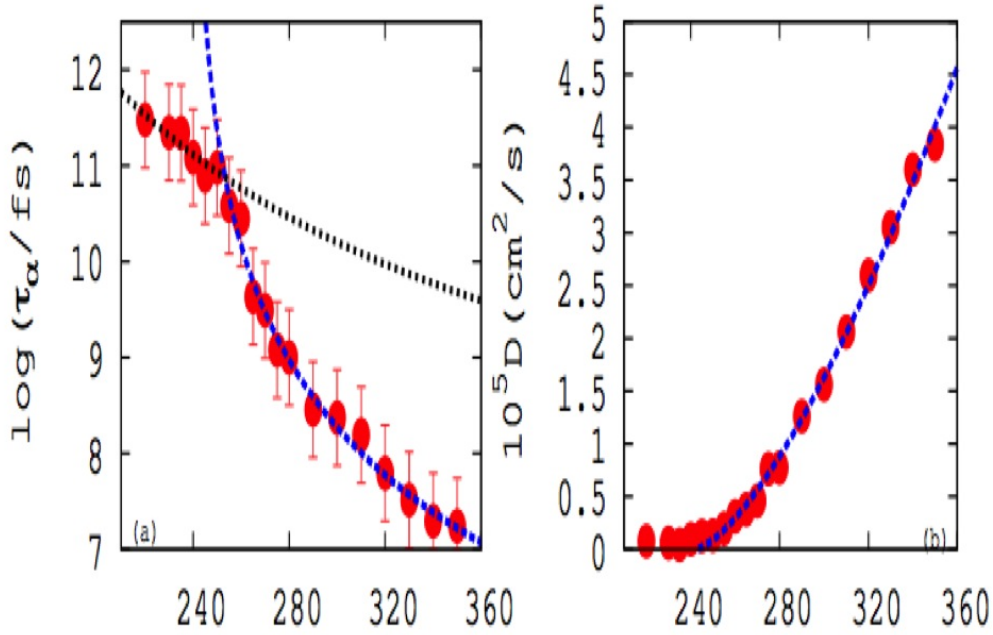
Orientational relaxation time and Diffusion

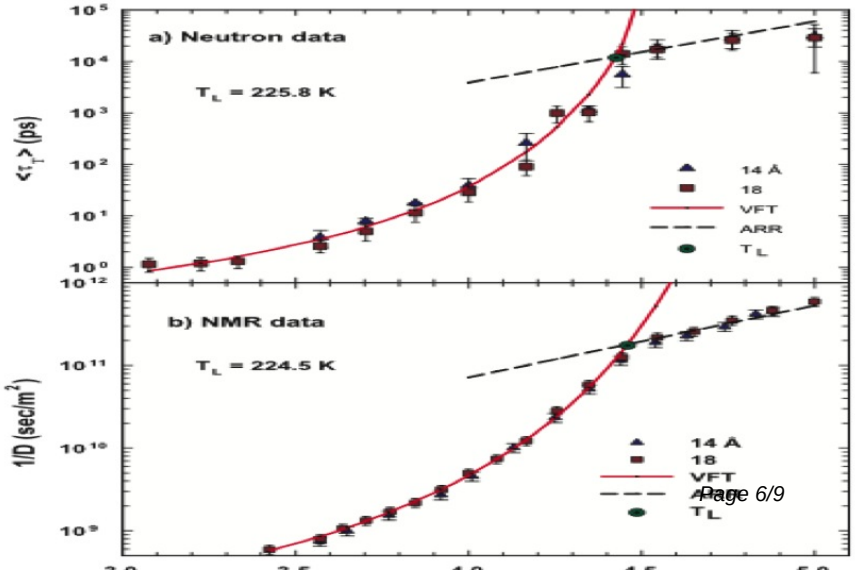
The high temp –MCT dynamics - fragile liquid

Arrhenius $\tau_0 \exp(E_a/k_B T)$ at lower temperatures E_a=9kJ/mol-

Crossover at -28°C (245 K) for water

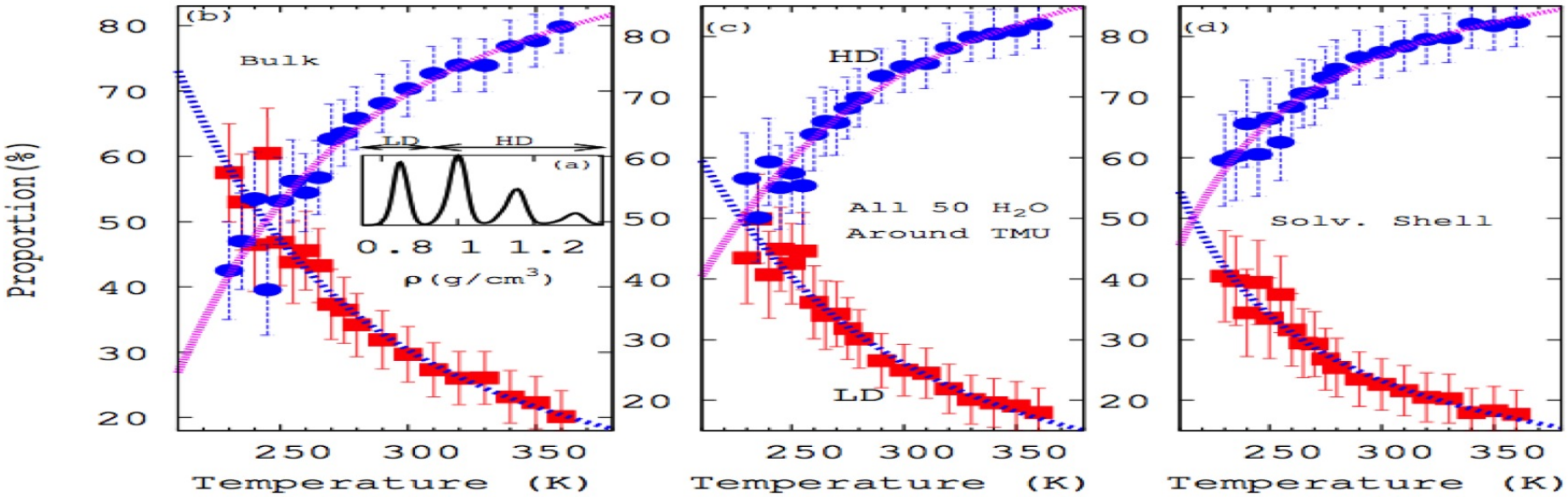
Good agreement with neutron spectroscopic and NMR measure-ments on nanoconfined water





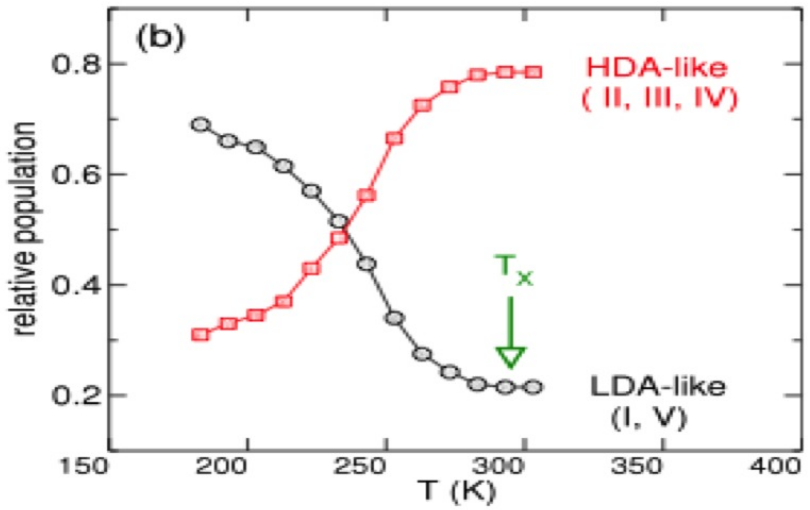
Mallamace et al. Transport properties of supercooled confined water, EPJ (2008)

Low density high density water



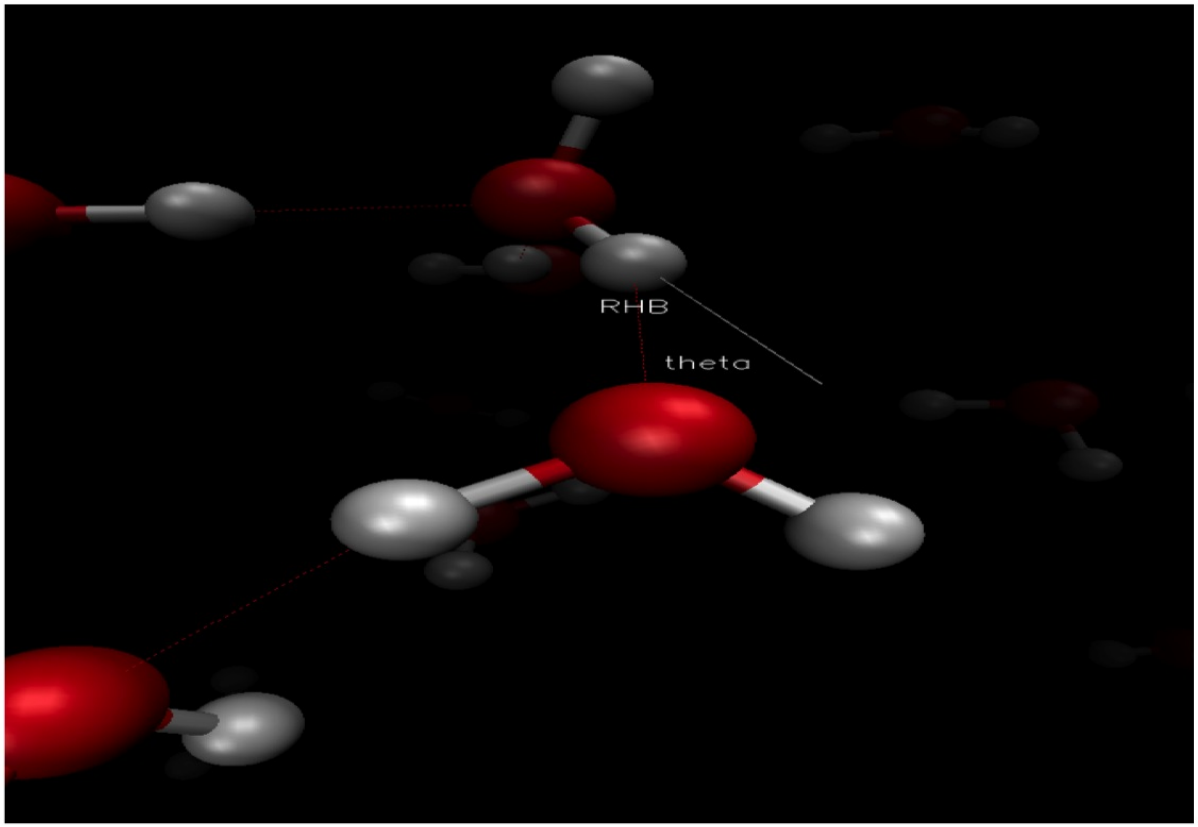
A crossover from dominantly HD to low density water at 245 K (-28 °C) => similar to dynamic crossover

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)

Strong HBs confirmed by long lived HBs



$$p_{\mathrm{HB}}(t) = \frac{\langle h(0)h(t)\rangle_0}{\left\langle (h(0))^2 \right\rangle_0}.$$

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

Summary

- 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 within the LD phase accounting for very long lived HB pairs.