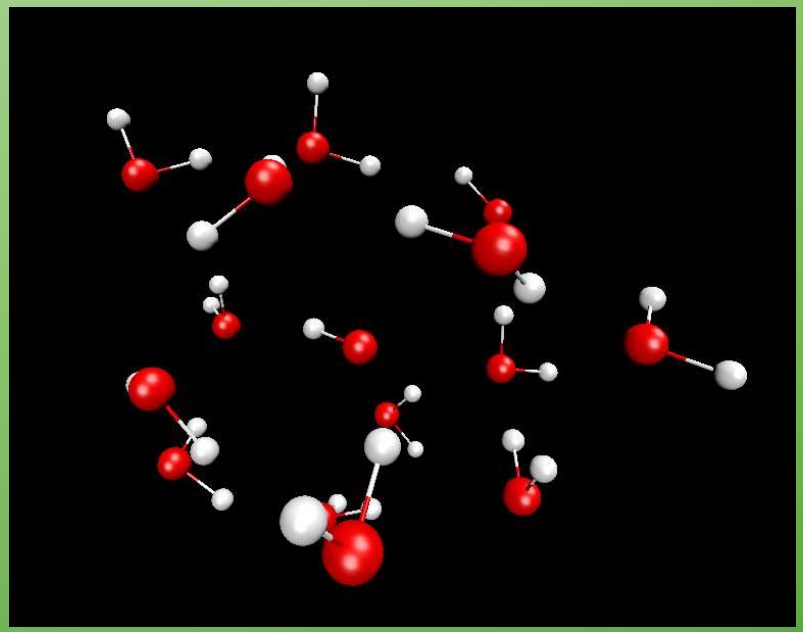
HYDROXYL RADICAL IN HIGH TEMPERATURE WATER – MECHANISM OF TRANSPORT



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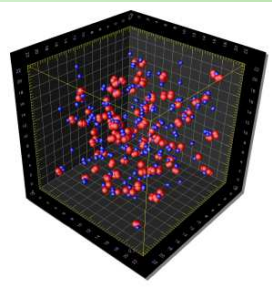


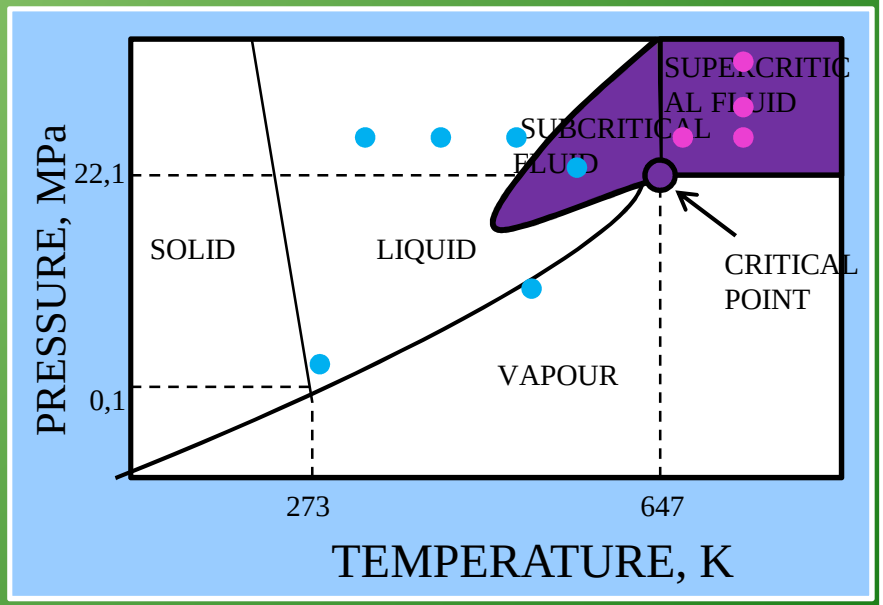
METHOD

- molecular dynamic simulation (NVE)
- flexible models of water and •OH radical
- simulation of solution and pure water
- simulation box of solution: 400 water molecules and one •OH radical
- simulation box of pure water: 400 water molecules

THERMODYNAMIC STATES

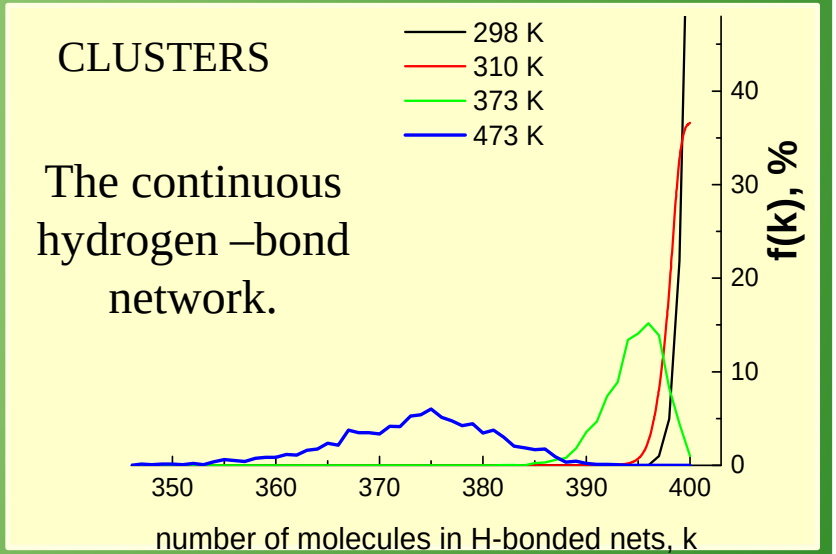
TEMPERATURE, K	DENSITY, g cm^{-3}	
298	0.997	
310	0.994	
373	0.969	LIQUID (COMPRESSED) WATER
473	0.881	
573	0.740	
573	0.720	
623	0.610	
673	0.660	SUPERCRITICAL WATER
653	0.451	
673	0.375	
673	0.167	

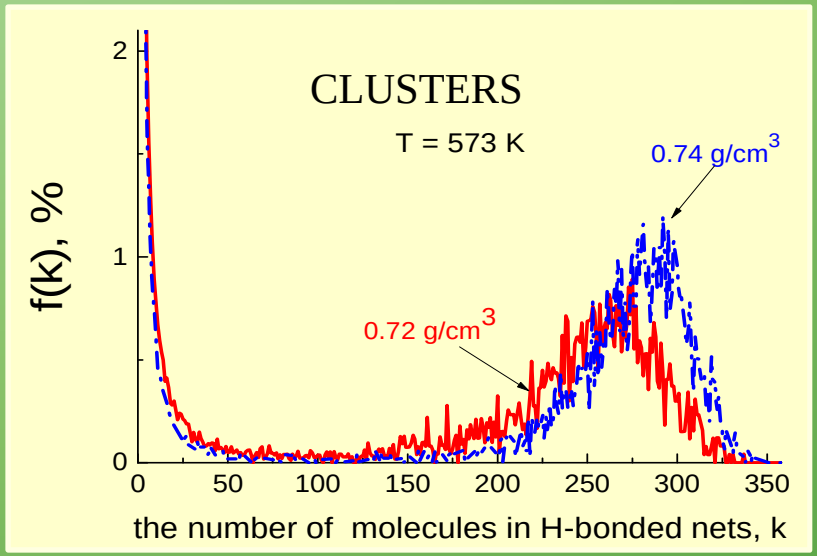
THE PHASE DIAGRAM

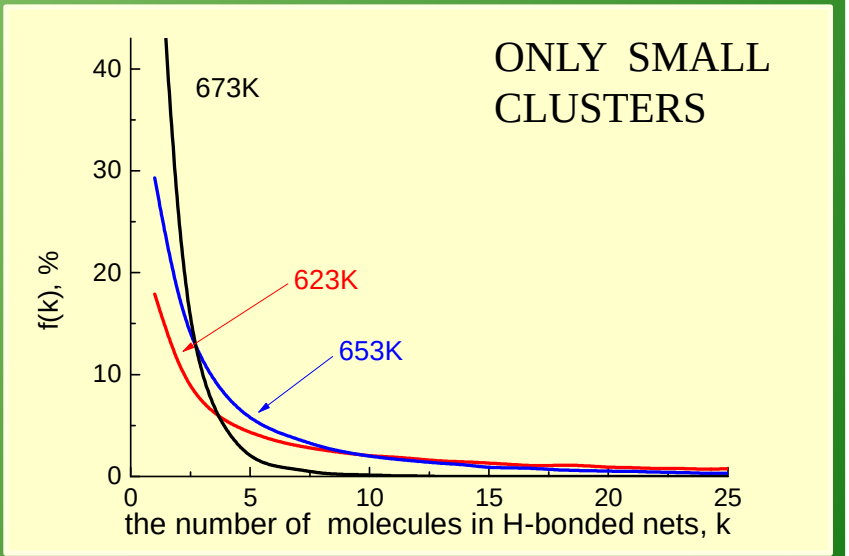


THE STRUCTURE OF WATER
THE HYDROGEN - BOND NETWORK

CLUSTER
net of molecules having at least one H-bond to other members

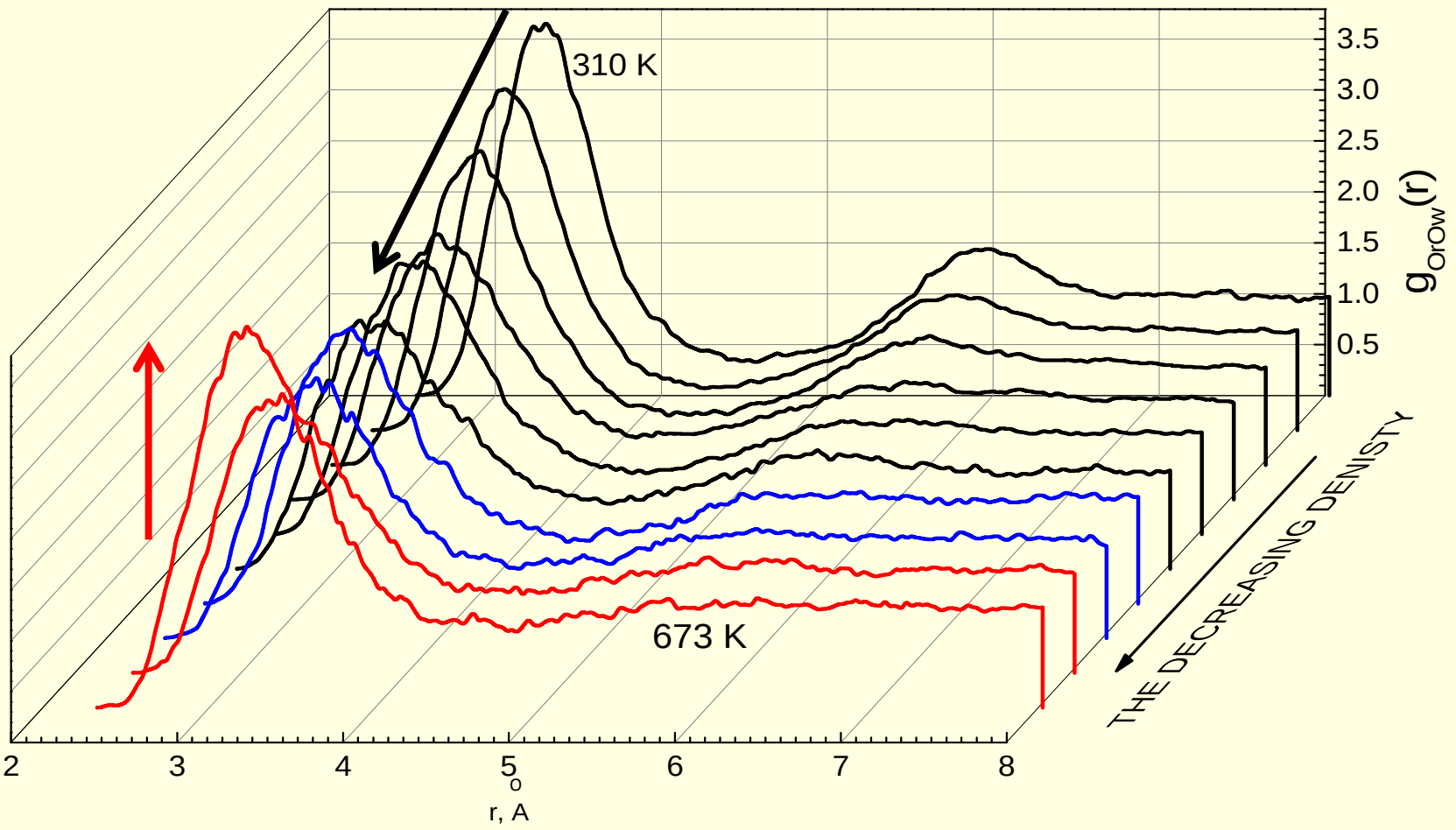






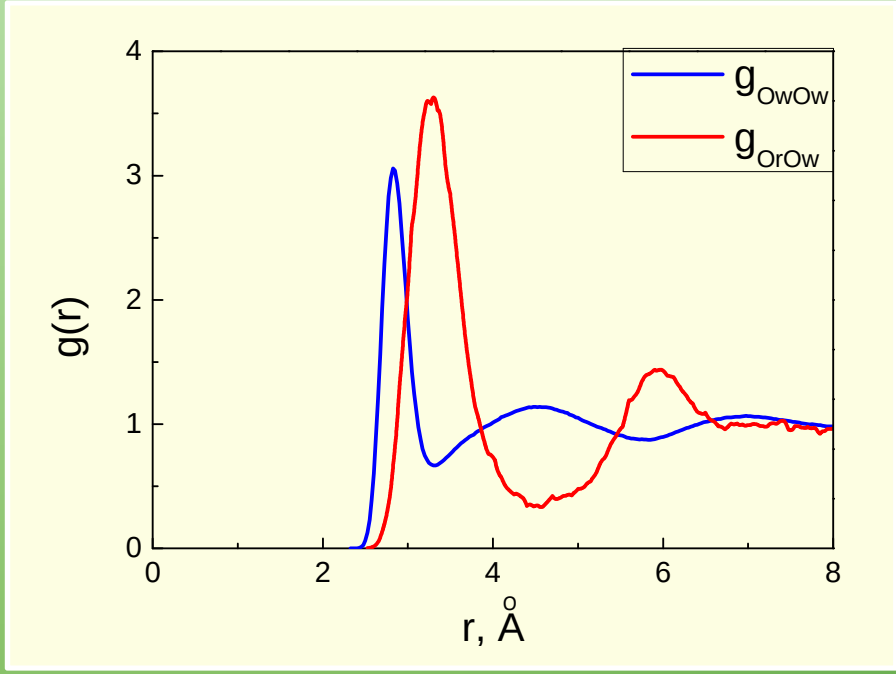
D.Swiatla-Wojcik, J.Szala-Bilnik, Transition form patchlike to clusterlike inhomogeneity arising from hydrogen-bonding in water, J.Chem.Phys.,**134,**054121(2011).

RADIAL DISTRIBUTION FUNCTION $g_{OrOw}(r)$

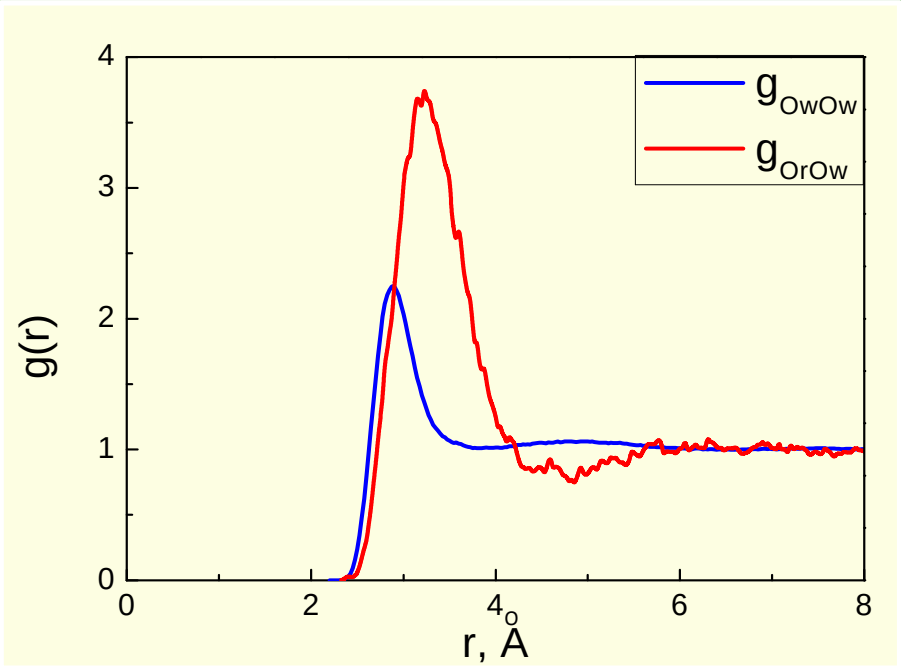


RADIAL DISTRIBUTION FUNCTION

T=310 K, ρ=0,994 gcm^{-3}

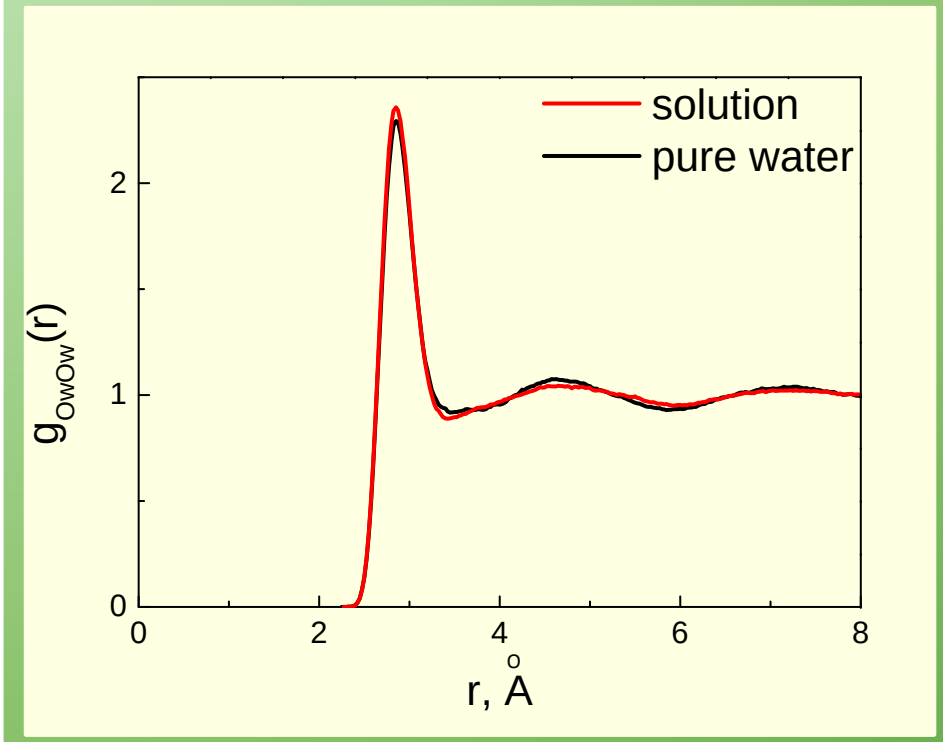


T=673 K, ρ=0,167 gcm^{-3}

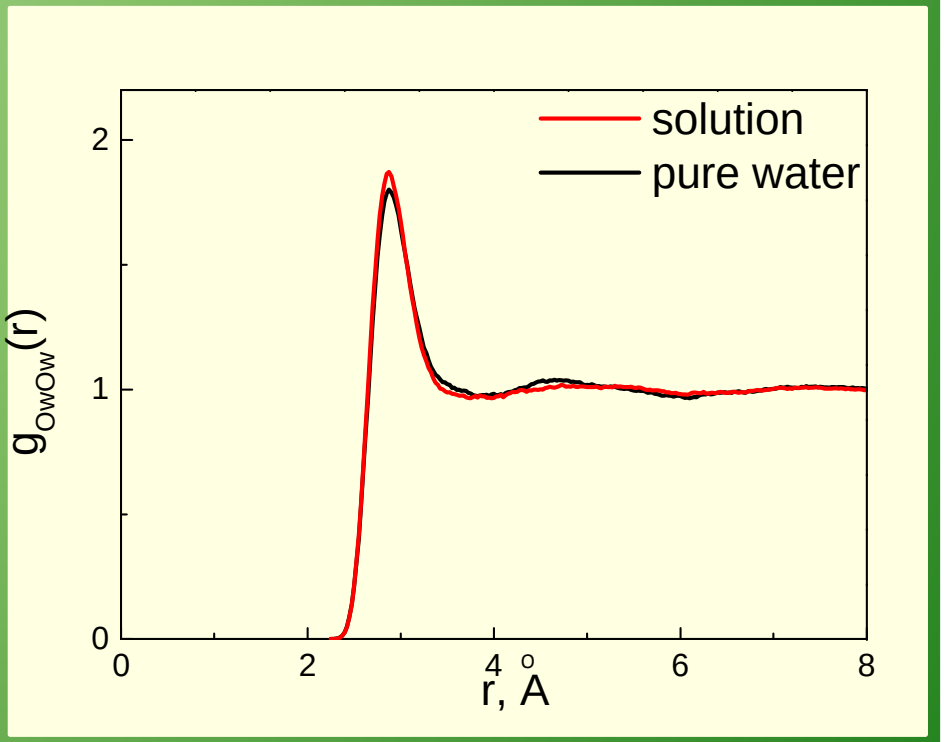


RADIAL DISTRIBUTION FUNCTION OF WATER

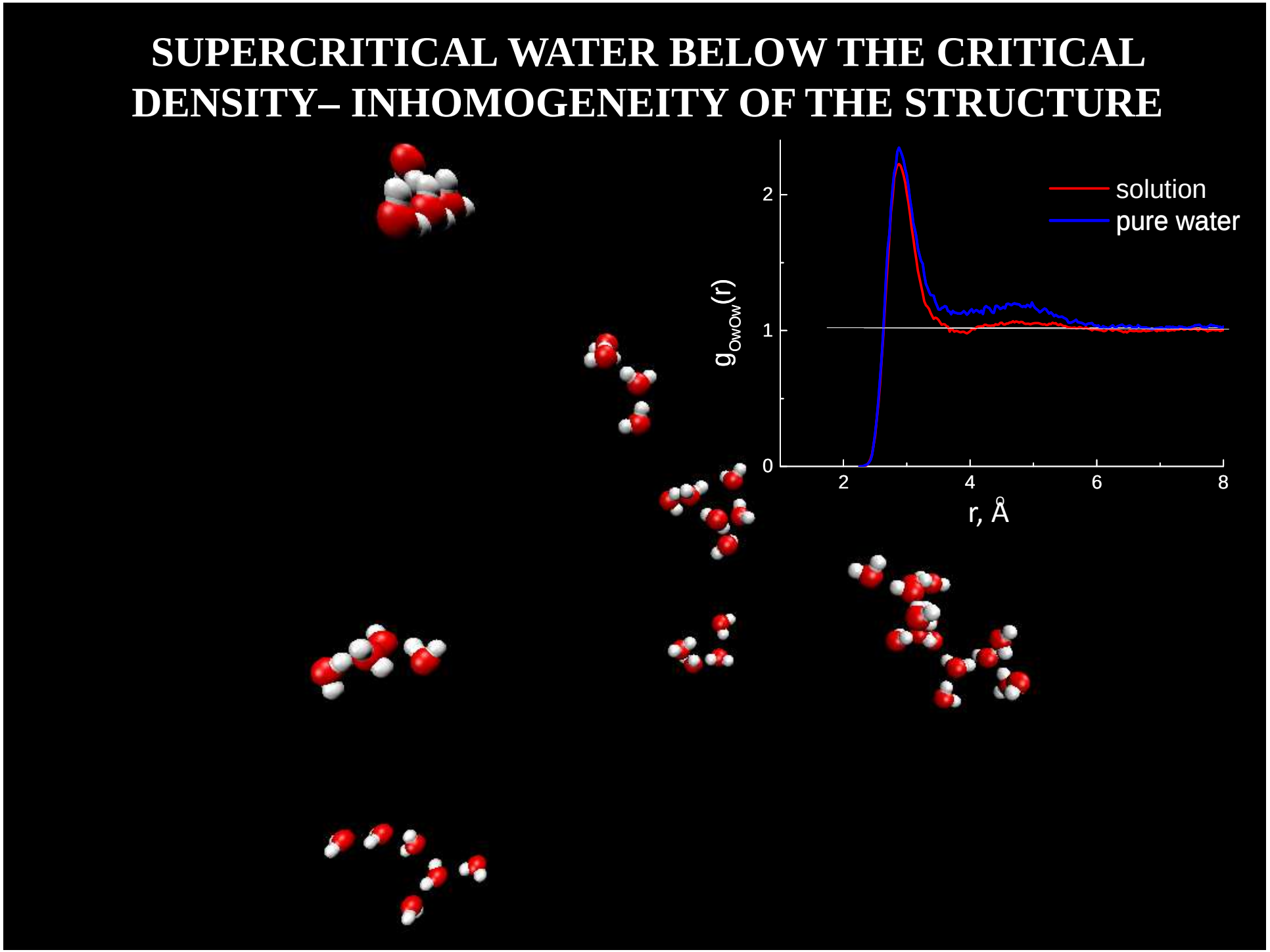
LIQUID WATER



SUPERCRITICL WATER
ABOVE THE CRITICAL DENISTY



SUPERCRITICAL WATER BELOW THE CRITICAL DENSITY– INHOMOGENEITY OF THE STRUCTURE



TWO HYDRATION MECHANSIMS

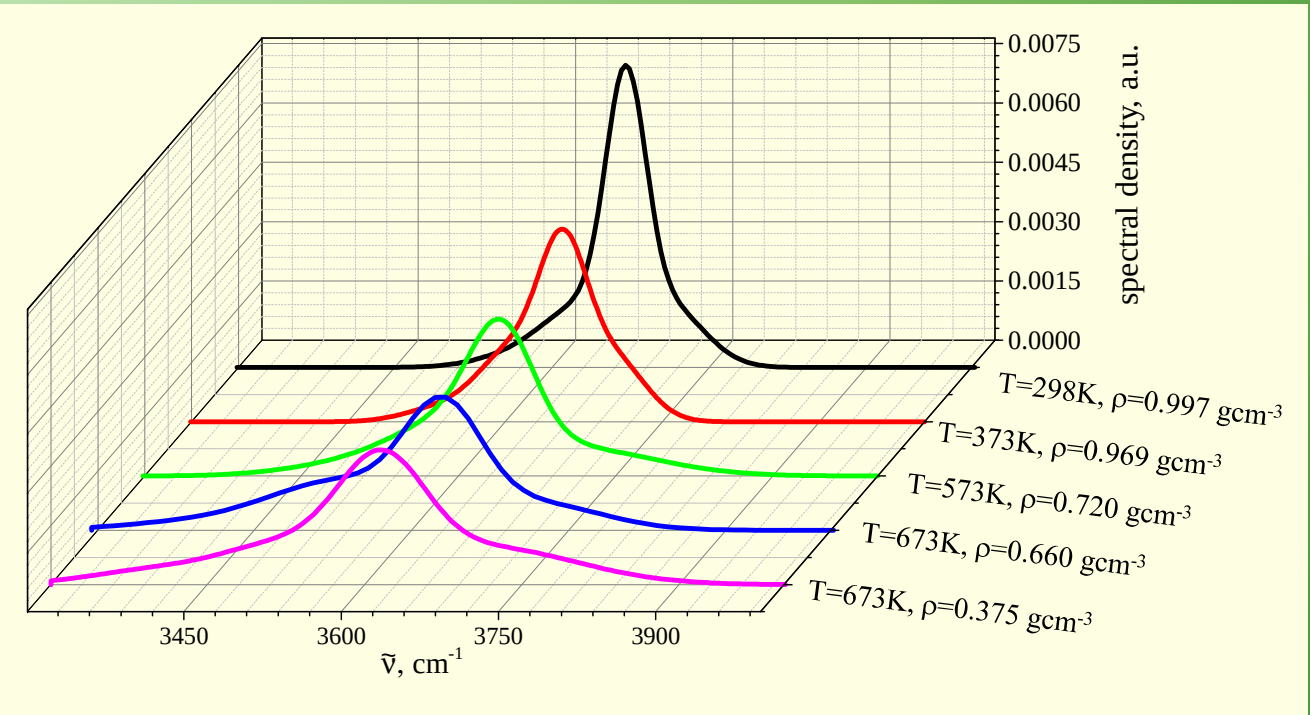
• LOCALISATION IN CAVITIES EXISTING IN THE SOLVENT STRUCTURE - LIQUID WATER AND SUPERCRITICAL WATER ABOVE THE CRITICAL DENISTY

•SELF – TRAPPING - SUPERCRITICAL WATER BELOW THE CRITICAL DENSITY

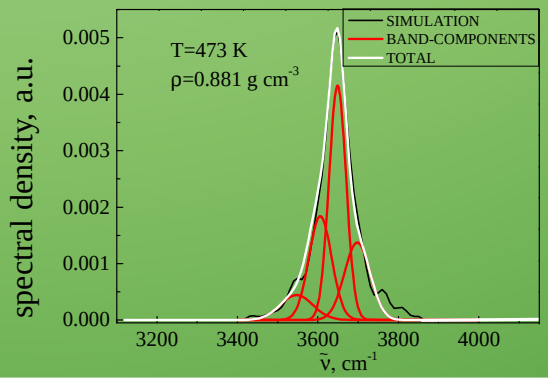
J.Szala-Bilnik, D. Swiatla-Wojcik, Hydration of OH radical in high temperature water, J.Mol.Liq. **164**,34 (2011),

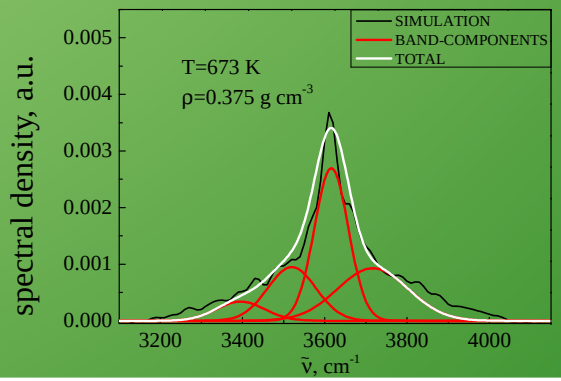
D.Swiatla-Wojcik, J.Szala-Bilnik, Mechanism of OH radical hydration: A comparative computational study of liquid and supercritical solvent, J. Chem. Phys. **136**,064510 (2012)

SPECTRAL DENSITY OF THE STRETCHING VIBRATIONS OF •OH



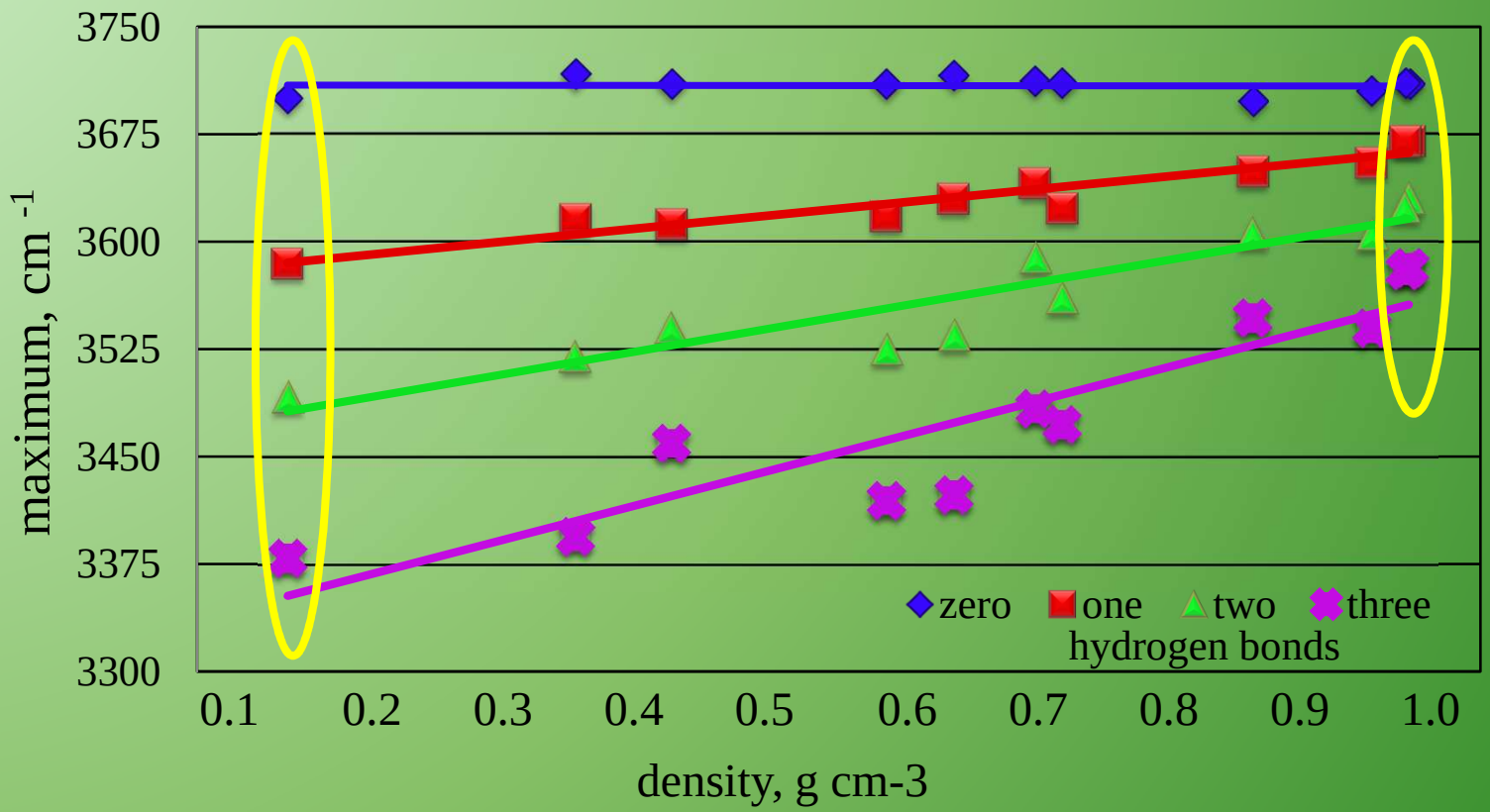
DECOMPOSITION OF THE SPECTRAL DENSITY





BAND-COMPONENTS WERE ASSIGNED TO STRETCHING VIBRATIONS OF •OH RADICAL FORMING 0, 1, 2 OR 3 HYDROGEN BONDS WITH WATER MOLECULES

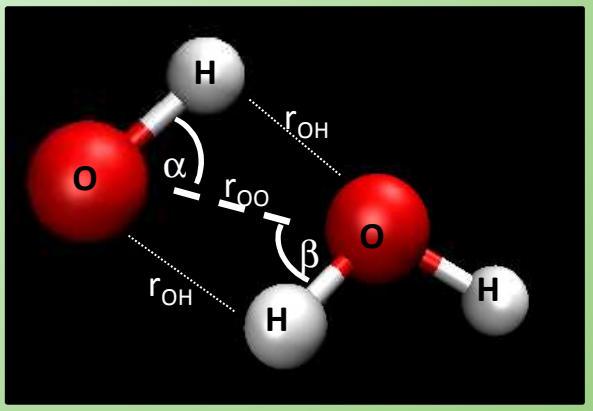
THE INFLUENCE OF DENSITY ON THE MAXIMUM OF BAND-COMPONENTS



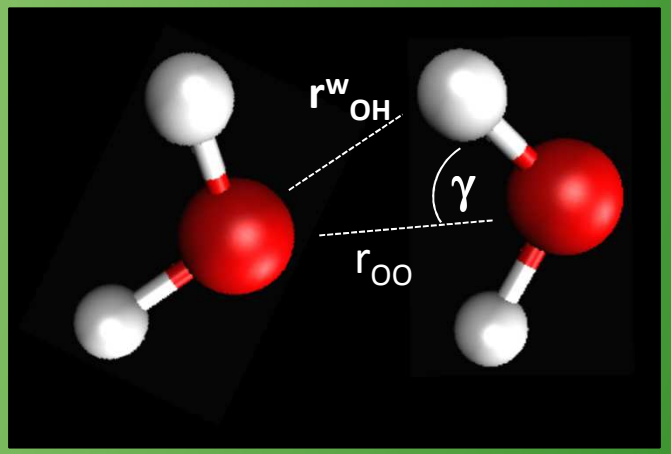
The position of band-components assigned to non-bonded OH radical is unaffected by thermodynamic conditions .

The shifts between band-components confirmed the hydration mechanism.

DEFINITION OF H - BONDS

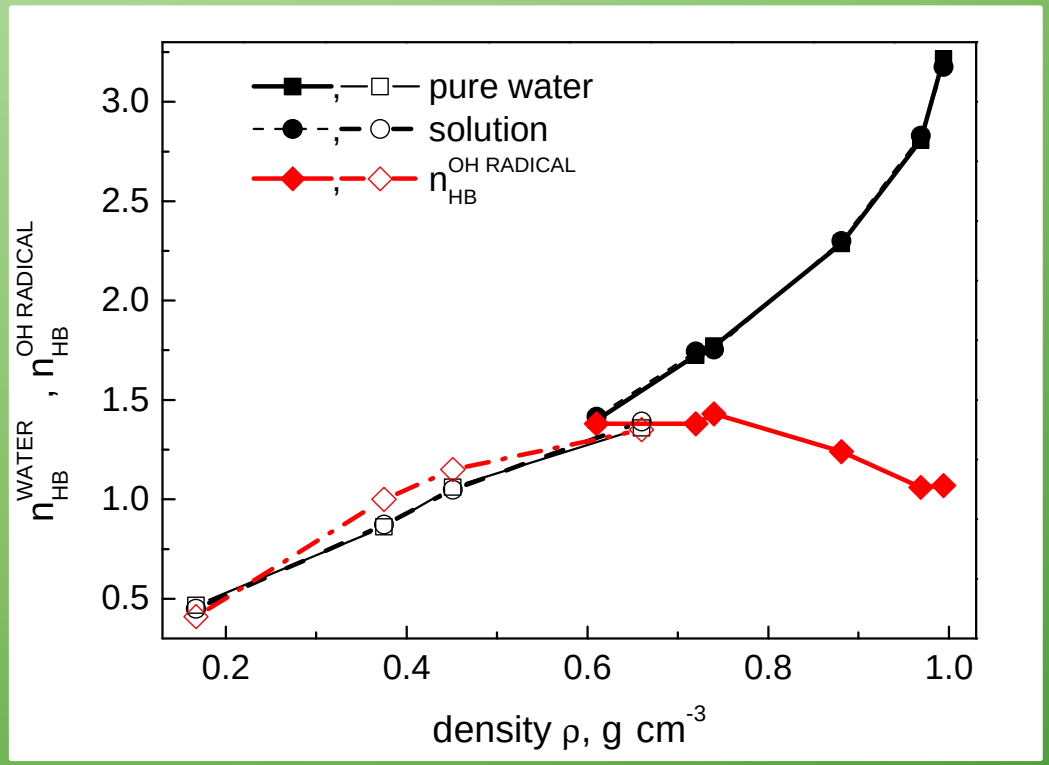


$r_{OH} \leq 2.7$ Å
$\alpha, \beta \leq 40^{o}$
$E \leq -6$ kJ mol^{-1}



$r^{w}_{OH} \leq 2.5$ Å
$\gamma \leq 30^{o}$
$E \leq -8$ kJ mol^{-1}

MEAN NUMBER OF HYDROGEN BONDS, n_{HB}



decrease with the decreasing density (water)

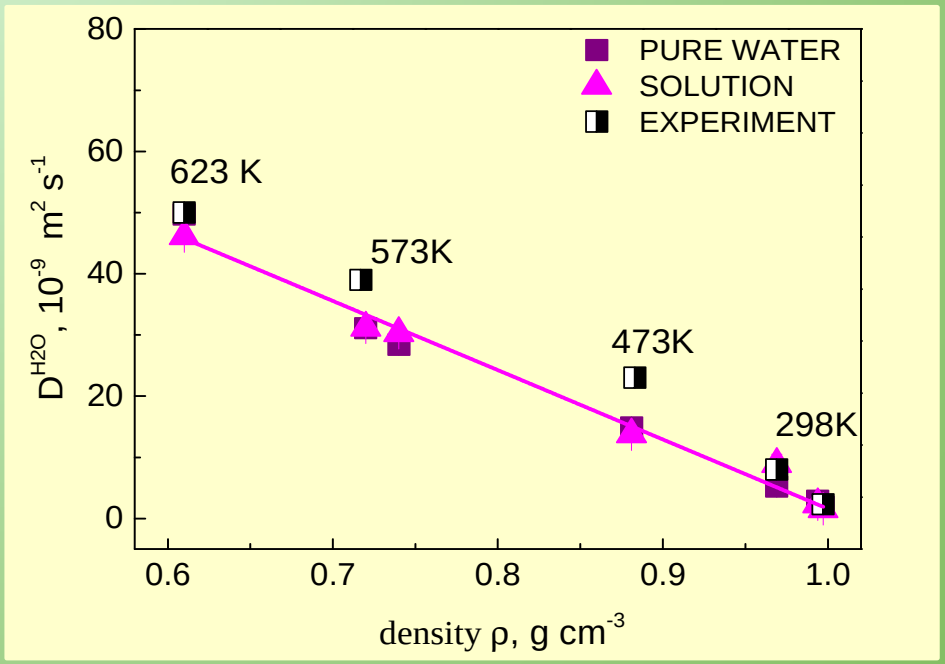
non-monotonic dependence (•OH radical)

SELF - DIFFUSION COEFICIENT OF WATER
DIFFUSION COEFICIENT OF •OH RADICAL

Green –Kubo relation

$$D^{ACF} = \lim_{t\to\infty} \frac{1}{3} \int_0^t \langle \vec{v}(0) \cdot \vec{v}(t') \rangle \, dt'$$

SELF- DIFFUSION COEFFICIENT OF WATER

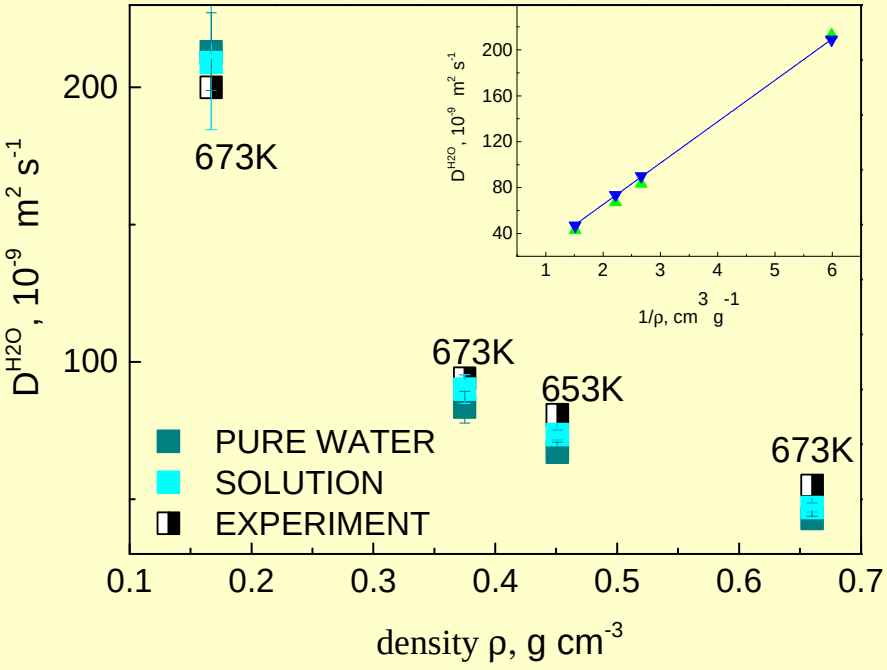


LIQUID WATER: D^{H2O}
similar for pure water and solution
linear increase with the decreasing density
good accordance with experiment

SUPERCRITICAL WATER: D^{H2O}
good accordance with experiment

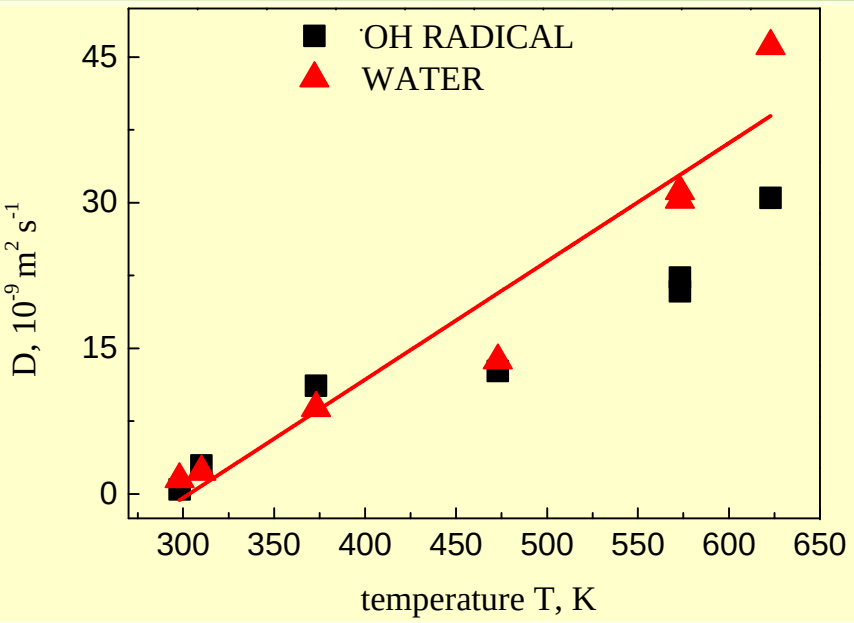
Above the critical density
similar for pure water and solution

Below the critical density
the significant increase

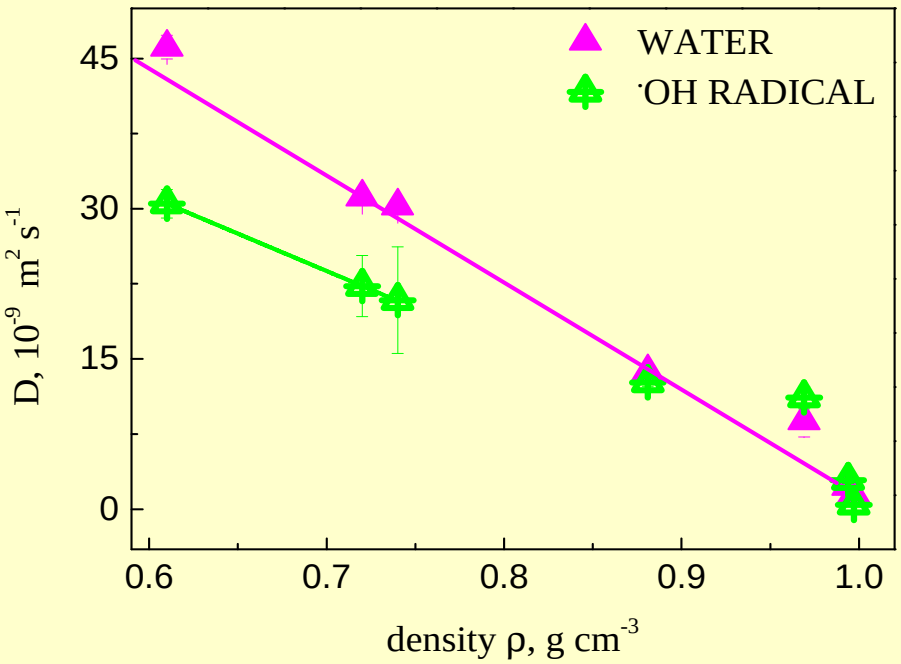


D.Swiatla-Wojcik, J.Szala-Bilnik, *Transition from patch-like to cluster-like inhomogeneity arising from hydrogen-bonding water*, J. Chem. Phys. **134,** 054121 (2011)

COMPARISON OF DIFFUSION AND SELF- DIFFUSION COEFFICIENT



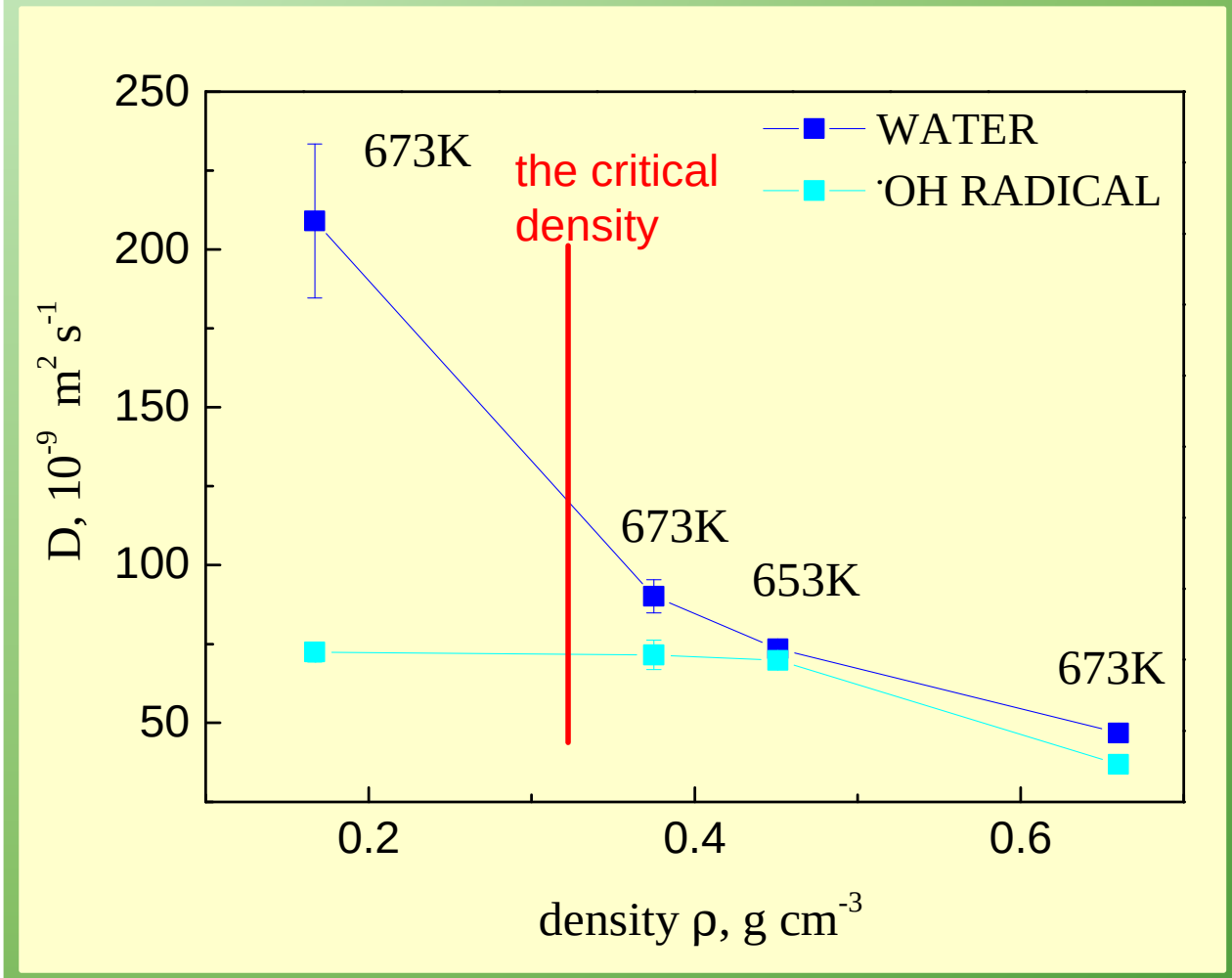
D^{H2O} and $D^{\bullet OH}$ increase with the decreasing density and the increasing temperature



($T < 473$ K) and ($\rho > 0.8$ g cm^{-3})
D^{H2O} and $D^{\bullet OH}$ are similar

($T > 573$ K) and ($\rho < 0.74$ g cm^{-3})
$D^{\bullet OH}$ is lower than D^{H2O}

COMPARISON OF DIFFUSION AND SELF- DIFFUSION COEFFICIENT – SUPERCRITICAL WATER



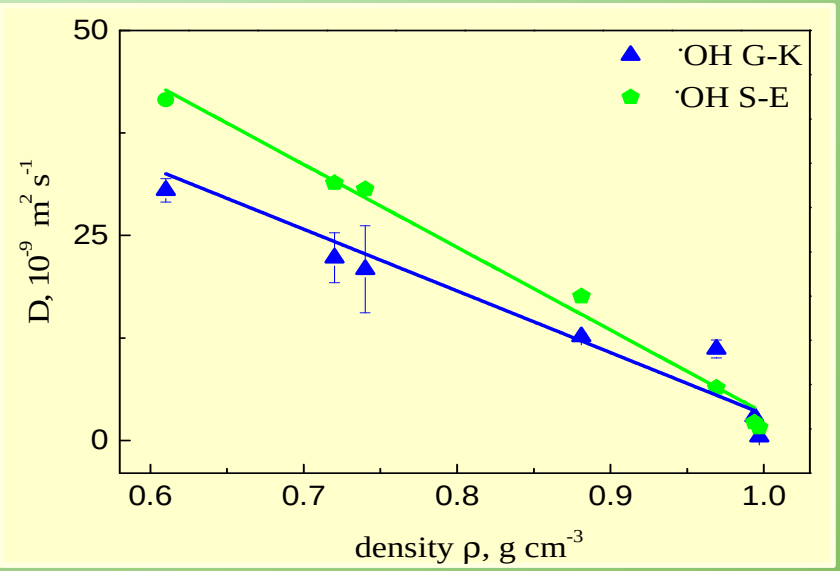
- Above the critical density

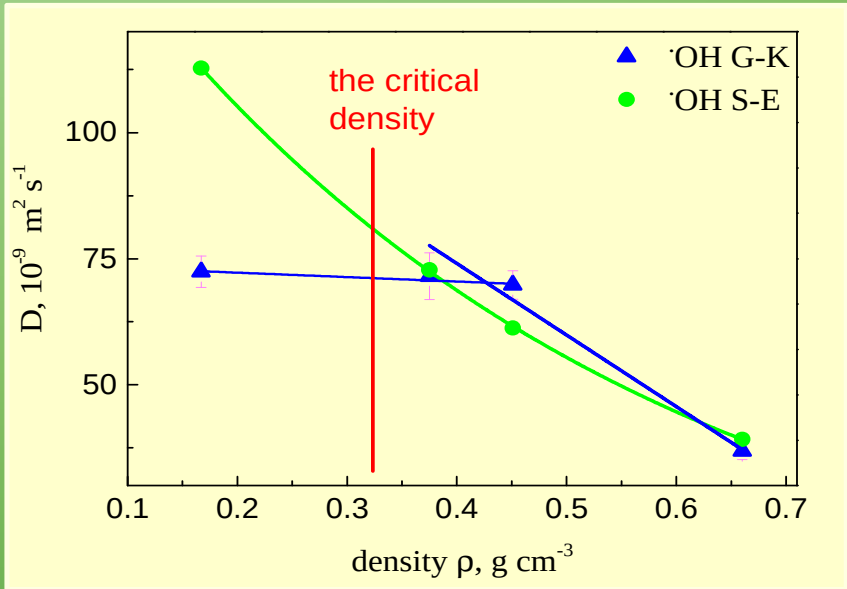
D^{H2O} and $D^{\cdot OH}$ increase with the decreasing density

- Below the critical density

D^{H2O} increases significantly
$D^{\cdot OH}$ does not change

DIFFUSION COEFFICIENT FOR •OH RADICAL





Stokes - Einstein relation

$$D = k_B T/(\alpha \eta \pi r)$$

the hydrodynamic radius r = 2.2 Å
the parameter α = 4

$D^{\bullet OH}$ in liquid water

• the hydrodynamic radius should increase to 3.3 Å to match $D^{\bullet OH}$ calculated from simulation

$D^{\bullet OH}$ in supercritical water

•below the critical density Stokes – Einstein relation predicts about 40% higher value.

CONCLUSIONS

1. In liquid compressed water up to ~473 K, in the presence of the continuous H-bond network, $D^{\bullet OH}$ scales with temperature like $D^{H2O.}$

2. Breakage of the continuous H-bond network causes lowering of $D^{\bullet OH}$ in relation to D^{H2O}, as the number of hydrogen bonds formed by •OH radical increases.

3. In the low density limit above the critical temperature self-trapping of •OH radical—noticeably hinders its diffusion.

Thank you for your attention