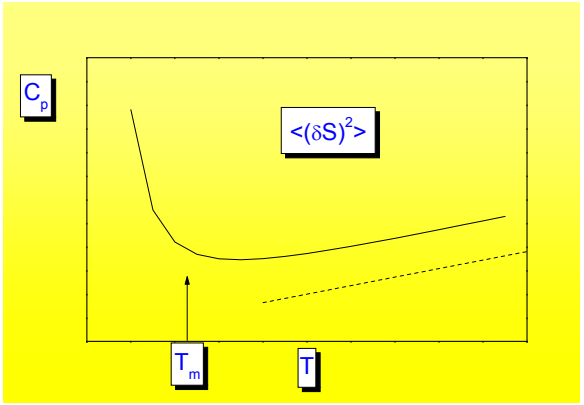
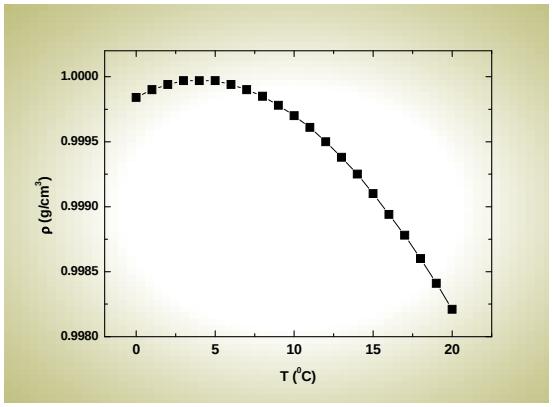
ROMA TRE
UNIVERSITÀ DEGLI STUDI

Clustering and percolation in supercritical aqueous fluids

Maria Antonietta Ricci

www.fis.uniroma3.it/liquidsgroup





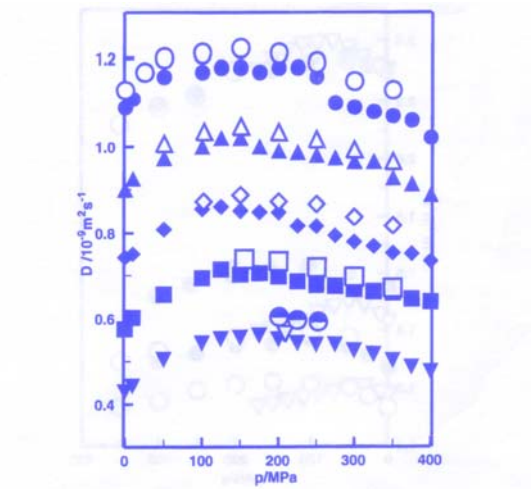
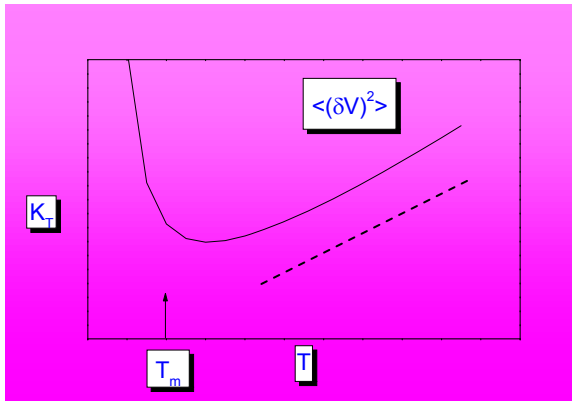
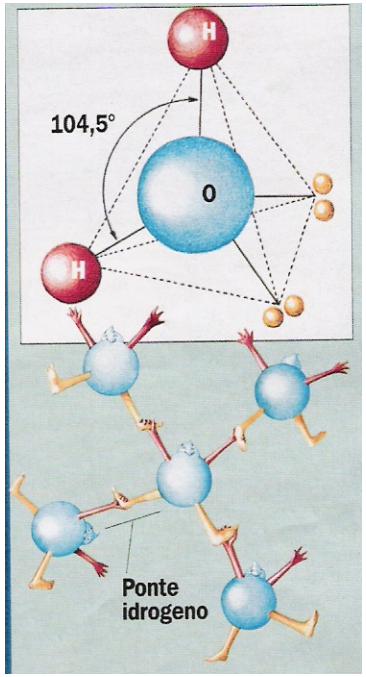


Figure 4. Comparison of the experimental self-diffusion coefficients of water with previous work below 0 °C: (open symbols) as in Figure 3; (●) 0 °C, (▲) −5 °C, (◆) −10 °C, (■) −15 °C, (▼) −21 °C, Prielmeier *et al.*, 1988.

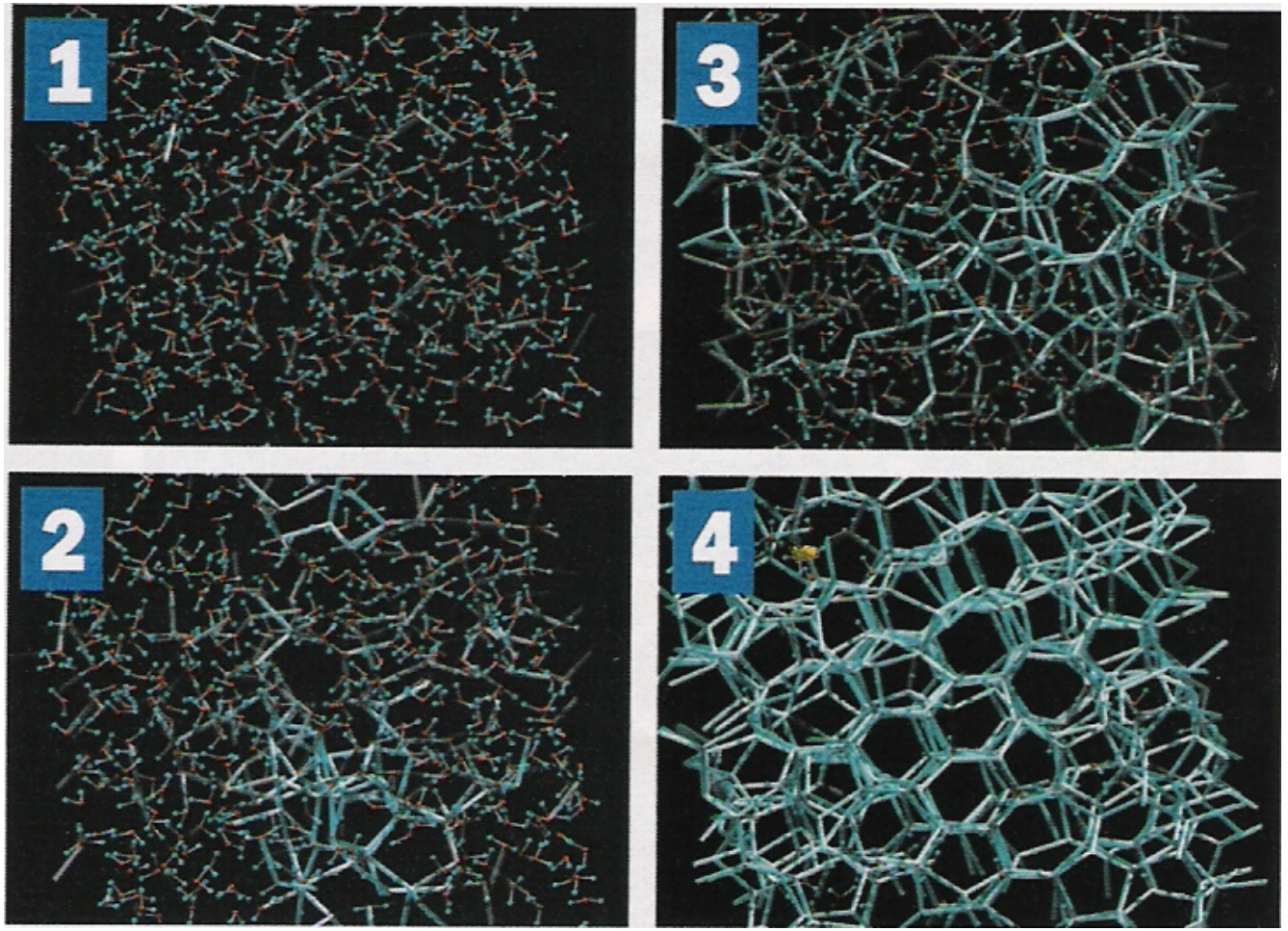




τ=0.000000000001 s (1 millesimo di miliardesimo di secondo)

Hbond energy: E_H=5Kcal/mole=10kT

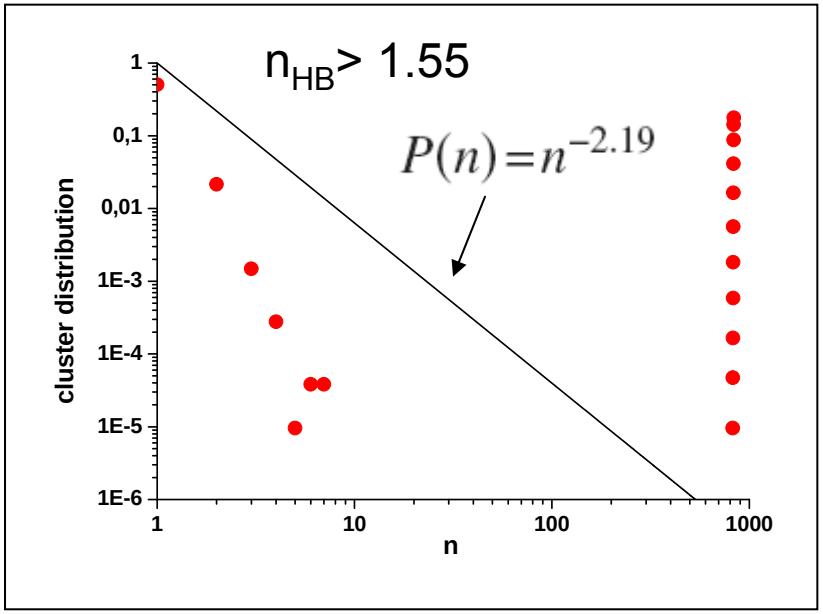
Covalent bond energy: E_c=200kT



H. E. Stanley, *J. Phys. A: Math. Gen.* **12**,L329 (1979).

H. E. Stanley, and J. Teixeira, *J. Chem. Phys.* **73**, 3404(1980).

Water at ambient conditions can be described as a percolating HB network



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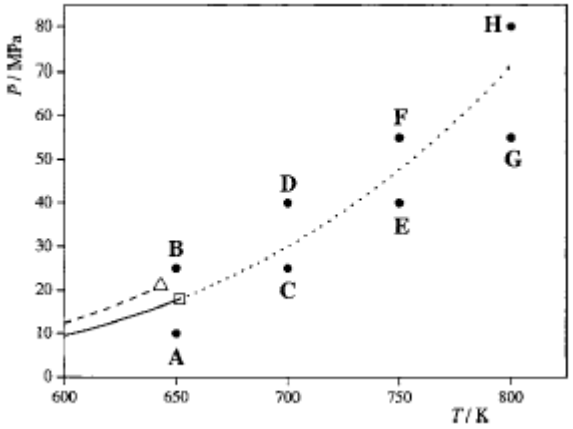
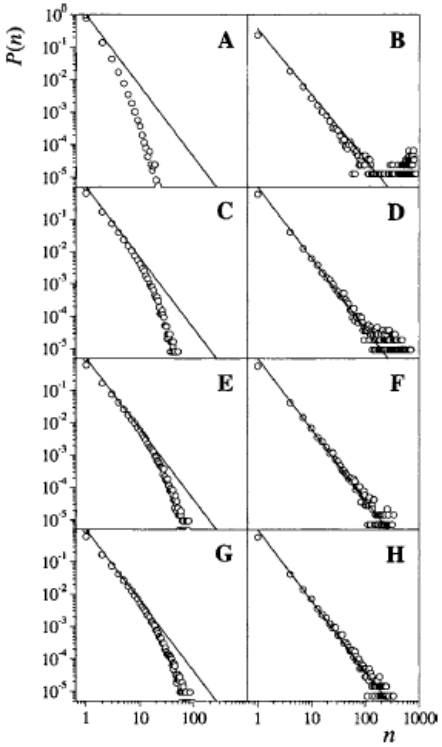
Line of percolation in supercritical water

Lívia Pártay and Pál Jedlovszky[a)]





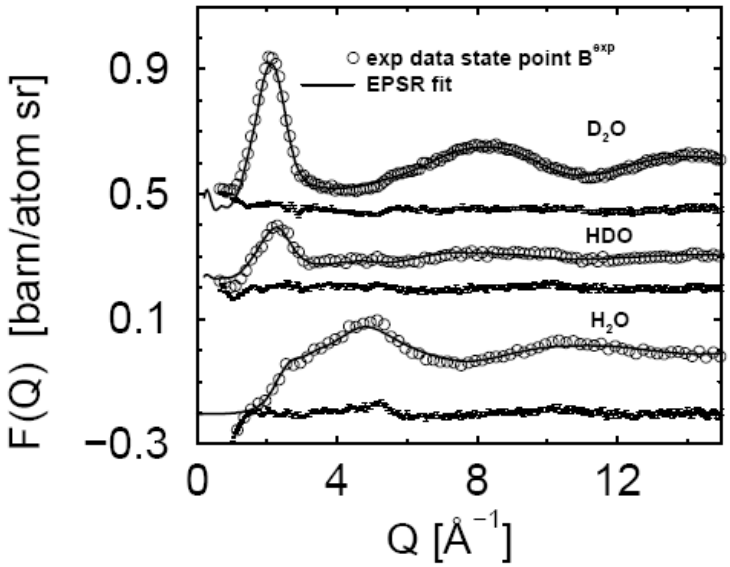
Questions:

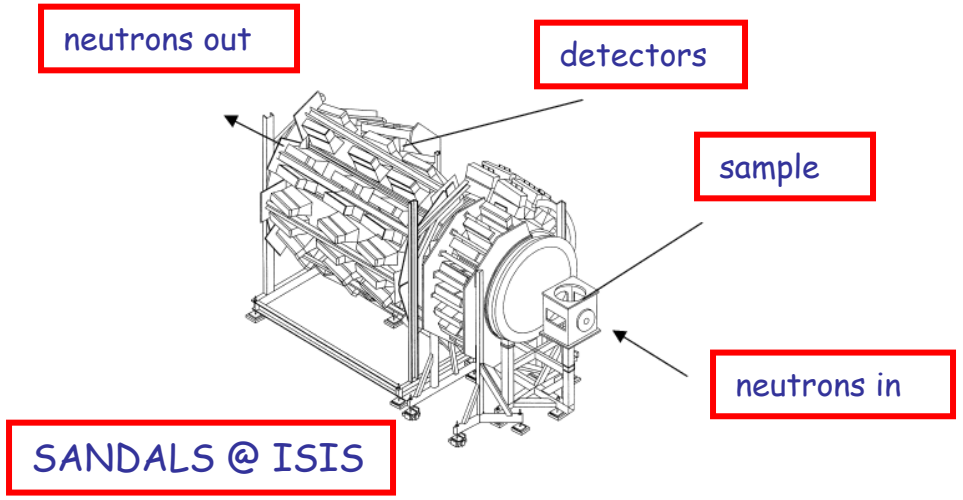
- Is it possible to test this idea against an experiment?
- What can we learn from this kind of data analysis?

- Is it possible to test this idea against an experiment?

YES

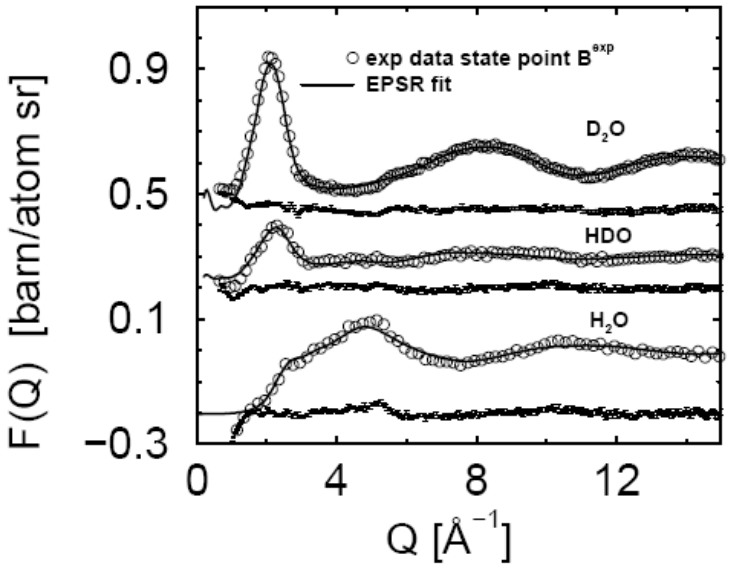
- Fully deuteriated
- Fully protiated
- 50% mixture





$$Q = \frac{4\pi}{\lambda} sin\theta$$

Is it possible to test this idea against an experiment?



$$F(Q) = \sum_{\alpha} \sum_{\beta \geqslant \alpha} w_{\alpha\beta}(S_{\alpha\beta}(Q) - 1)$$

$$w_{\alpha\beta} = c_\alpha c_\beta b_\alpha b_\beta (2 - \delta_{\alpha\beta})$$

$$(S_{\alpha\beta}(Q) - 1) = 4\pi\rho \int_0^\infty r^2 (g_{\alpha\beta}(r) - 1) \frac{sin(Qr)}{Qr} dr$$

Is it possible to test this idea against an experiment?

EPSR Monte Carlo Simulation

MC simulation with reference potential

Comparison with data

feedback

MC simulation with new effective potential

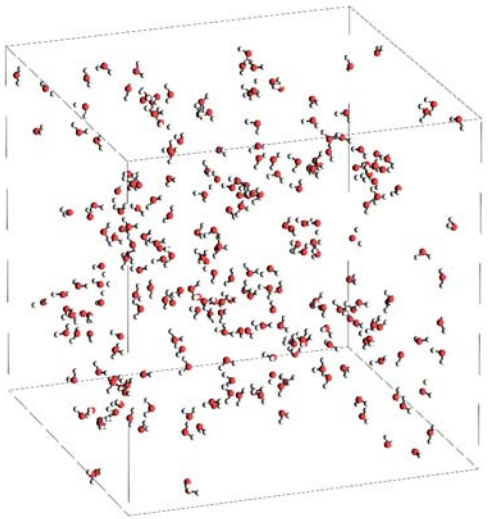
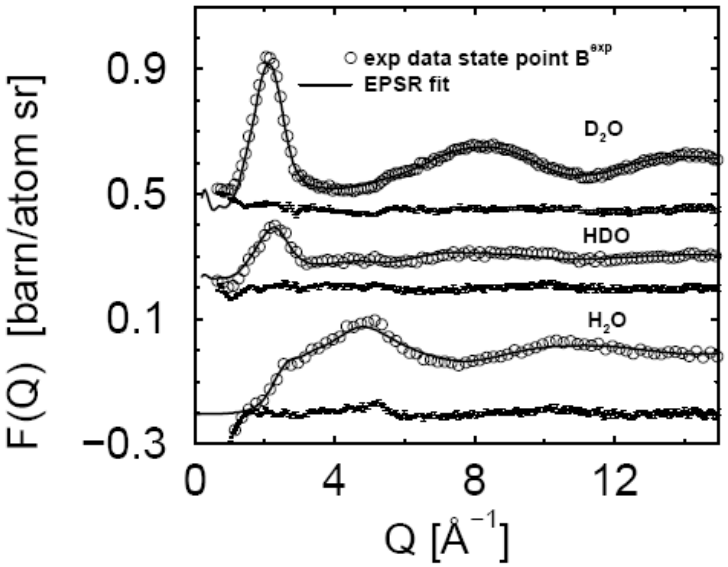
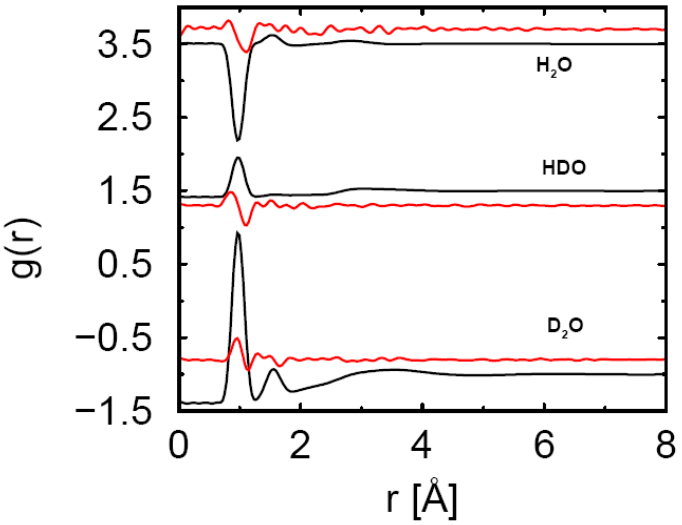
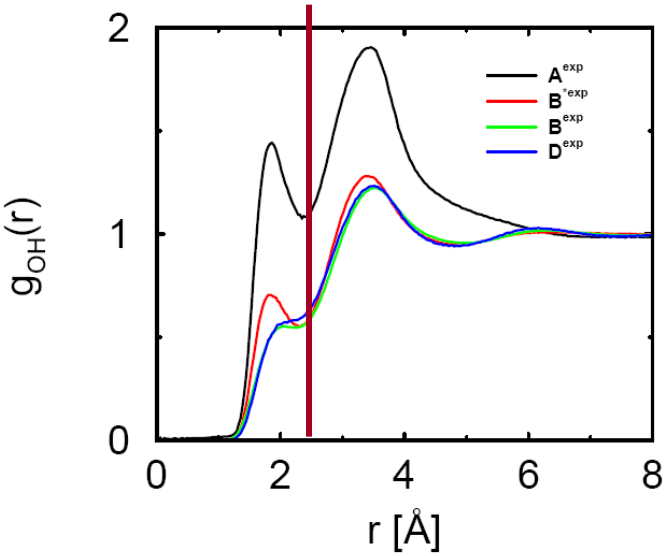


TABLE II. Parameter of the reference potential used to start the EPSR routin. The intramolecular bonds used were l_{C-O}=1.161 Å, l_{O-O}=2.32 Å, $l_{O_w}-H_w$=0.976 Å, and H_w-H_w=1.54 Å (Refs. 28 and 29).

	ϵ (kJ/mol)	σ (Å)	q (e)
O_w	0.65	3.166	−0.847 6
H_w	0	0	0.423 8
C	0.241	2.785	0.664 5
O	0.689 85	3.064	−0.332 25







Definitions:

- Two molecules are H-bonded if the OH distance is below the I minimum of g_{OH}.
- A group of molecules forms a cluster if each pair of molecules is bonded to at least one other molecule in the cluster.

Pure supercritical water

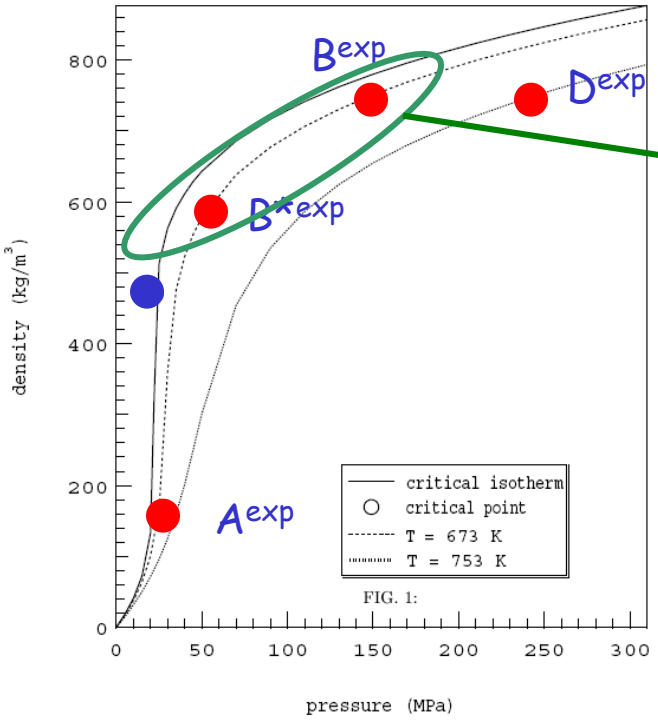


FIG. 1:

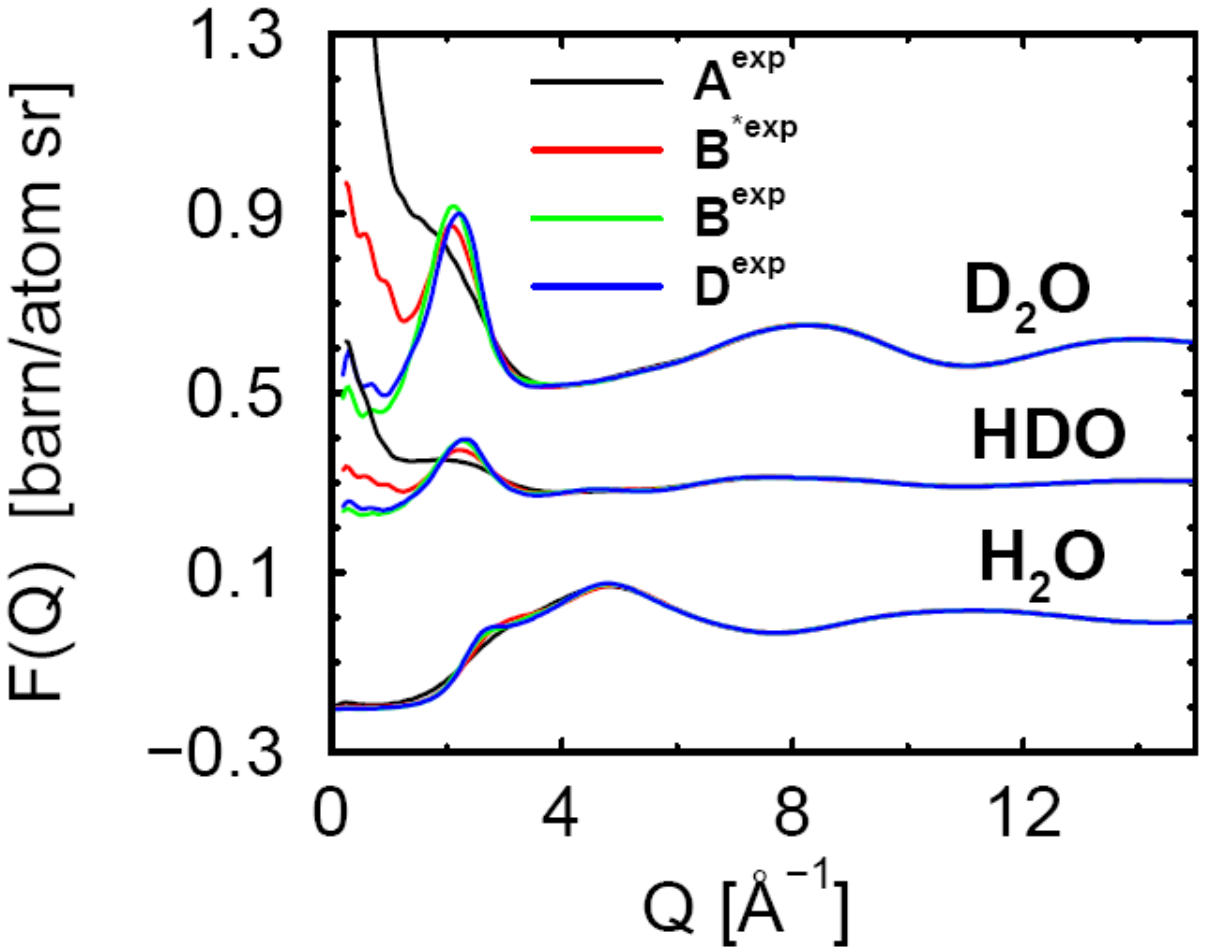
Supercritical water- CO_2 mixtures

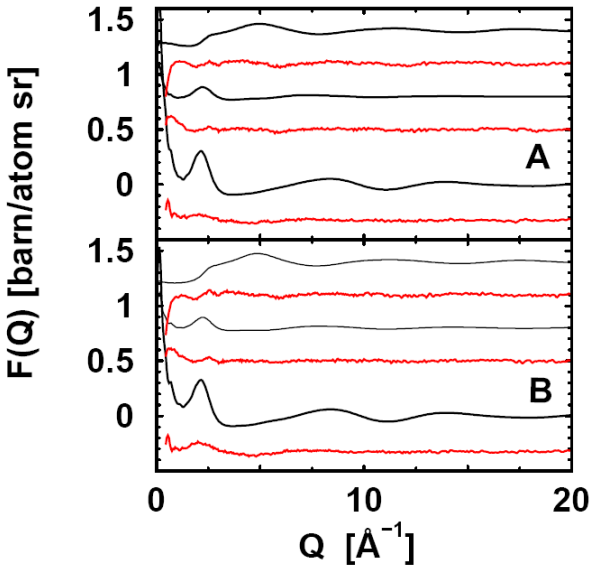
TABLE I. Thermodynamic parameters of the investigated water-CO_2 mixtures and pure water states.

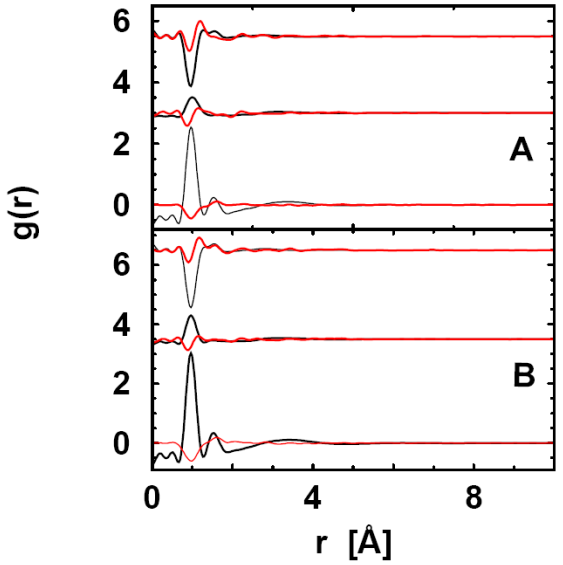
CO_2 concentration (%)	T (K)	P (bar)	ρ(at./Å^3)
0.92	673	1300	0.0458
9.2	673	1300	0.049
0	673	1500	0.0753
0	673	500	0.0552

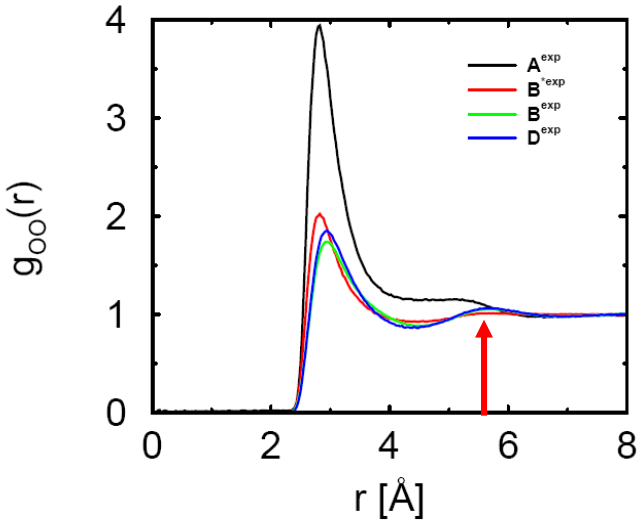
Excess volume

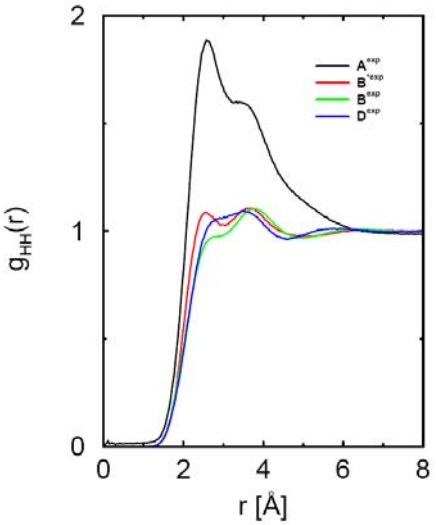
Pure supercritical water

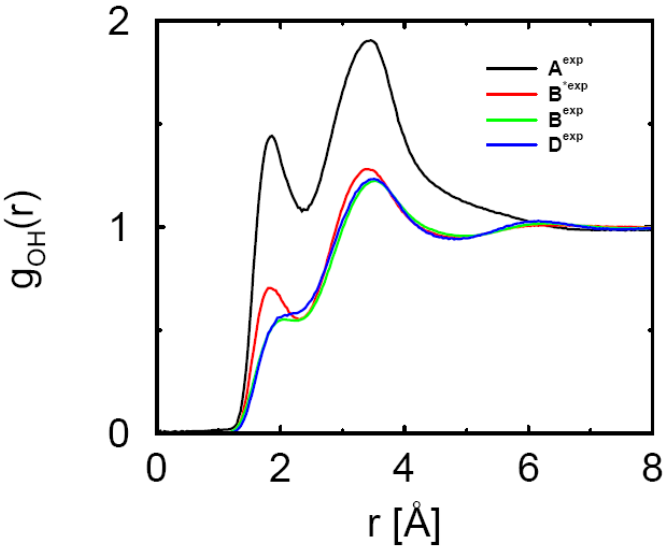




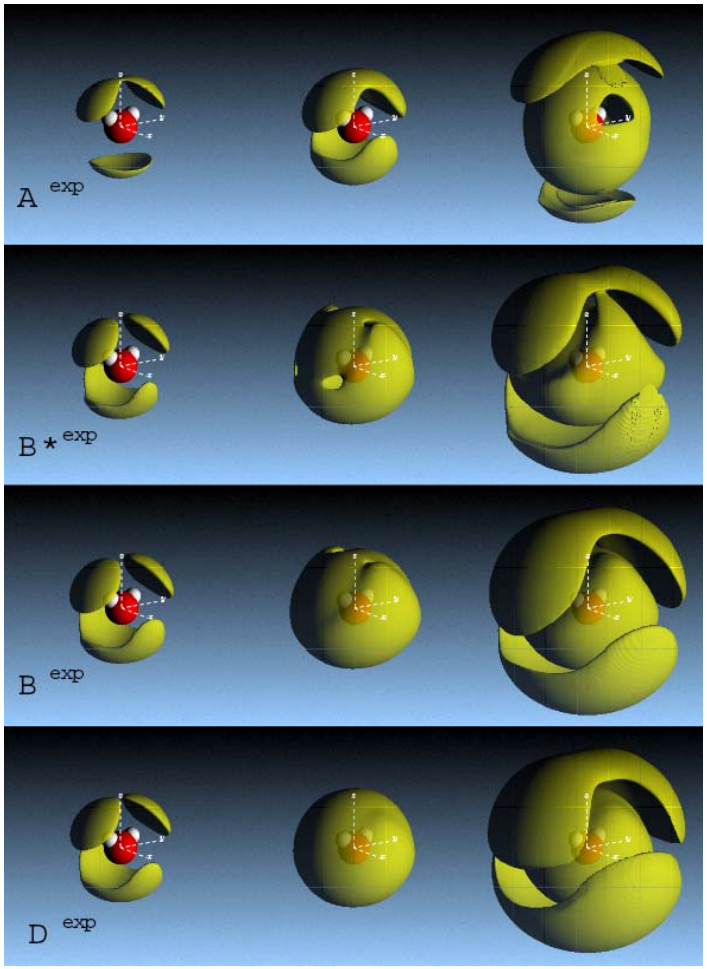




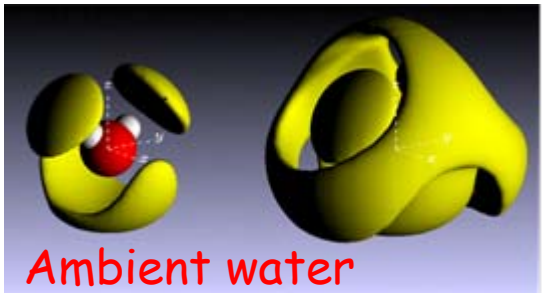


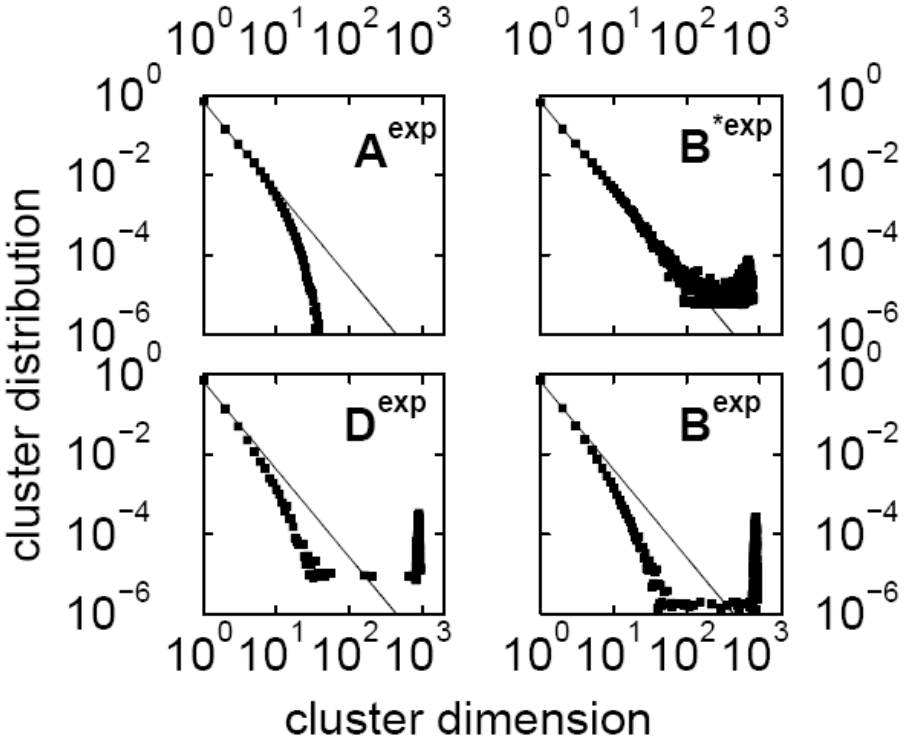


- Pure supercritical water
- gas- like vs liquid-like behavior
- signature of HB
- II peak of g_{OO} at ~ 5.6Å

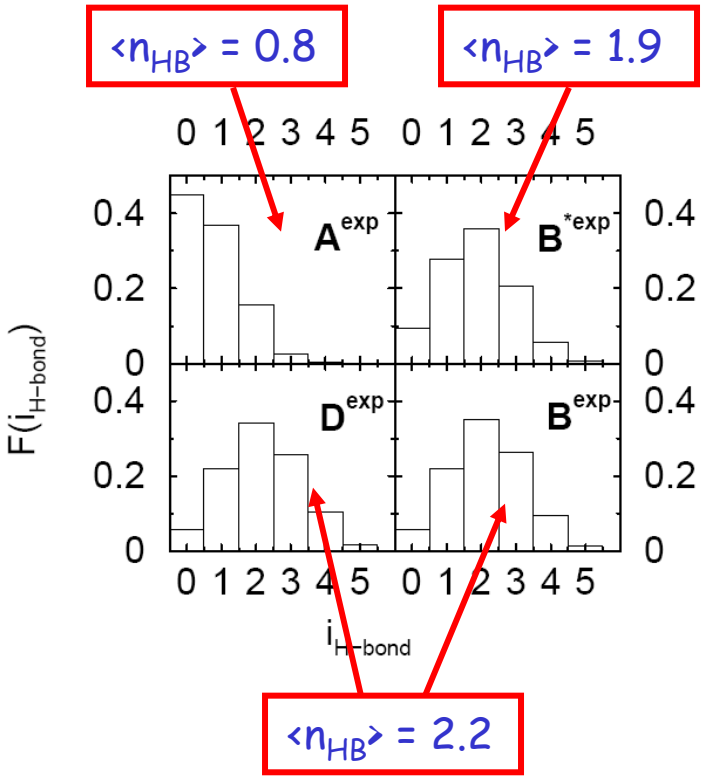


- Pure supercritical water
- triangular symmetry at state A^{exp}
- tetrahedral symmetry at liquid-like states
- lowering the contrast the symmetry becomes sferical
- II shell has the same symmetry as I shell





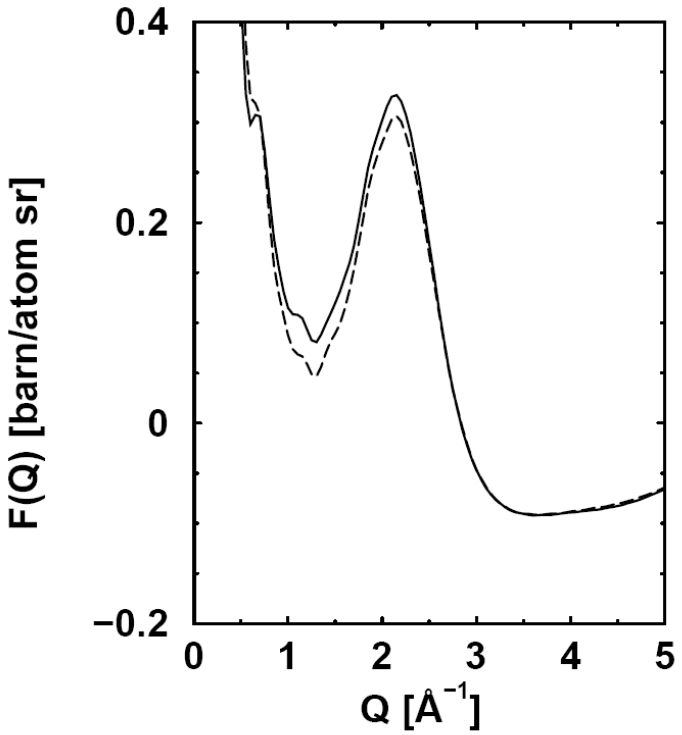
- Pure supercritical water
- liquid-like states are above the percolation threshold



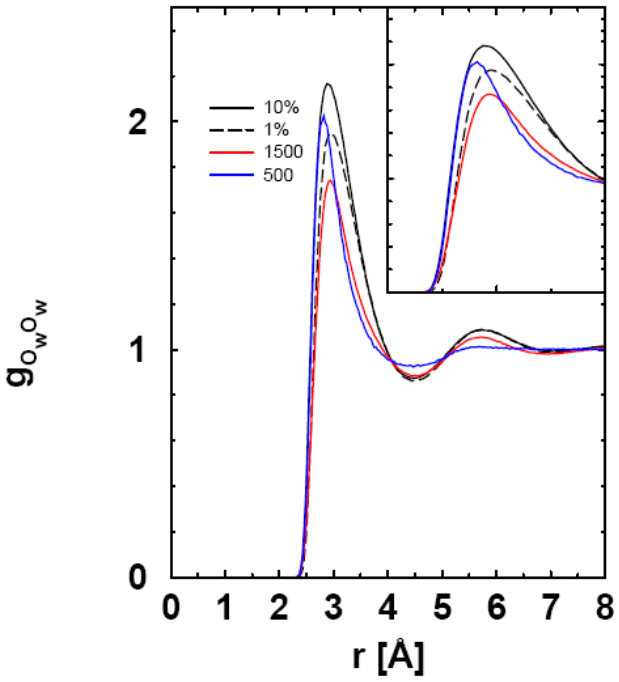
- Pure supercritical water- I take home message
- a percolation line separates 2 structurally different supercritical fluids:
- gas-like, with triangular I shell
- liquid-like with tetrahedral I shell
- n_{HB} decreases from ~ 2 to ~ 0.8 upon crossing PL
- 3D HB clusters or branched chains at liquid-like states
- 2D HB sheets or oligomers at gas-like states
- Question for the theoreticians:

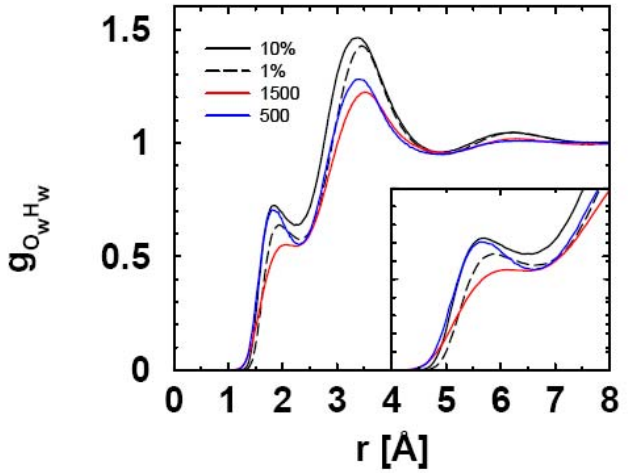
  PL and Fisher-Widom line can be identified?

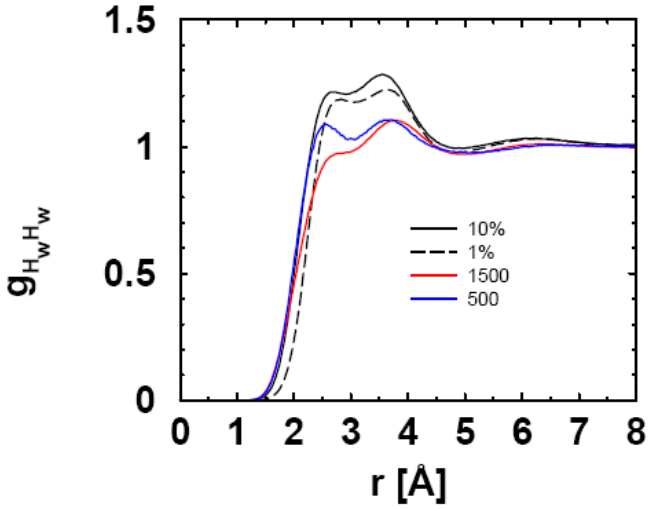
Supercritical water- CO_2 mixtures



- Supercritical water- CO_2 mixtures
- both states are liquid-like
- more defined peaks compared to pure water

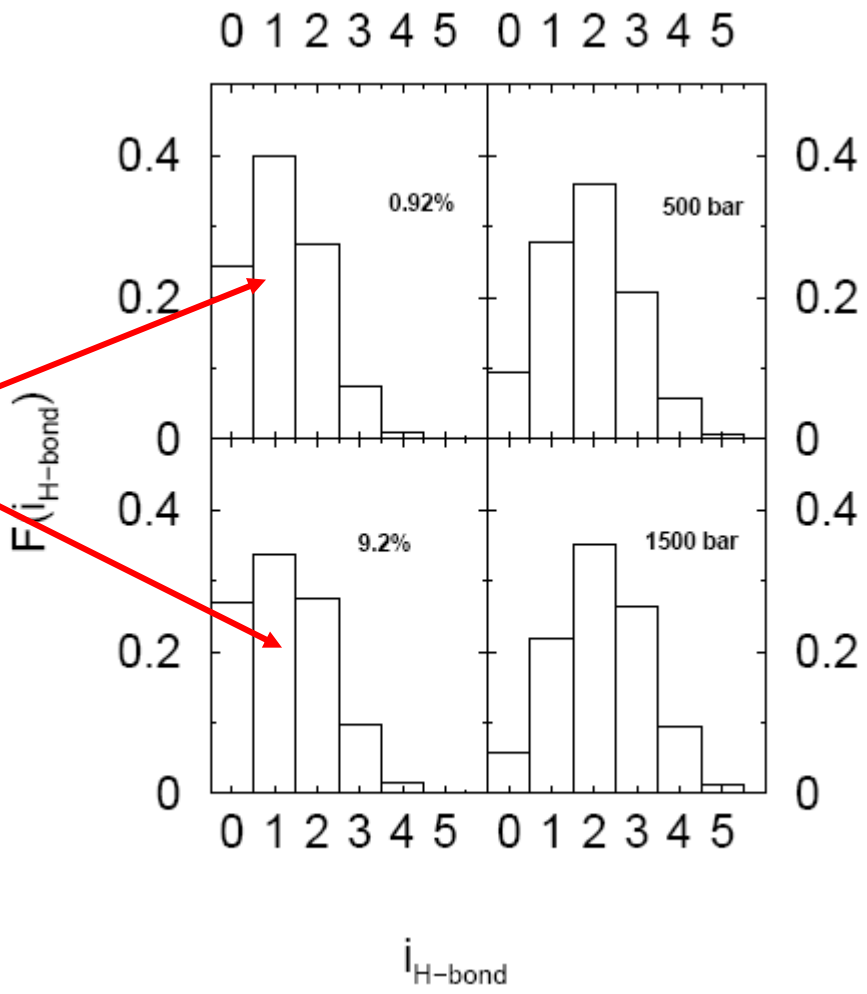




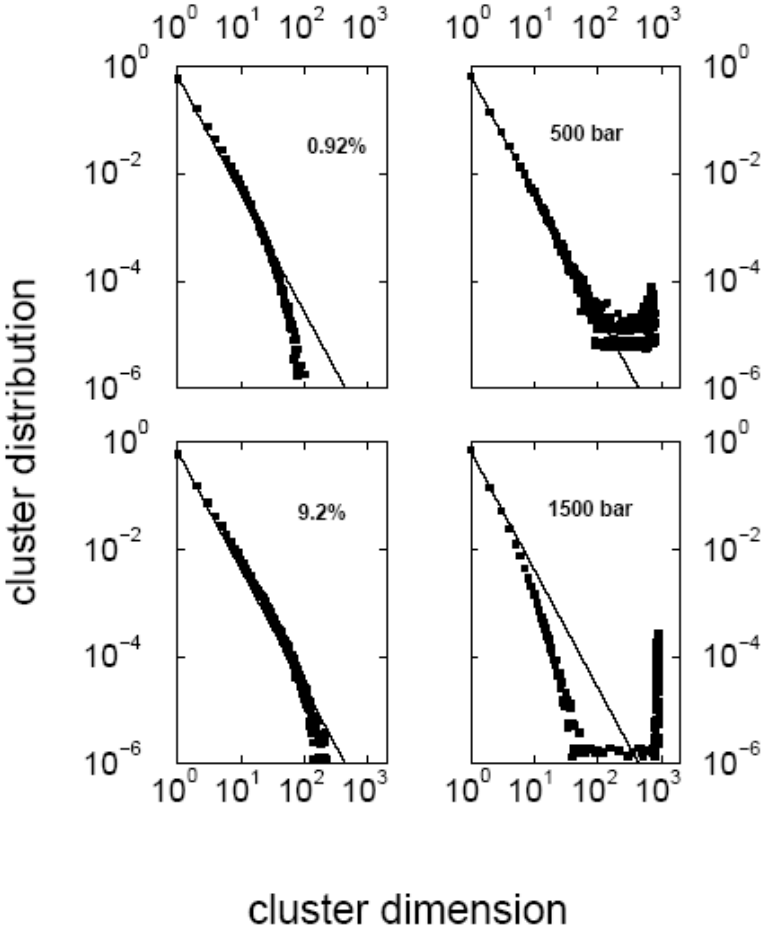


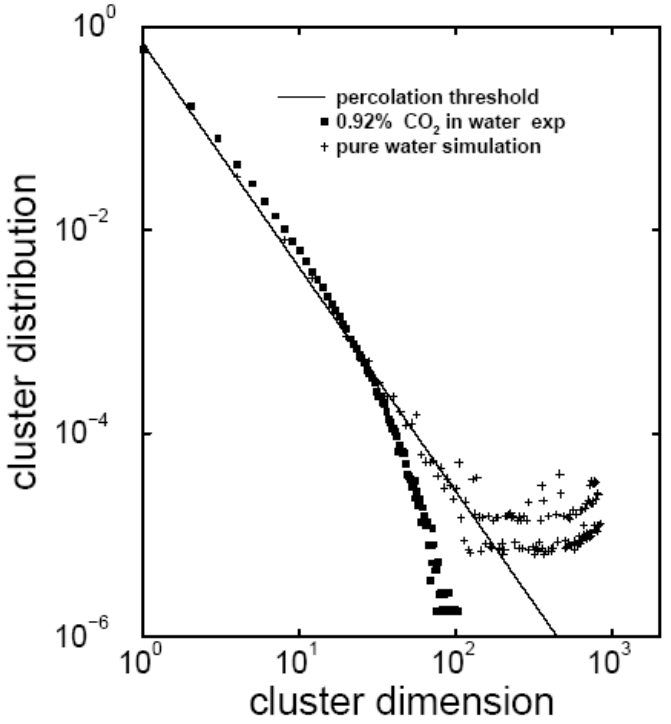
Supercritical water- CO_2 mixtures

n_{HB} ~ 1.2

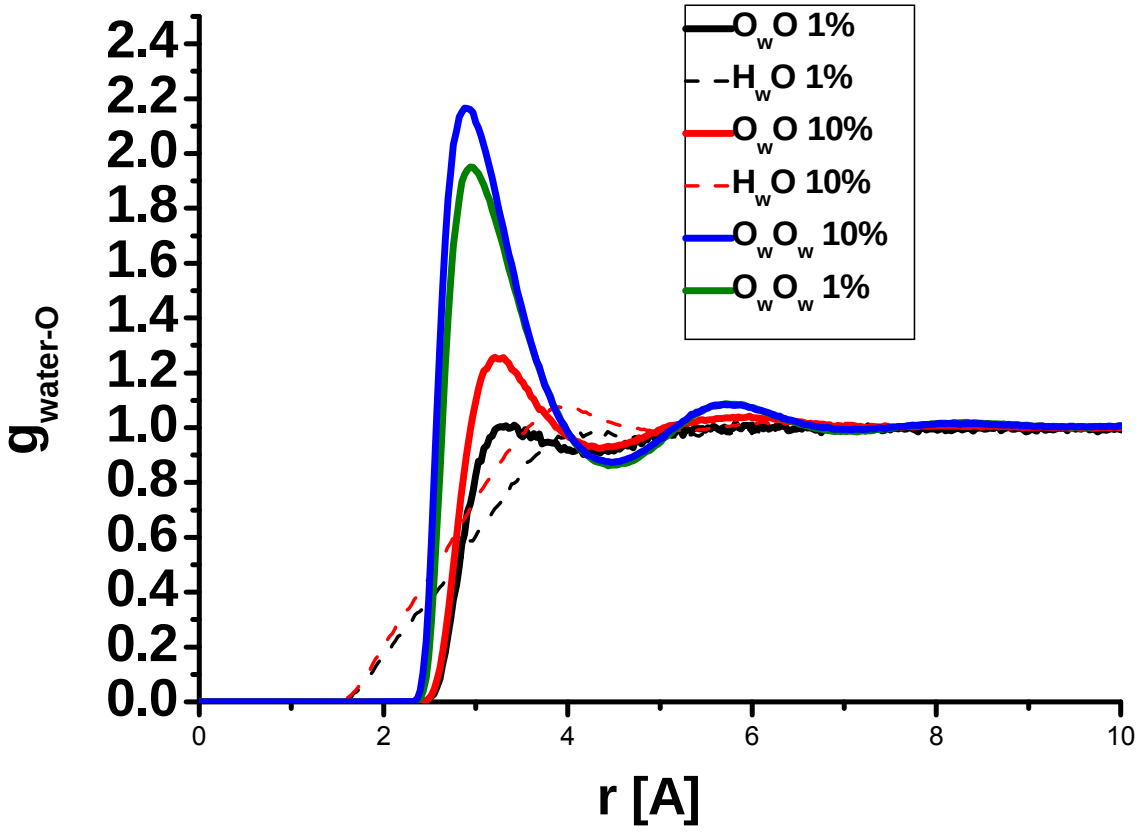


- Supercritical water- CO_2 mixtures
- the absence of percolation is not a trivial effect of the excess volume





- Supercritical water- CO_2 mixtures
- both minimum approach distance and average Ow -Ow distance are shorter than Ow-O distances.



- Supercritical water-CO_2 mixtures - II take home message
- liquid-like states
- better definition of shells compared to pure water
- $\langle n_{HB} \rangle$ lower than 1.55 → no percolation
- this is not a trivial effect of the excess volume
- the excess volume is localized around the CO_2 molecules
- clusters are fragmented.

Fabio Bruni	Roma Tre
Marco Bernabei	Roma Tre - UPV San Sebastian (ES)
Alan Soper	ISIS Facility (UK)

Thanks to:

ISIS Facility

CNR

MIUR

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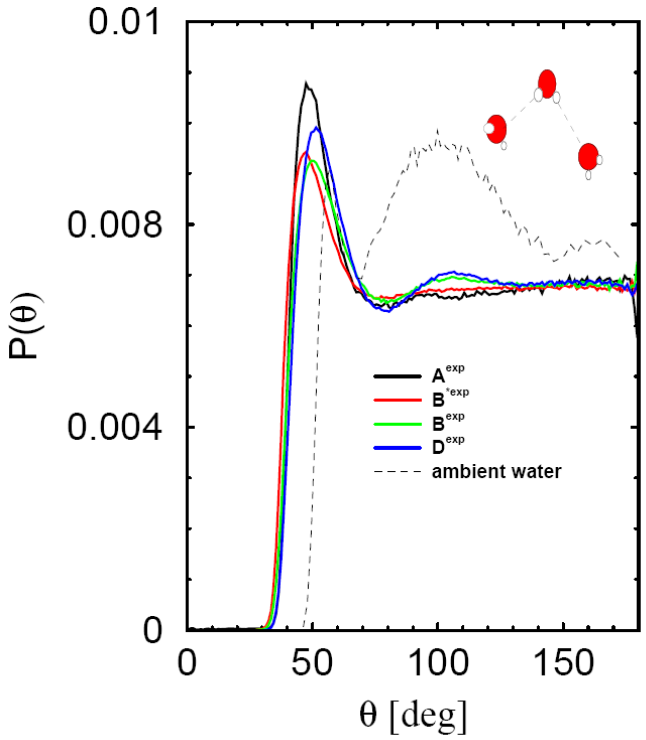

0.01
0.008
0.004
0
P(θ)
0
50
100
150
θ [deg]
A^exp
B'^exp
B^exp
D^exp
ambient water

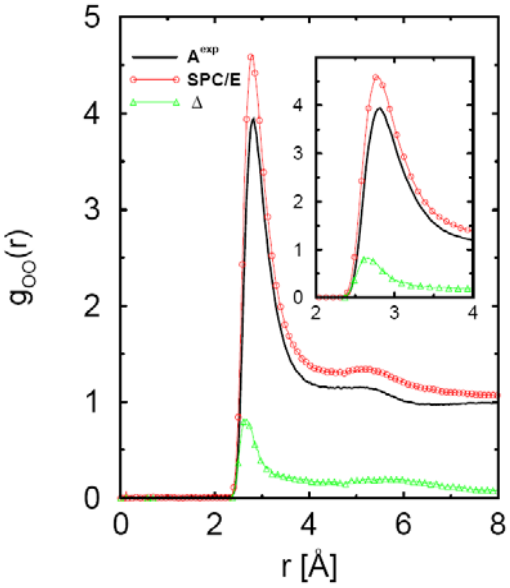
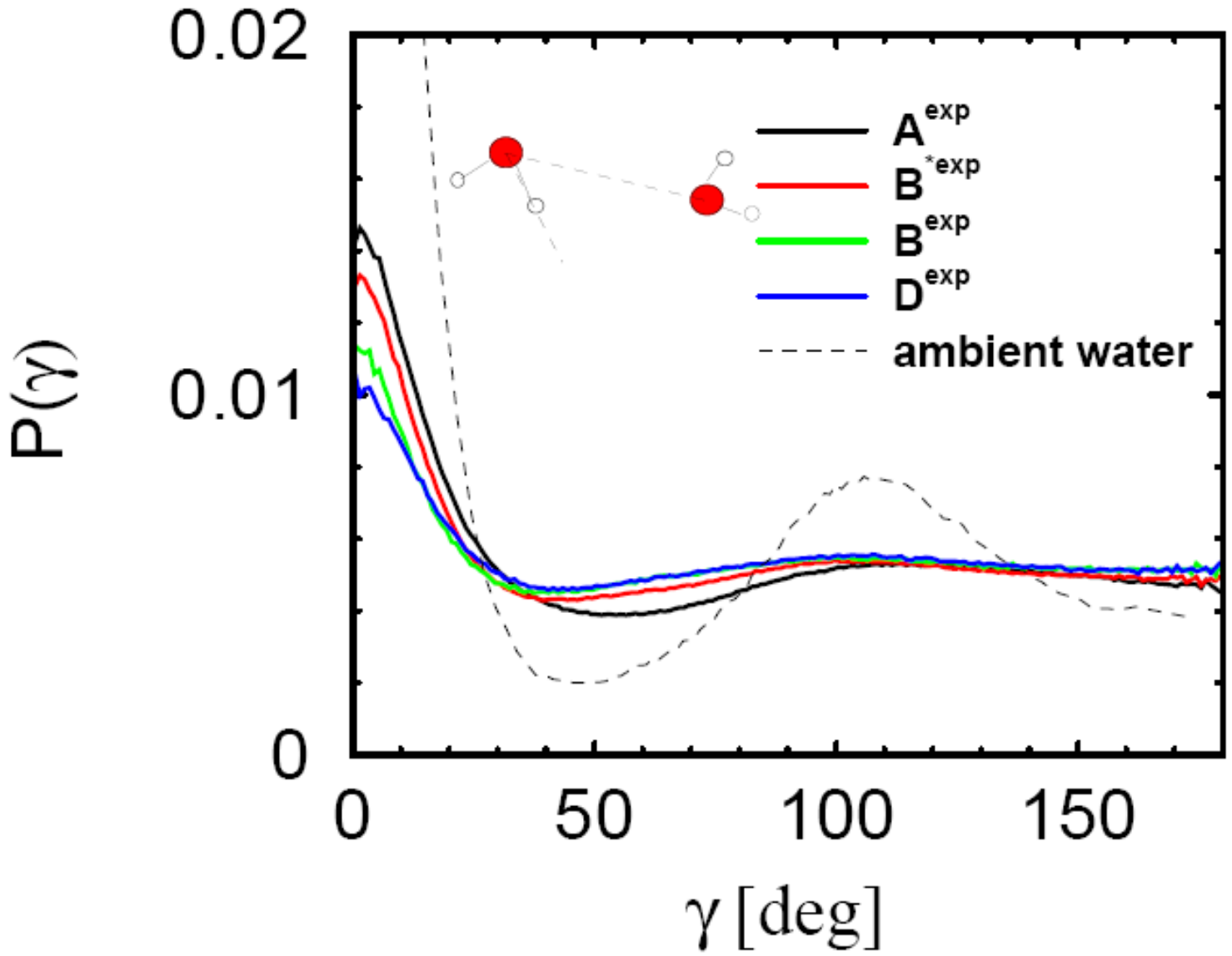
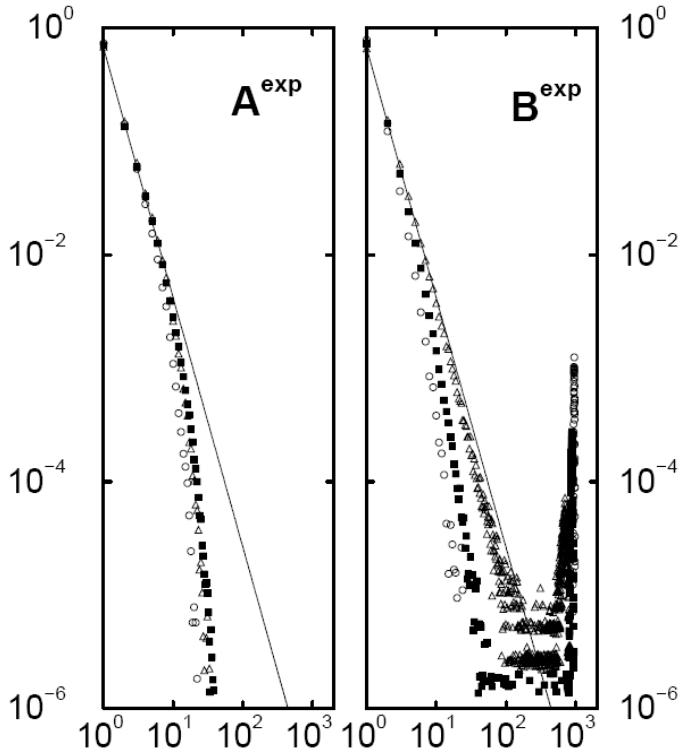
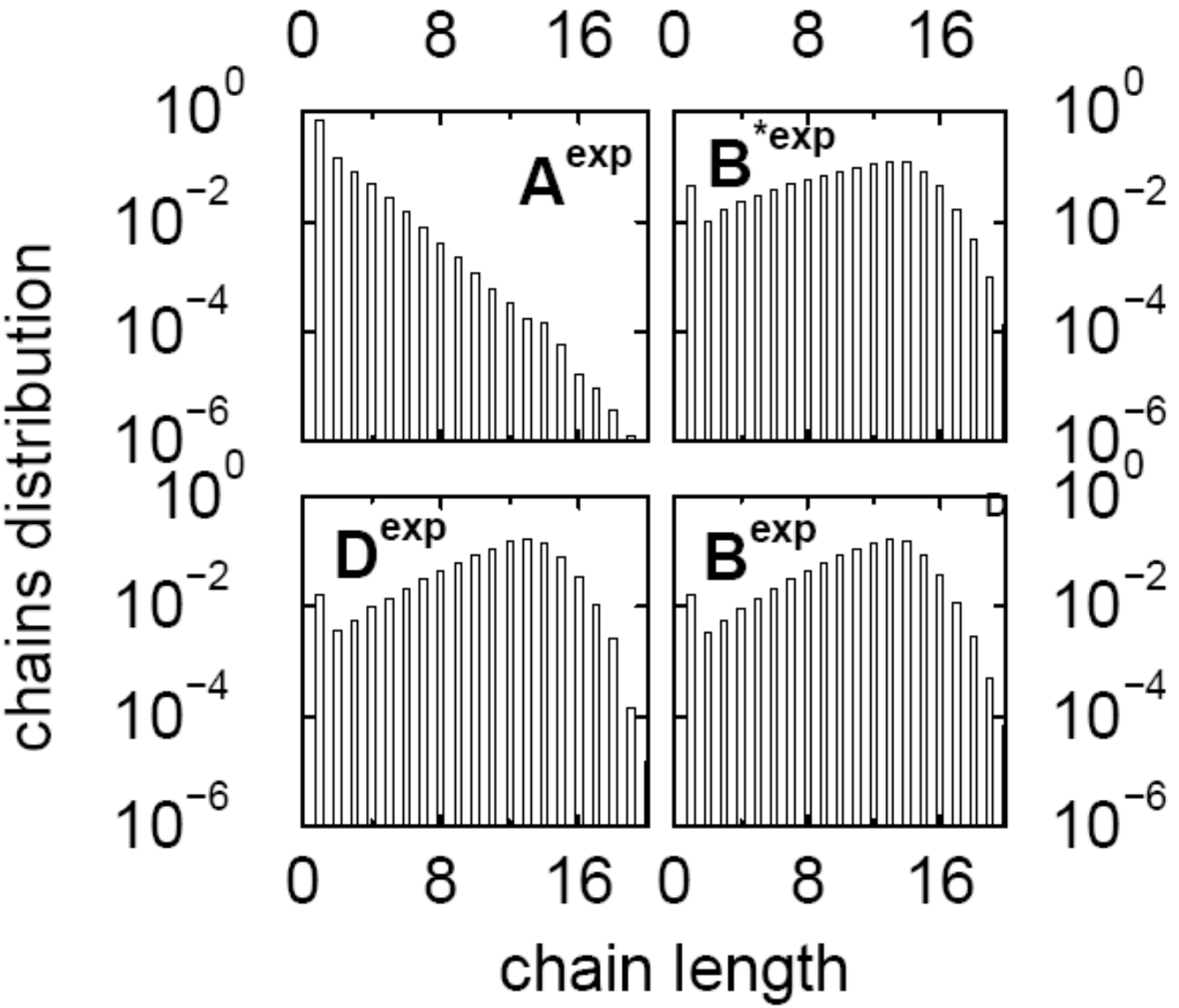

5
4
3
2
1
0
g_OO(r)
0
2
4
6
8
r [Å]
A^exp
SPC/E
Δ

FIG. 3:


0.02
0.01
0
P(γ)
0
50
100
150
γ [deg]
A^exp
B^*exp
B^exp
D^exp
ambient water


A^exp
B^exp
10^0
10^-2
10^-4
10^-6
10^0
10^1
10^2
10^3


0
8
16
0
8
16
10^{0}
10^{-2}
10^{-4}
10^{-6}
A^{exp}
B^{*exp}
D^{exp}
B^{exp}
chains distribution
chain length