Equation of State and the Topology of Hydrogen Bonding Networks in Water at High Temperatures and Pressures

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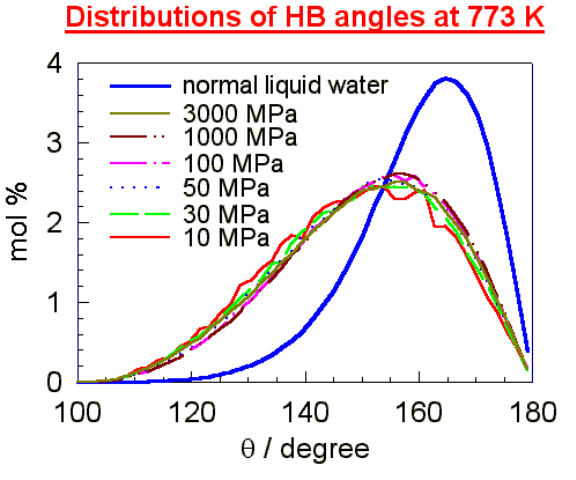

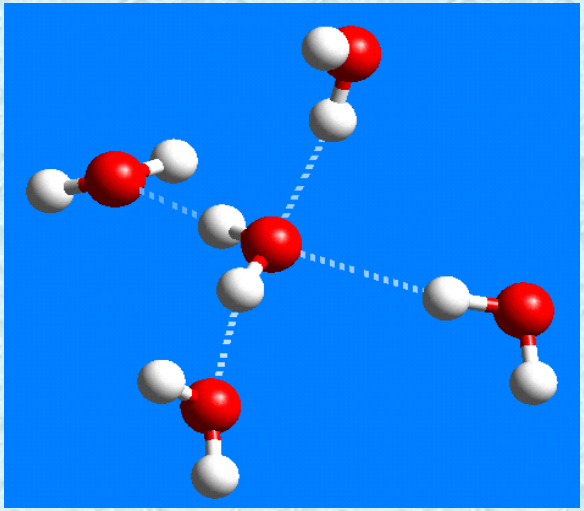

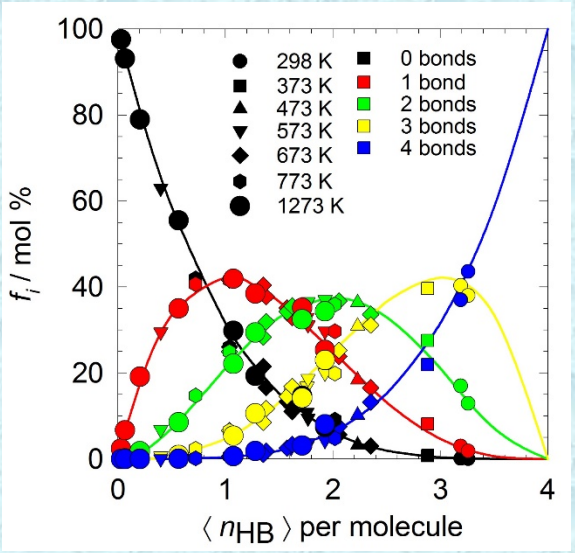

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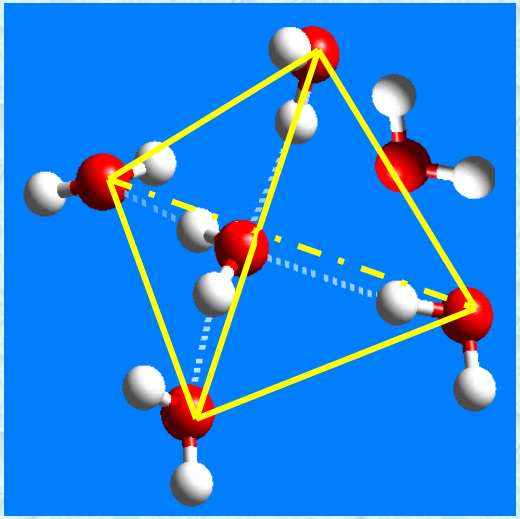
Acknowledgments

V.E.Fortov – *IPCP RAS, Chernogolovka*
K.I.Shmulovich – *IEM RAS, Chernogolovka*

Medeo, September 1981

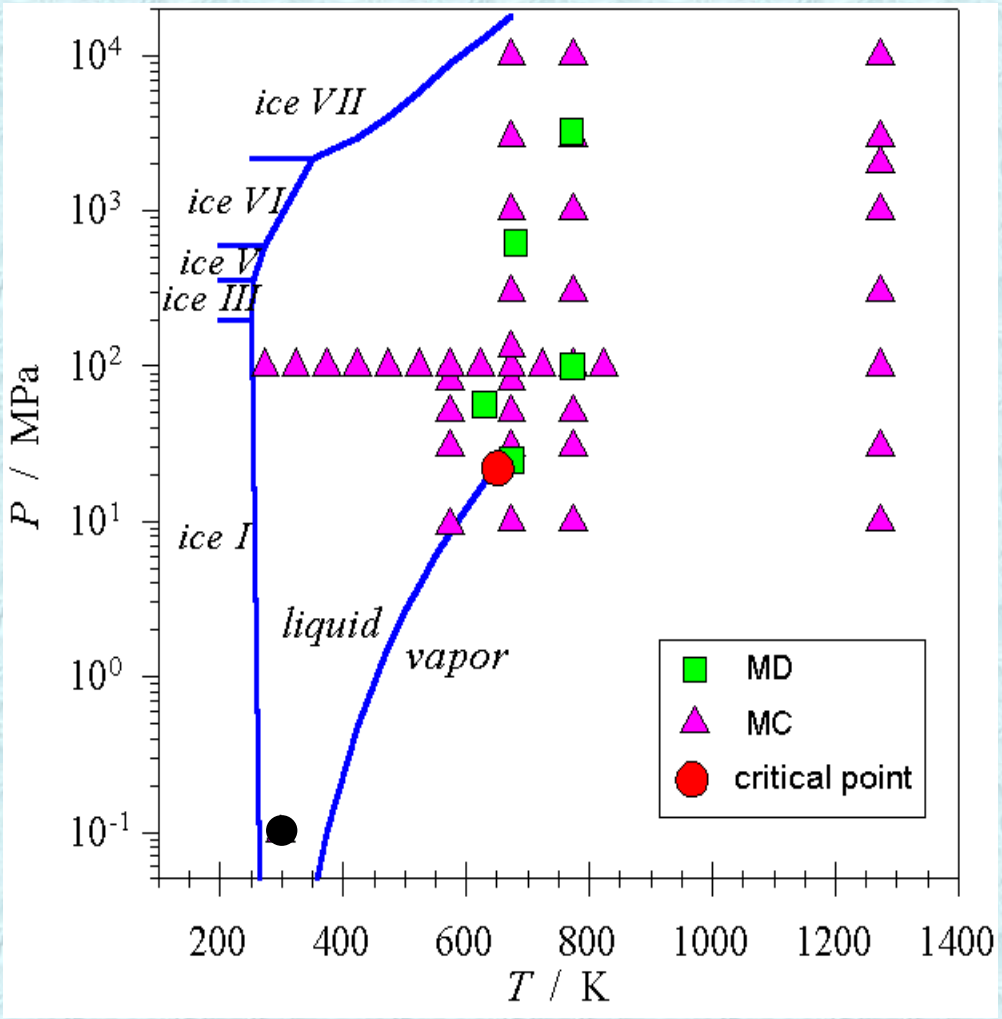
Atomistic computer simulations of water at high pressures and temperatures

Water Phase Diagram and the Thermodynamic Conditions of Present MC and MD simulations

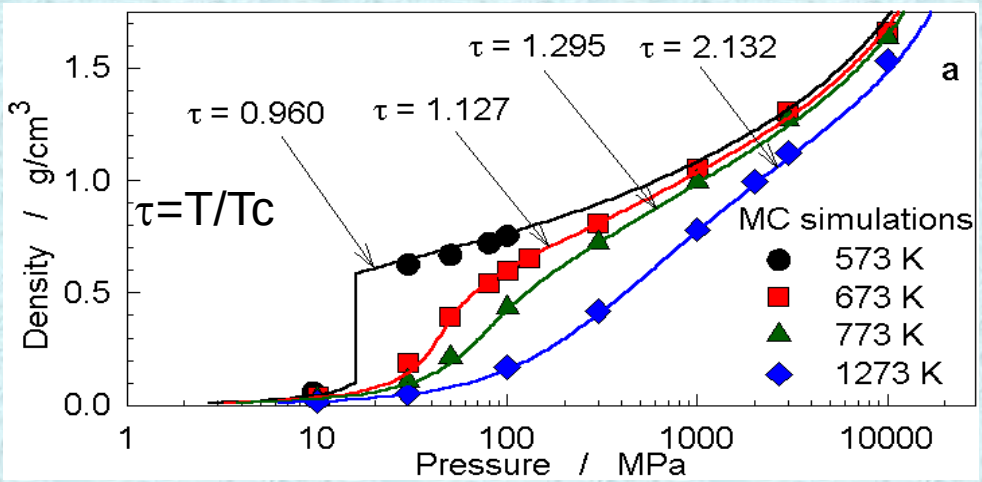


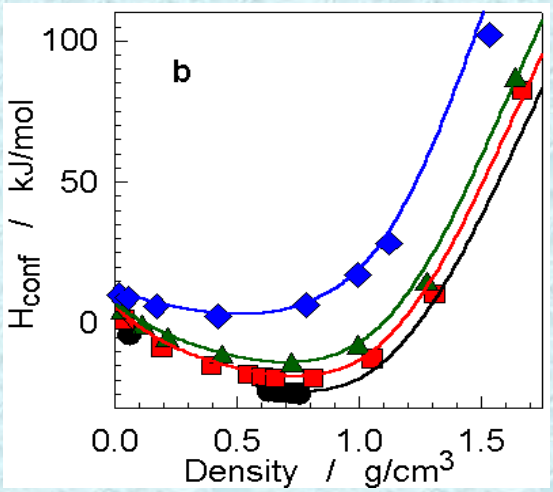
- **Ice-I:** Tetrahedrally ordered O in the diamond-like H-bond network
- H positions are disordered
- Proton diffusion; proton hopping

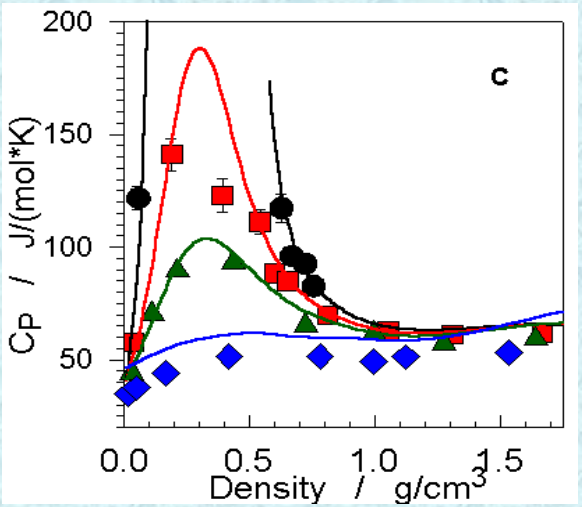
- **Liquid:** Only short-range tetrahedral ordering remains

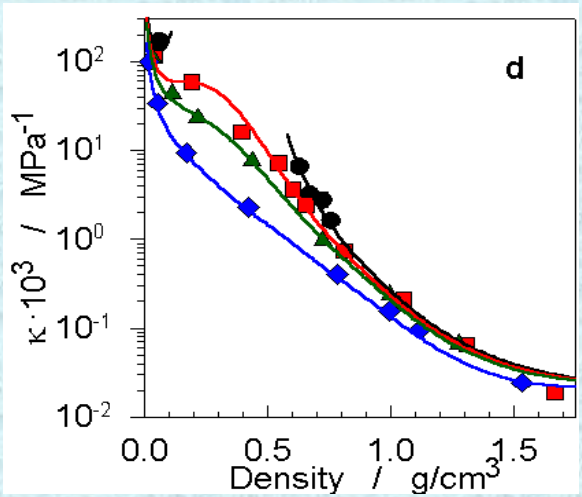


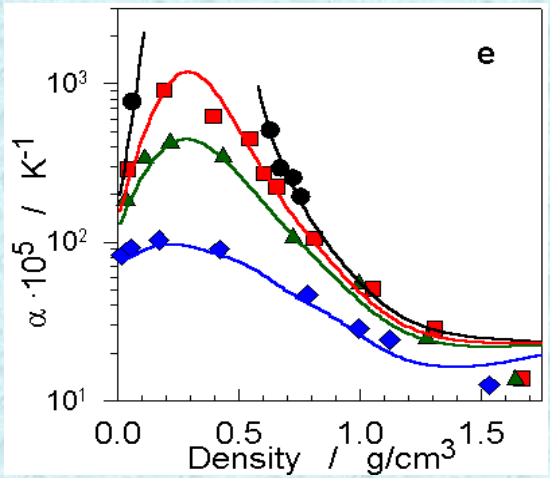
Thermodynamic Properties of Water
Monte Carlo Simulations with TIP4P potential







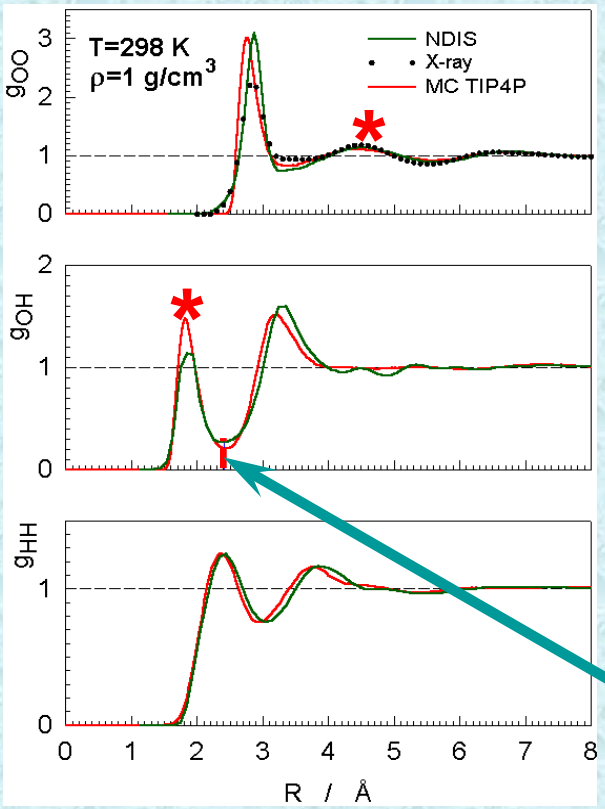


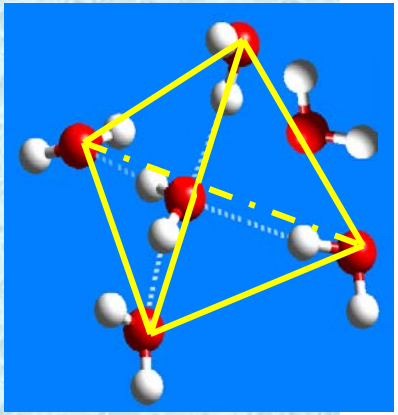


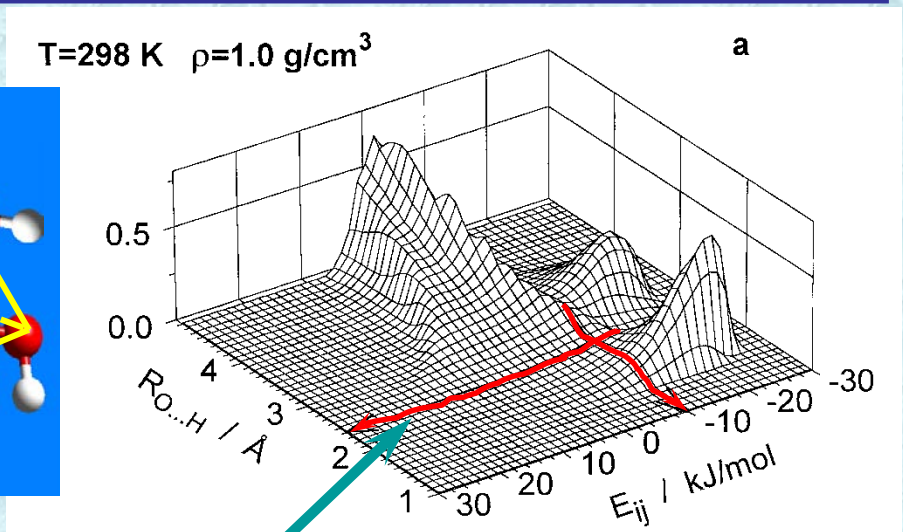
Kalinichev, *Rev. Mineral. Geochem.*, **42**, 83-129 (2001)

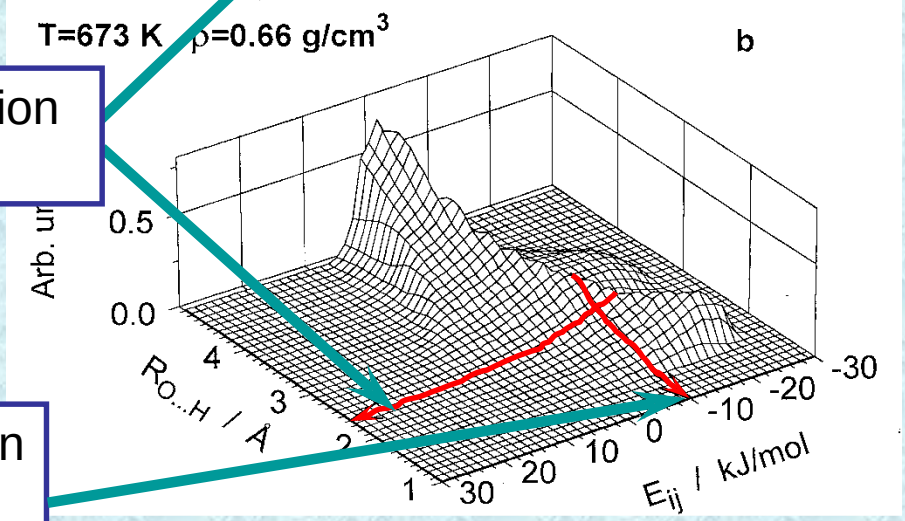
H-bond Definitions

Distance-Energy Distribution Functions

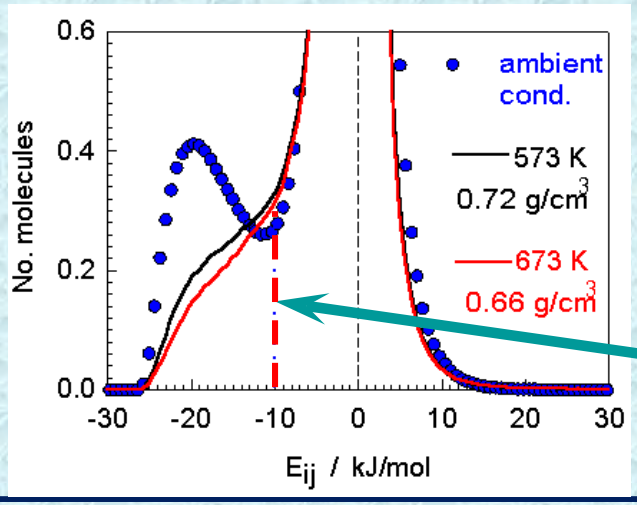






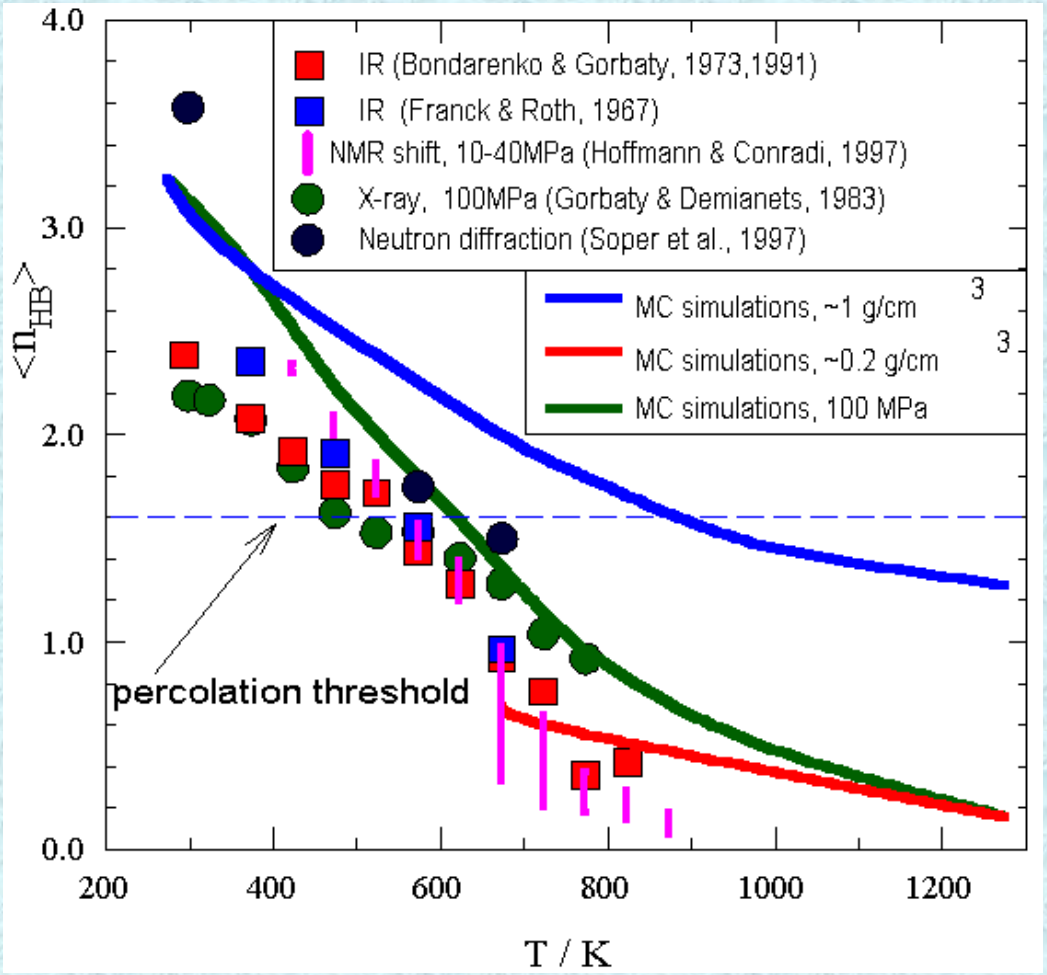


Distance criterion for H-bonding

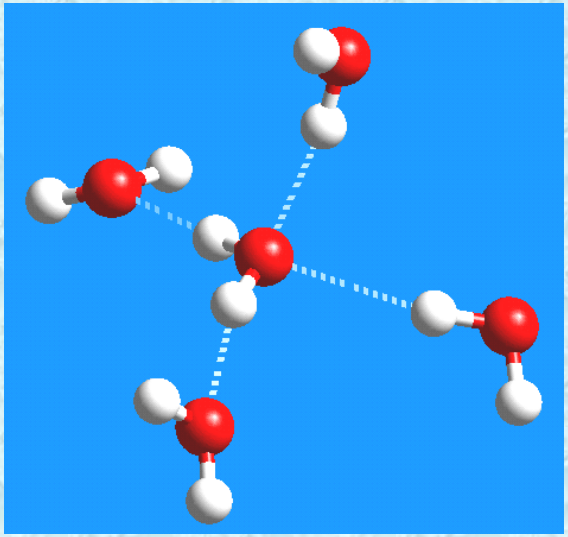


Energy criterion for H-bonding

Temperature and Pressure Dependence of the Number of H-bonds per Water Molecule

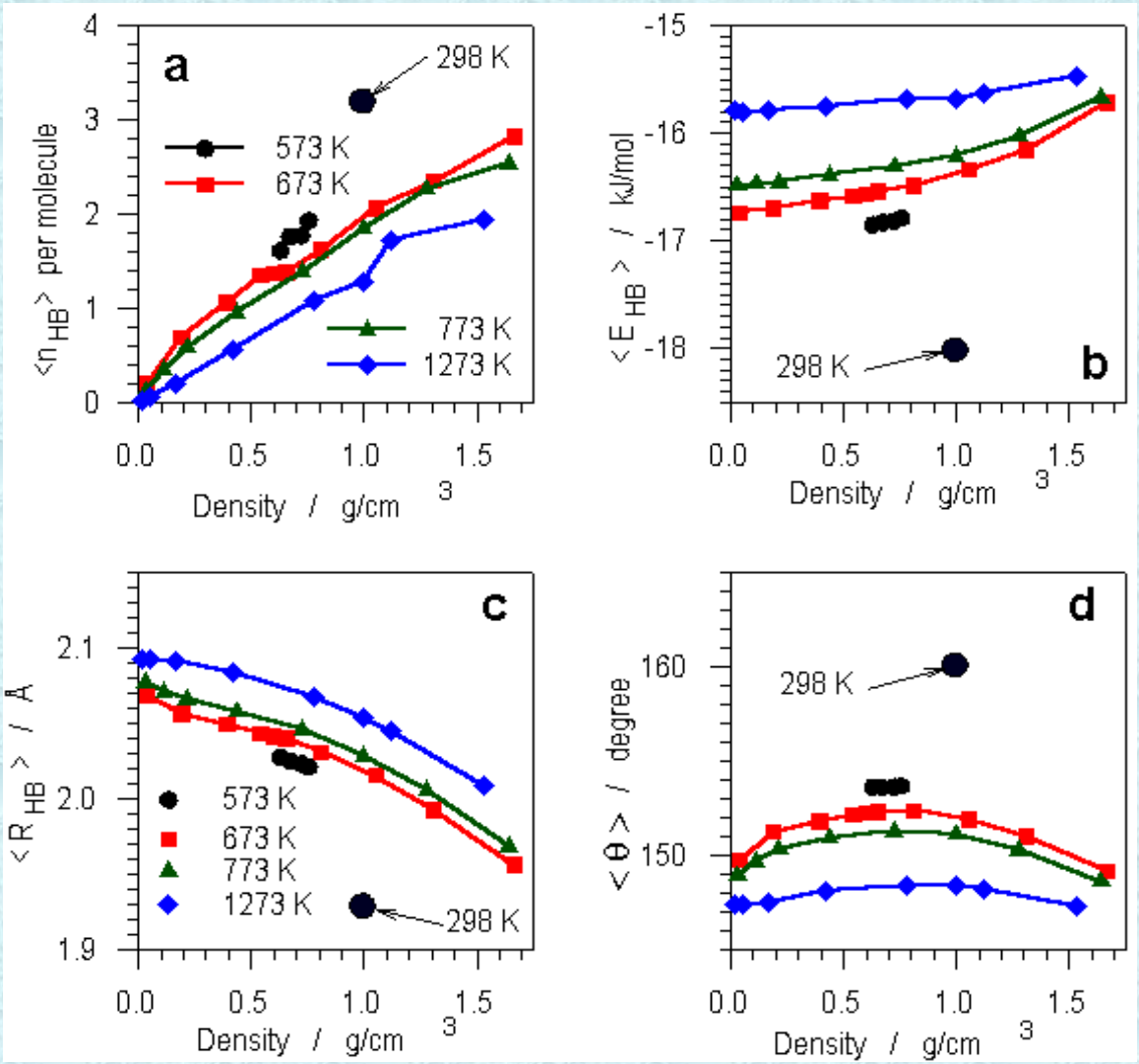


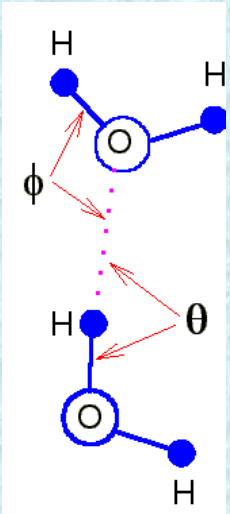
***H-bonding*:**
molecular simulations ***vs*** spectroscopic and diffraction evidence from various sources



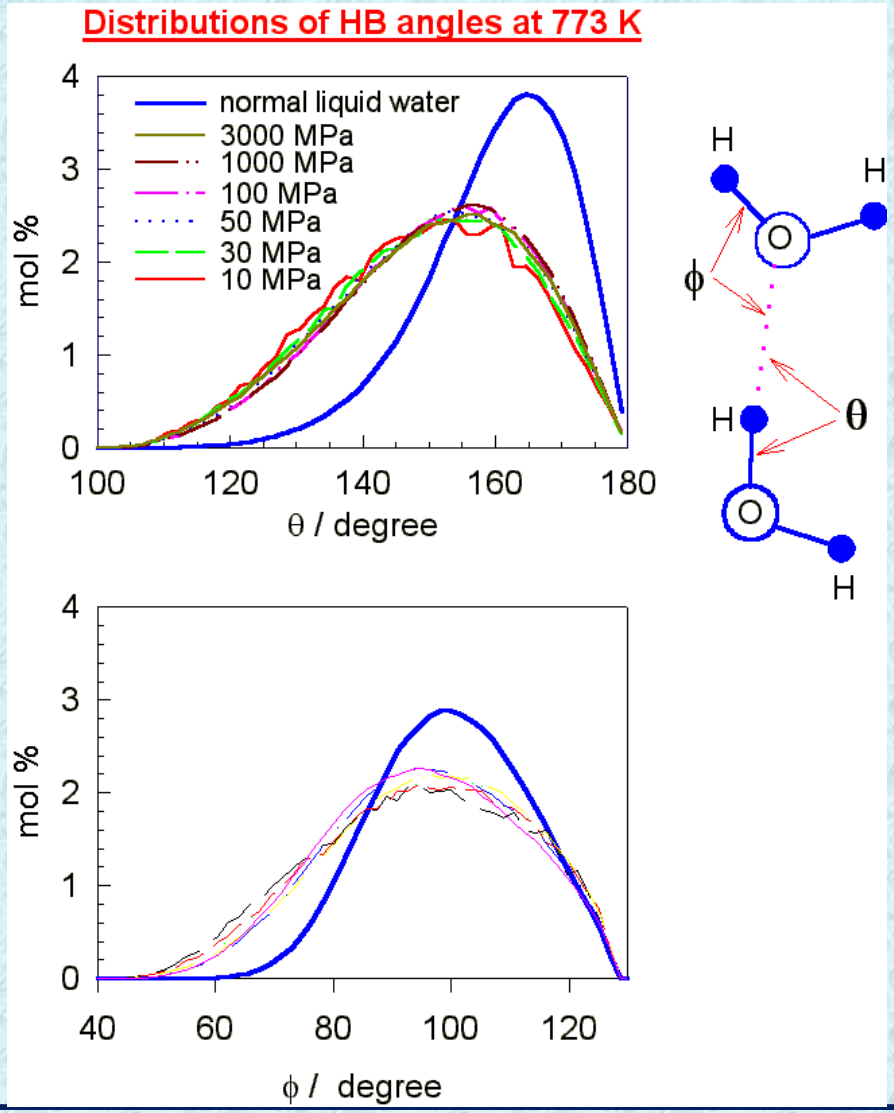
Kalinichev, *Rev. Mineral. Geochem.*, **42**, 83-129 (2001)

Average Parameters of H-bonds in Liquid and Supercritical Water

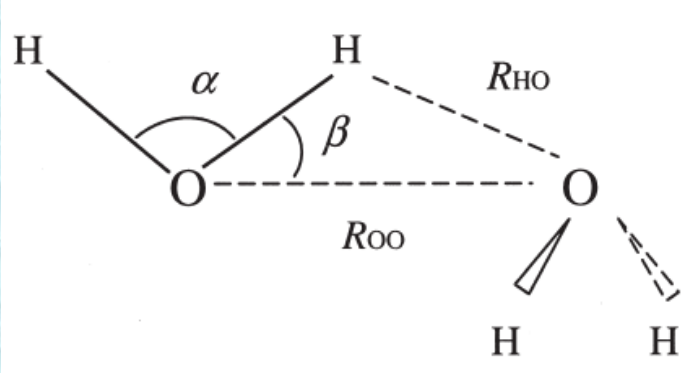




Angular Distributions of H-bonds in Water



Angular criterion of H-bonding can in many cases be used instead of the energetic criterion



$R_{OO} \leq$ 3.3-3.5 Å

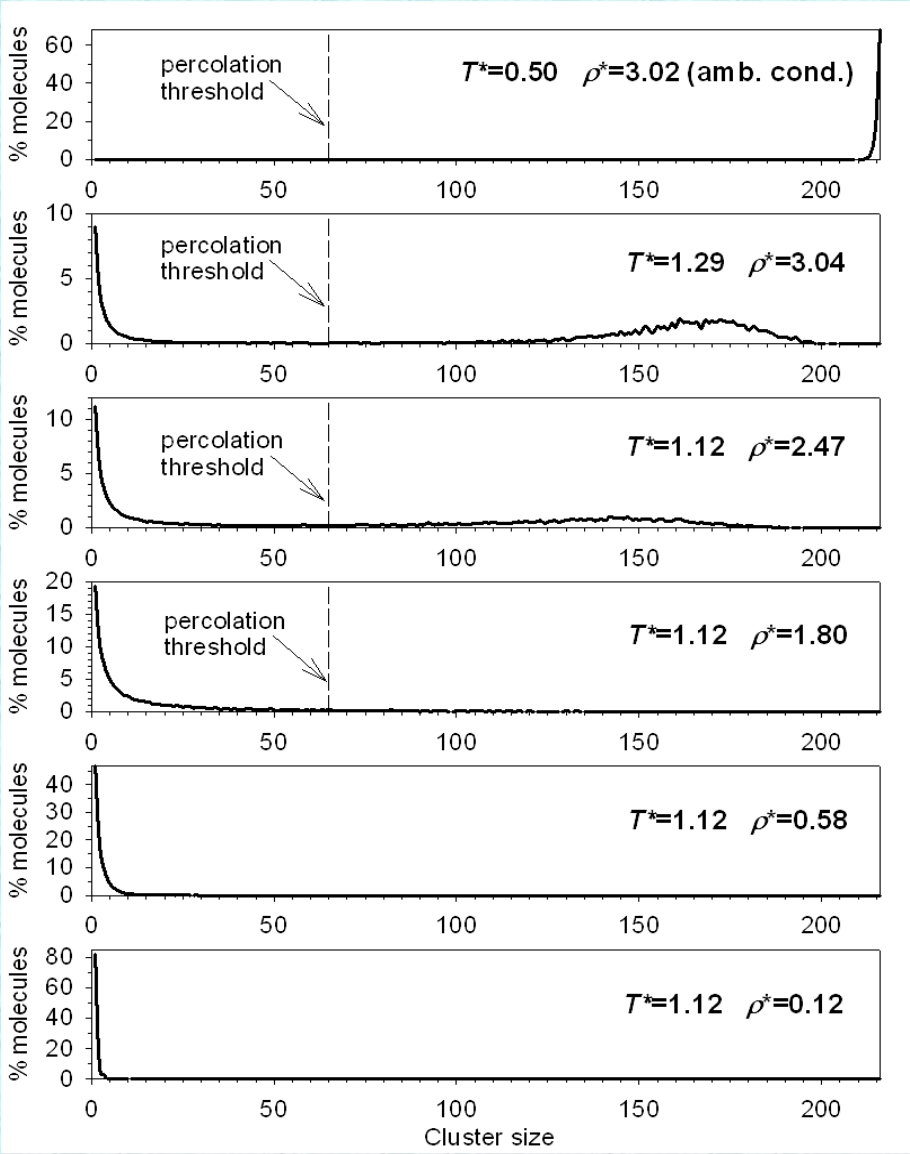
or

$R_{OH} \leq$ 2.45-2.5 Å

and

$\beta \leq 30^{o}$

Cluster Size distributions and Topology of H-bonding Network in SCW



Percolating H-bond network *vs* H_2O molecular clusters

$T^*=T/T_c$

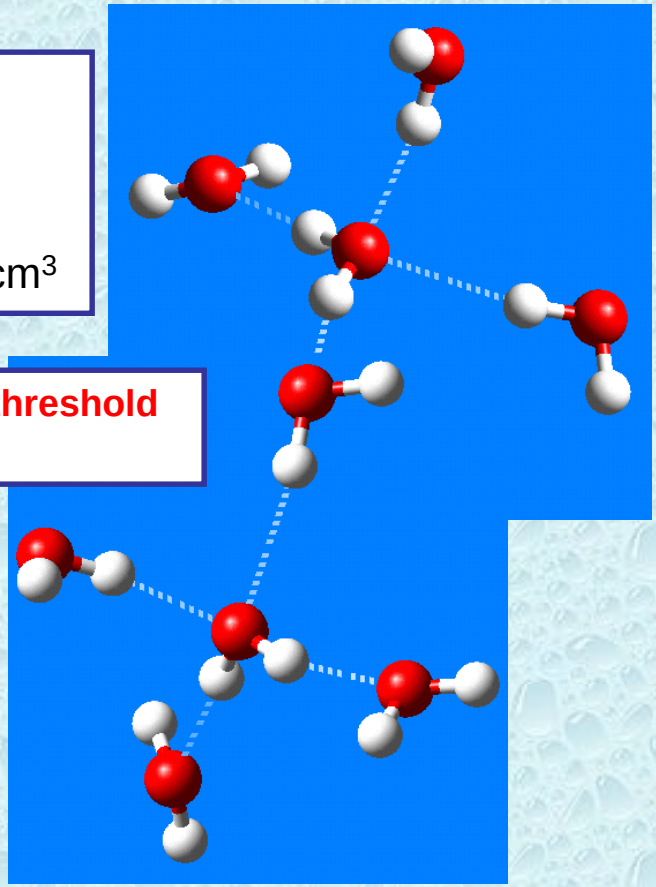
$\rho^*=\rho/\rho_c$

T_c=647 K

ρ_c=0.31 g/cm^3

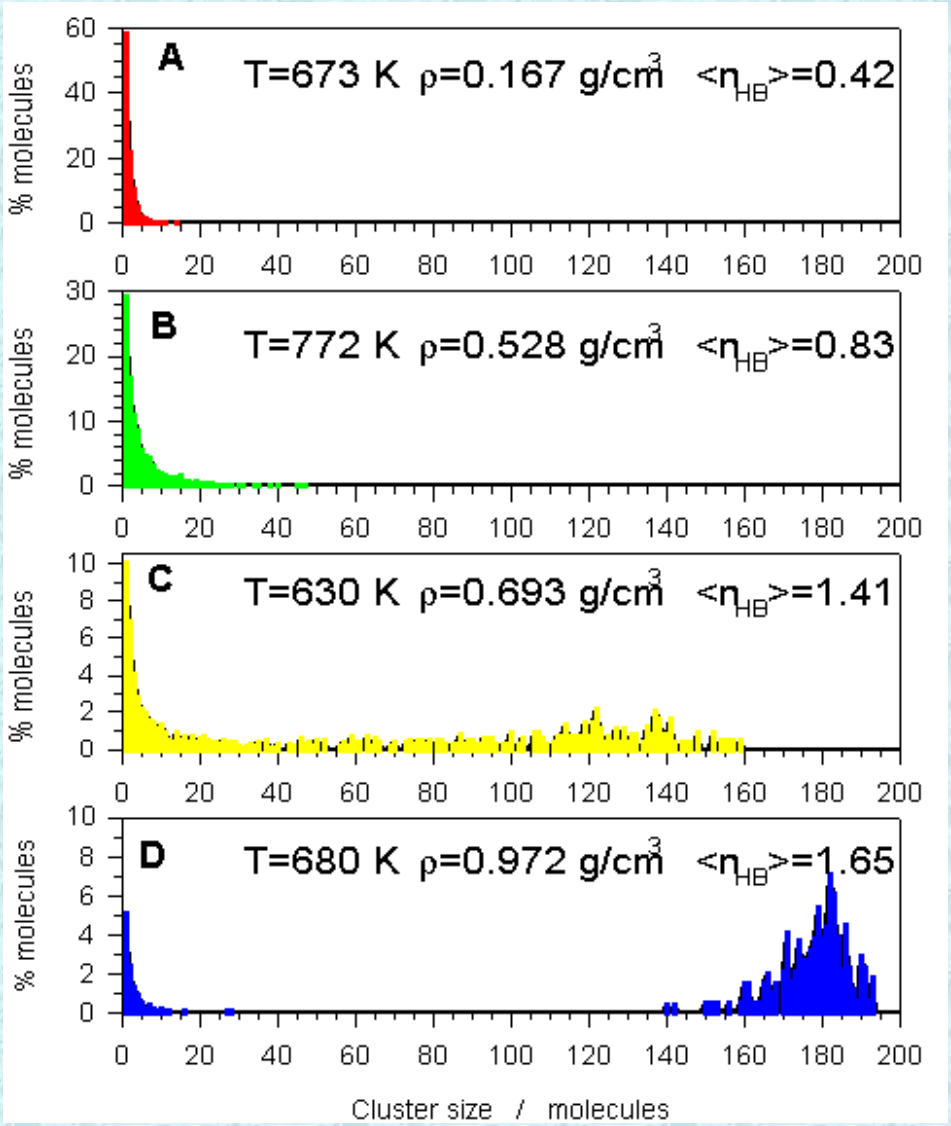
Percolation threshold

$\langle n_{HB} \rangle$ ~ 1.6

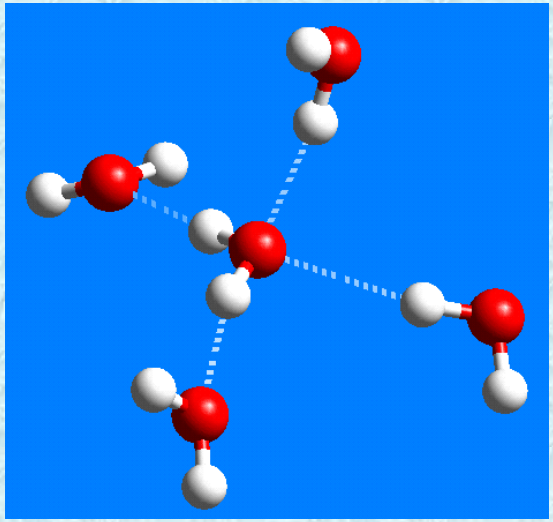


Kalinichev & Churakov, 1999, 2001

Molecular Clusterization in Supercritical Water



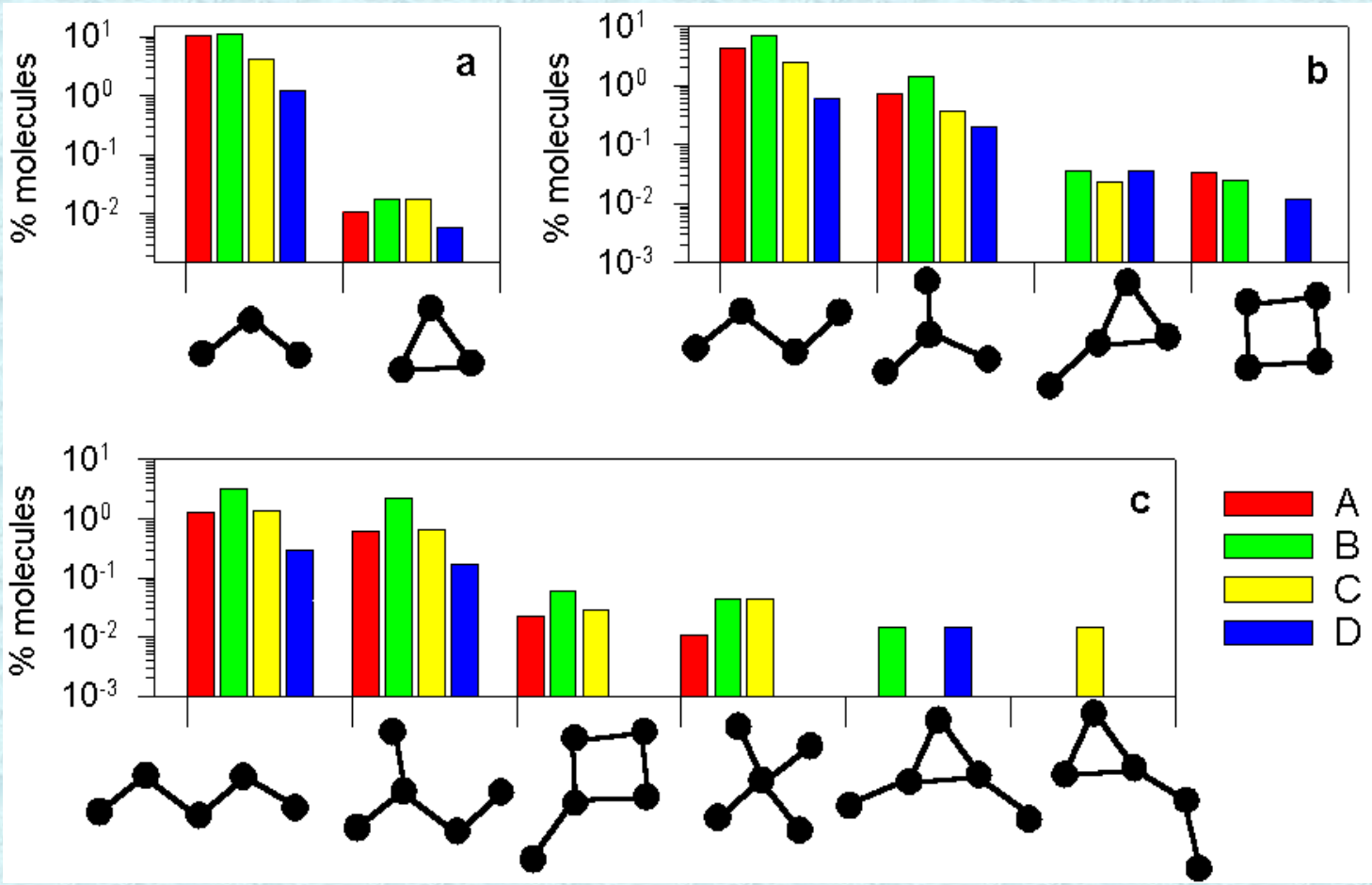
H-bonded cluster size distributions



Kalinichev & Churakov, 1999, 2001

Molecular Clusterization in Supercritical Water

Abundance of topologically different H_2O clusters



Kalinichev & Churakov, 1999, 2001

Molecular Clusterization in Supercritical Water

Average Parameters of H-bonded Clusters

Cluster topology	3a	3b	4a	4b	4c	4d	5a	5b	5c	5d	5e
$\langle \angle O\cdot\cdot O\cdot\cdot O_1\rangle$/°	109	60	110	107	114	87	110	108	112	107	105
$\langle \angle O\cdot\cdot O\cdot\cdot O_2\rangle$/°					60				86	60	
$\langle \angle O\cdot\cdot O\cdot\cdot O_3\rangle$/°										119	
$\langle R_{O\cdot\cdot H}\rangle$ / Å	2.04	2.07	2.04	2.04	2.06	2.03	2.04	2.04	2.05	2.06	2.05
$\langle R_{O\cdot\cdot O}\rangle$ / Å	2.90	2.89	2.91	2.91	2.90	2.90	2.91	2.91	2.91	2.90	2.92
$\langle \angle O\cdot\cdot H–O\rangle$ / °	149	143	150	150	146	150	150	150	149	146	150
$\langle U_{HB}\rangle$ / kJ/mol	-16.9	-16.4	-16.9	-16.7	-16.3	-17.0	-16.9	-16.8	-16.7	-16.3	-16.8

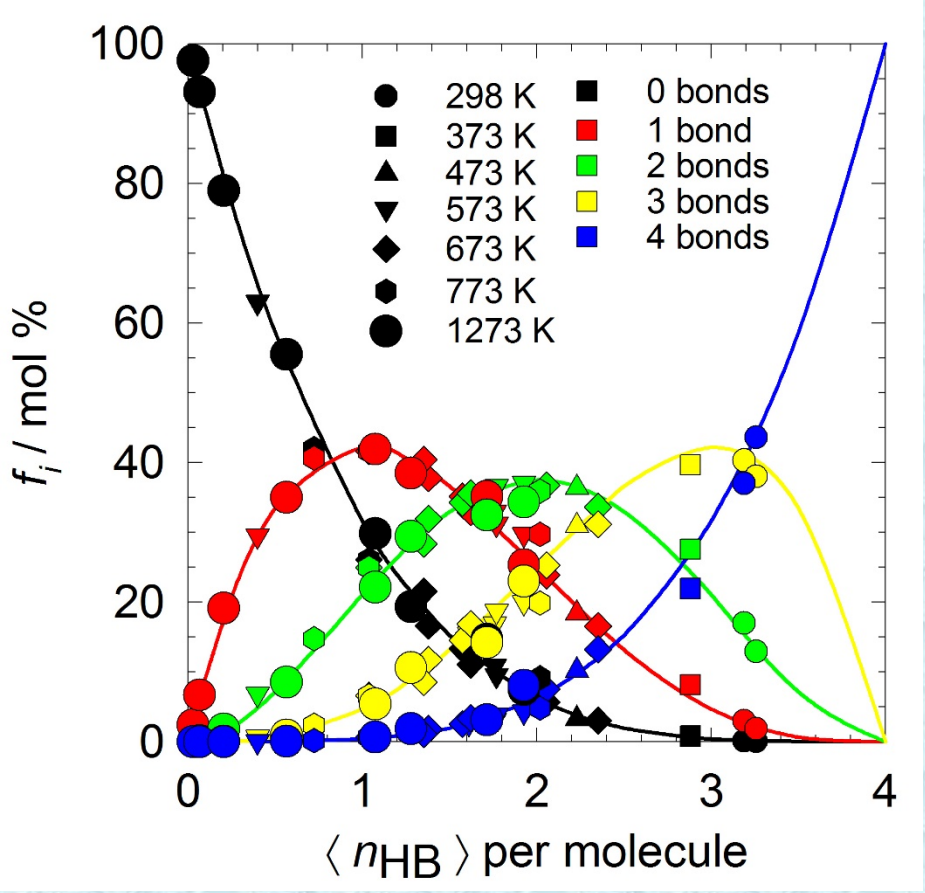
Distributions f_i of H_2O Molecules Involved in i H-bonds in Liquid and Supercritical Water as a Function of the Average Number of H-bonds per Molecule in the System, $\langle n_{HB} \rangle$

Theory of independent bonds

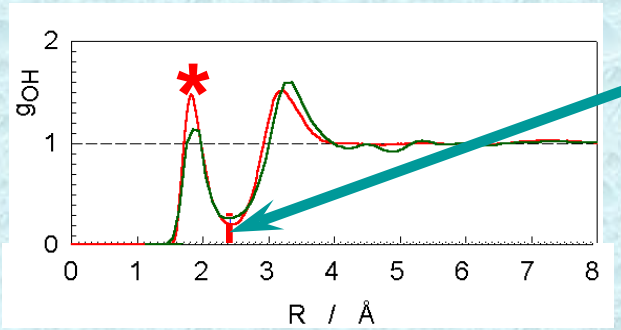
The interconnected percolating network of H-bonds in liquid water can be quite accurately described by a simple binomial distribution

$$f(i) = \left(\frac{m}{i}\right)\left(\frac{\langle n_{HB}\rangle}{m}\right)^{i}\left(1-\frac{\langle n_{HB}\rangle}{m}\right)^{m-i}$$

Blumberg et al. (1984) Connectivity of hydrogen bonds in liquid water. *J. Chem. Phys*, **80**, 5230-5241

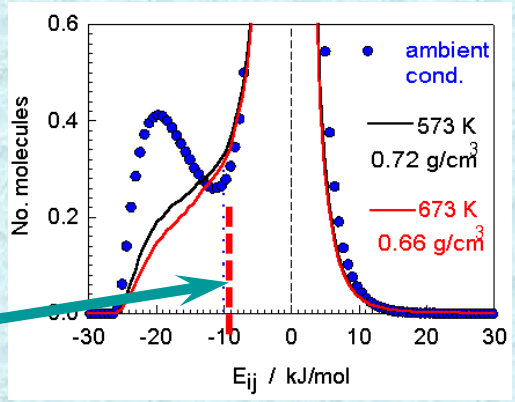


Lifetime of H-bonds in Supercritical Water



Distance criterion for H-bonding

Energy criterion for H-bonding



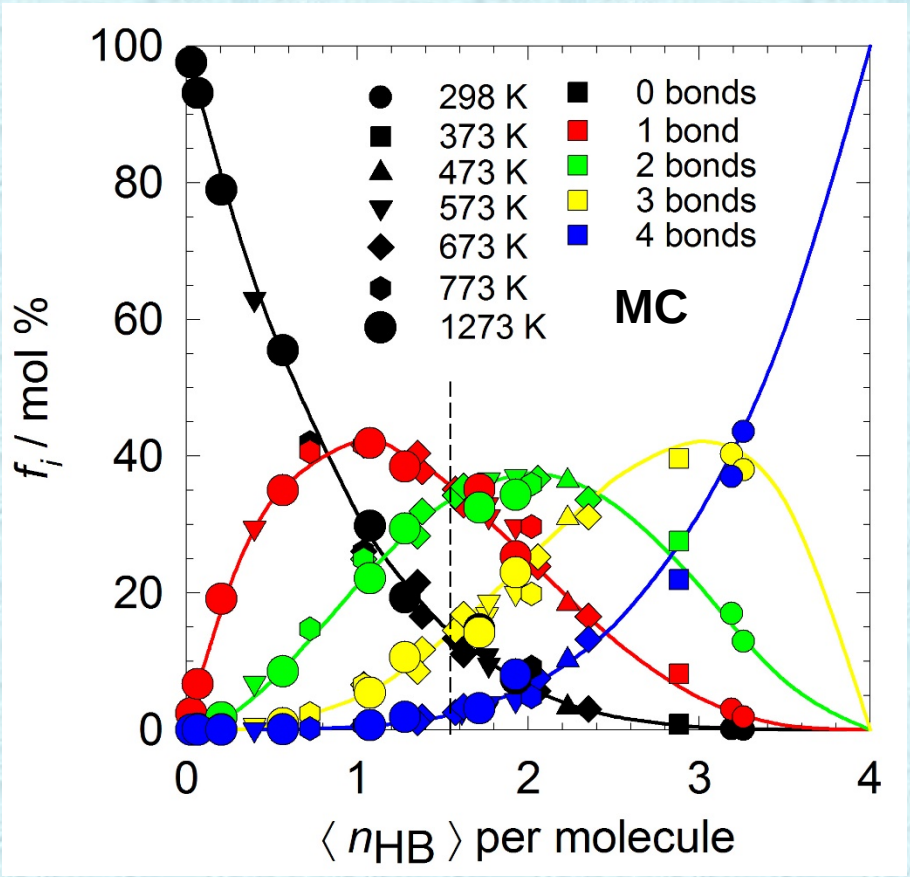
Average number of H-bonds per H_2O molecule and concentration of H-bonded species in supercritical BJH water at 630 K and 0.692 g/cm^3 as a function of a lifetime criterion for H-bonds.

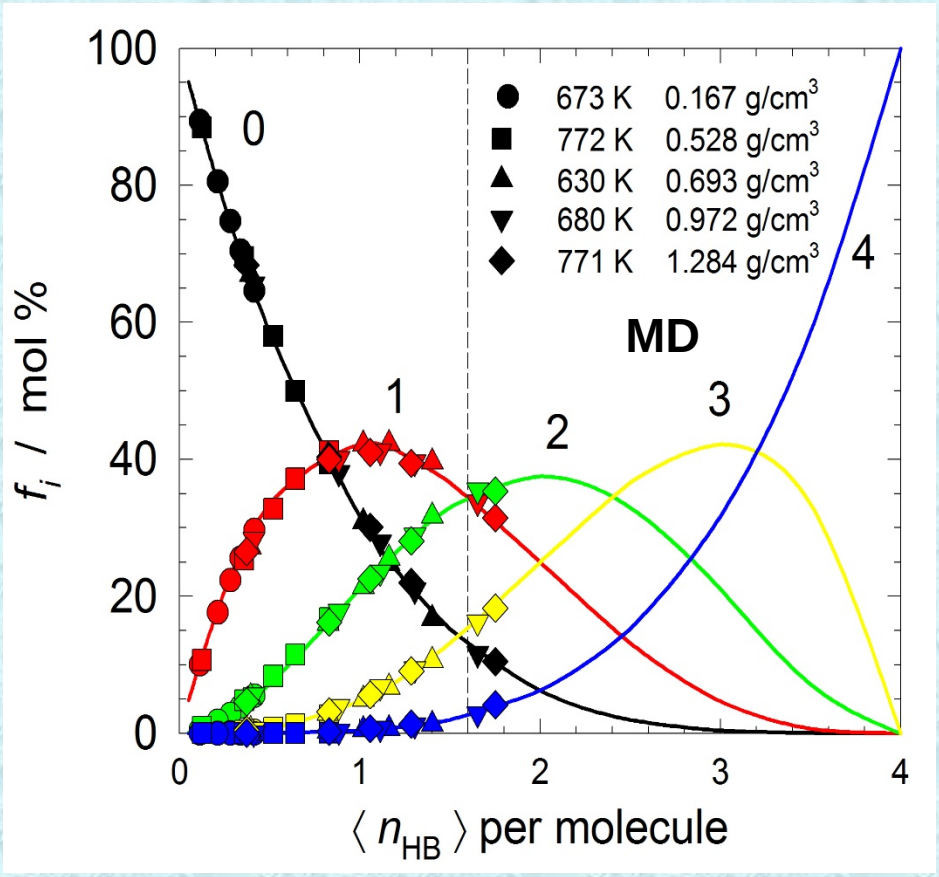
$\Delta\tau$ / ps	$\langle n_{HB} \rangle$	% of monomers (0 bonds)	% of dimers (1 bond)	% of trimers (2 bonds)	% of tetramers (4 bonds)
0.01	1.41	16.6	39.4	31.9	10.7
0.1	0.83	40.2	40.2	16.3	3.0
0.2	0.57	55.0	34.2	9.5	1.2

Distributions f_i ($\langle n_{HB} \rangle$) from MC and MD Simulations with TIP4P and BJH Potentials

$$f(i) = \left(\frac{m}{i}\right)\left(\frac{\langle n_{HB}\rangle}{m}\right)^{i}\left(1-\frac{\langle n_{HB}\rangle}{m}\right)^{m-i}$$

Kalinichev (2017) Universality of hydrogen bond distributions in liquid and supercritical water. *Journal of Molecular Liquids*, **241**, 1038-1043





Conclusions and Outlook

- MC and MD simulations of supercritical water (SCW) are performed over a very wide range of thermodynamic conditions and demonstrate very good agreement with all available thermodynamic and structural experimental data.
- Energetic, geometric, and angular parameters of H-bonds are quantitatively analyzed as functions of temperature and pressure (density).
- It is demonstrated that temperature affects the characteristics of H-bonding in SCW much stronger than density along any supercritical isotherm and that at any given temperature H-bonding characteristics remain almost independent of density over a very wide range from a dilute vapor (~0.03 g/cm^3) to a highly compressed liquid (~1.5 g/cm^3).
- Compared to H-bonds in normal liquid water, H-bonds at 773 K (and the same density of 1 g/cm^3) are by ~10% weaker, by ~5% longer and somewhat less linear on average.
- With increasing temperature and/or decreasing density, the continuous network of H-bonds in water is broken into separate fragments and clusters below the percolation threshold.
- However, independent of the percolation threshold the fractions of H_2O molecules forming simultaneously 0-, 1-, 2-, 3-, 4- H-bonds obey a universal binomial distribution as functions of the average number of H-bonds per molecule at these specific *T-P* conditions.
- These universal distributions remain intact even when dynamic criteria of H-bonding lifetimes are additionally applied.

Atomistic Computational Modeling Team at Subatech - Institut Mines-Télécom Atlantique, Nantes, France

In 2021, there is a fully funded open PhD position in my group in France for 3-3.5 years (or a postdoc for 1.5-2 years)

Atomistic / multiscale modeling of interactions between aqueous solutions and solid surfaces relevant in the technologies of geological disposal of radioactive waste:

1) Distribution of H_2O-H_2 mixtures in clay and cement nano-porous space. (This can also include the development and addition of some limited reactive capabilities to our ClayFF force field).

2) Effects of organics on the adsorption and transport of aqueous radionuclides (Cs^+, Sr^{2+}, UO_2^{2+}) radionuclides in clay and cement nano-porous space.

3) Possibility to develop a small local CPU-GPU cluster for these simulations.

http://www.imt-atlantique.fr/en/person/andrey-kalinichev