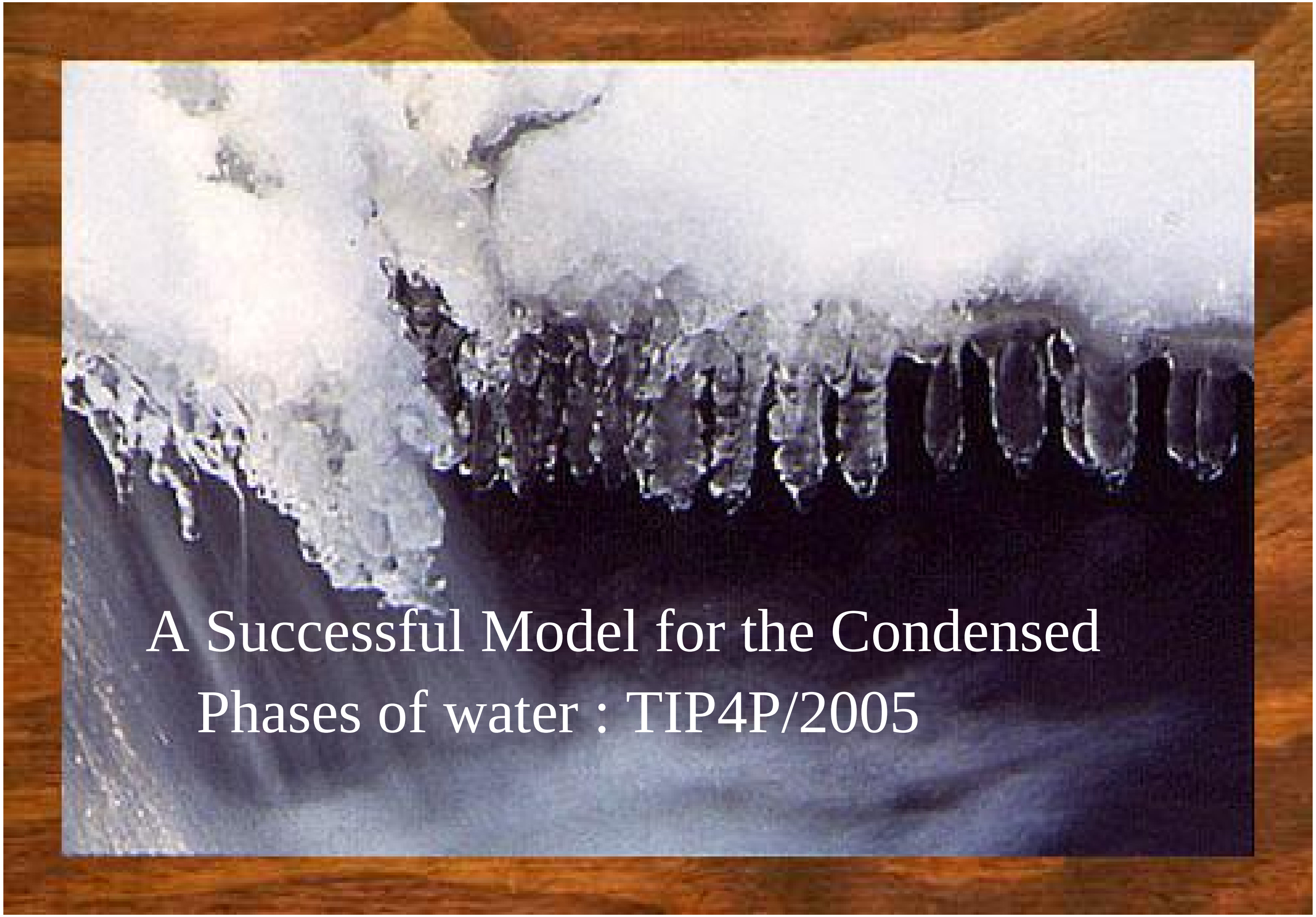


A Successful Model for the Condensed Phases of water : TIP4P/2005

A Successful Model for the Condensed Phases of Water : TIP4P/2005

Departamento de Química Física

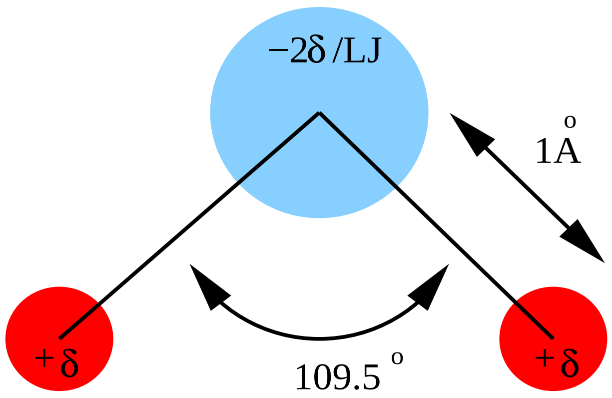
Universidad Complutense

Madrid, SPAIN

- Carlos Vega
- Jose Luis F. Abascal
- Maria M. Conde
- Juan L. Aragones

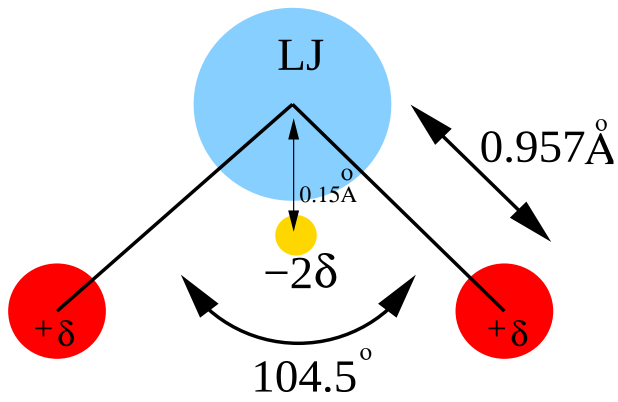
MODELS OF WATER

SPC/E Berendsen et al. 1987



$$\begin{aligned} \delta/|e| &= 0{,}4238 \\ \sigma &= 3{,}16557\text{Å} \\ \epsilon/k &= 78{,}2\text{K} \\ \mu &= 2{,}35D(1{,}85) \end{aligned}$$

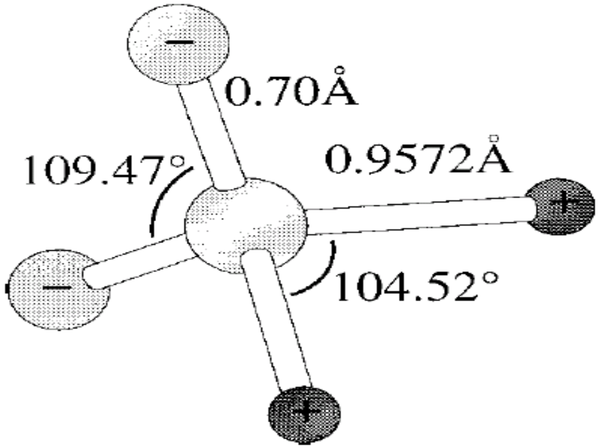
TIP4P Jorgensen et al. 1983



$$\begin{aligned} \delta/|e| &= 0{,}52 \\ \sigma &= 3{,}154\text{Å} \\ \epsilon/k &= 78{,}02\text{K} \\ \mu &= 2{,}18D \end{aligned}$$

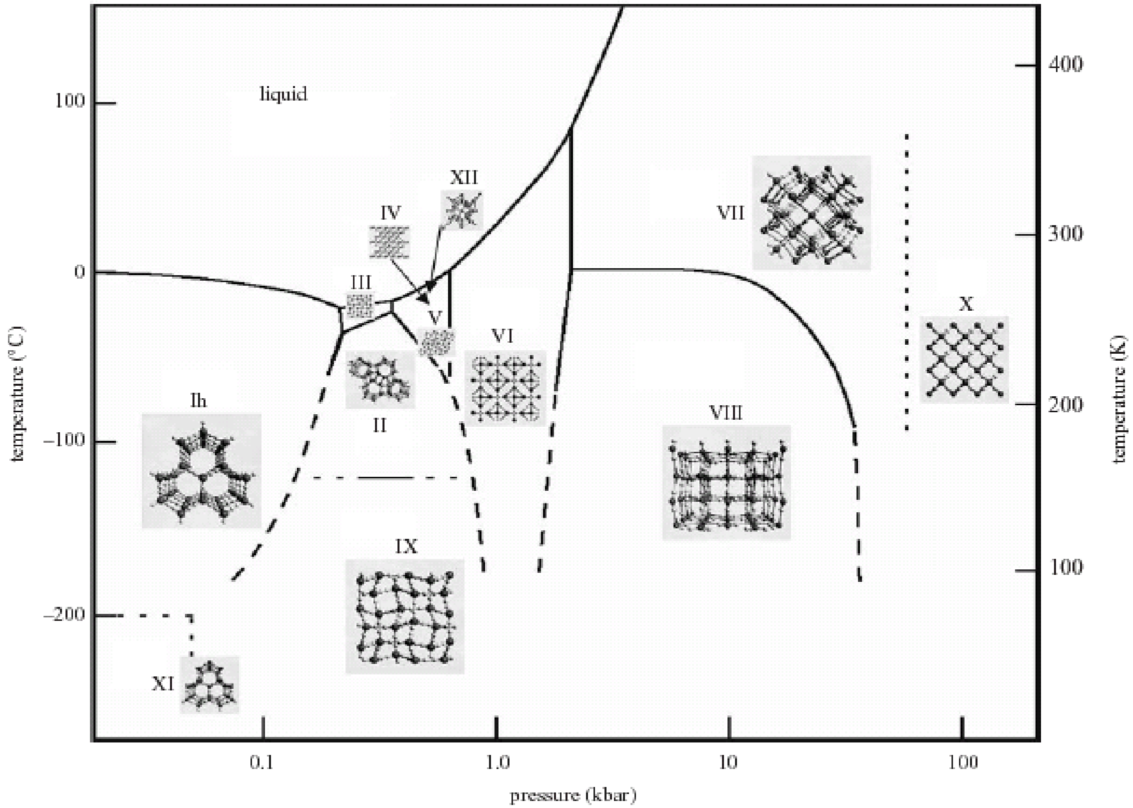
MODELS OF WATER

TIP5P , Mahoney and Jorgensen , JCP, 2000



$$\begin{aligned} \delta/|e| &= 0{,}241 \\ \sigma &= 3{,}12\text{Å} \\ \epsilon/k &= 80{,}52K \\ \mu &= 2{,}29D \end{aligned}$$

The phase diagram of water



J.Finney, Phyl.Trans.R.Soc.Lond.B,(2004)

1900 Tammann , 1912 Bridgman, 1968 Whalley , 1998 Finney et al.

Obtaining free energies for the solid (or fluid-solid coexistence)

- Cell occupancy W. G. Hoover and F. H. Ree, JCP, 1968
- Direct coexistence A. J. C. Ladd and L. V. Woodcock,CPL, 1977.
- Constrained fluid lambda-integration

  G. Grochola , JCP, 2004, 2005.

  D. M. Eike and J. F. Brennecke and E. J. Maginn, JCP, 2005.
- Self referential method M. B. Sweatman, PRE, 2005.
- Phase switch N. B. Wilding and A. D. Bruce, PRL, 1997, 2000.
- Einstein crystal D. Frenkel and A. J. C. Ladd, JCP, 1984.

  J. M. Polson and E. Trizac and S. Pronk and D. Frenkel, JCP, 2000.

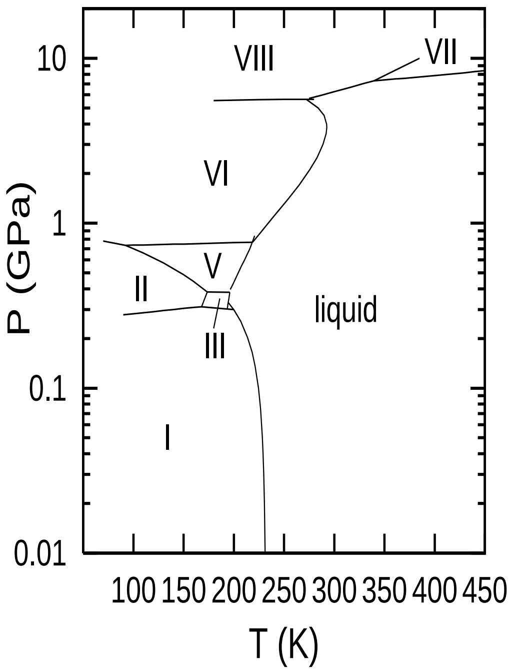
  Water. C.Vega and P. A. Monson, JCP, 1998

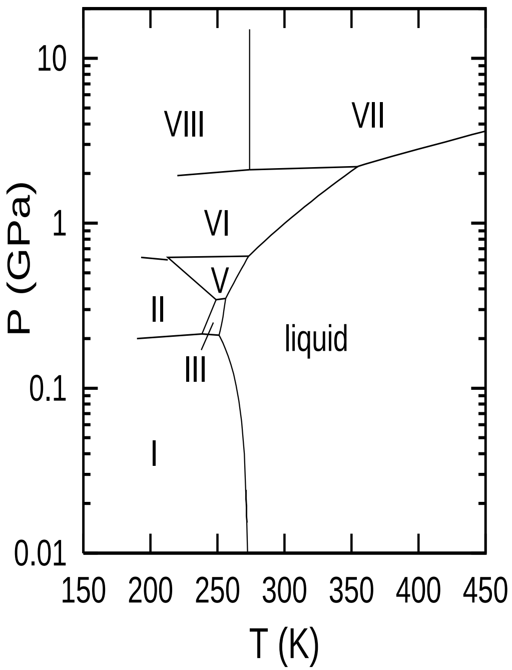
  Water. E.G.Noya, M.M.Conde and C. Vega , JCP, 2008.
- Lattice dynamics Water.G. T. Gao and X. C. Zeng and H. Tanaka, JCP, 2000.

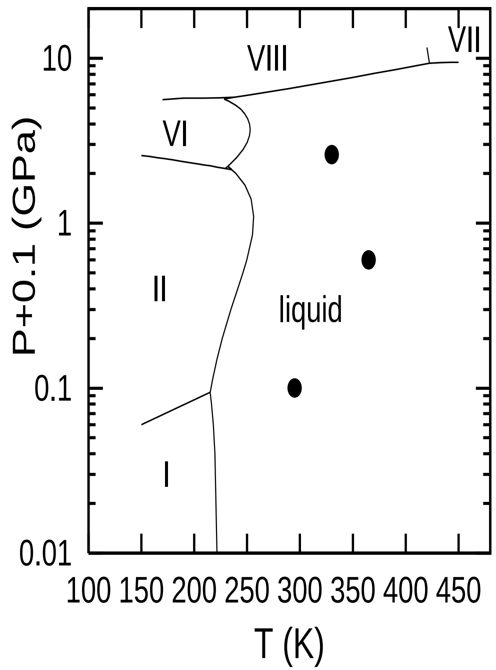
PHASE DIAGRAMS FOR THE TIP4P AND SPC/E MODELS

E.Sanz, C.Vega, J.L.F.Abascal and L.G.MacDowell,PRL, 92, 255701, (2004)

Strategy : Free energy calculations + Gibbs Duhem integration (Kofke, 1993)







TIP4P *Experiment* *SPC/E*

The ideas leading to TIP4P/2005

J.L.F.Abascal and C.Vega, JCP, 123, 234505, (2005)

- The model takes from TIP4P the geometry of the charge distribution, since it reproduces correctly the phase diagram of water (due to a good balance between dipolar and quadrupolar forces).
- The model takes from SPC/E the idea of reproducing the vaporization enthalpy after including the vaporization correction.
- The model takes from TIP5P the idea of using the maximum in density of water as a target property.
- The model also includes as target properties the density of several ice polymorphs and the melting point of ice Ih.

Potential models of water

Model	d_{OH}	H-O-H	σ	(ϵ/k_B)	q_H	d_{OM}	d_{OL}
TIP3P	0.957	104.5	3.150	76.5	0.417	0	-
TIP4P	0.957	104.5	3.154	78.0	0.52	0.15	-
TIP4P/2005	0.957	104.5	3.158	93.2	0.556	0.155	-
TIP5P	0.957	104.5	3.120	80.5	0.241	-	0.70

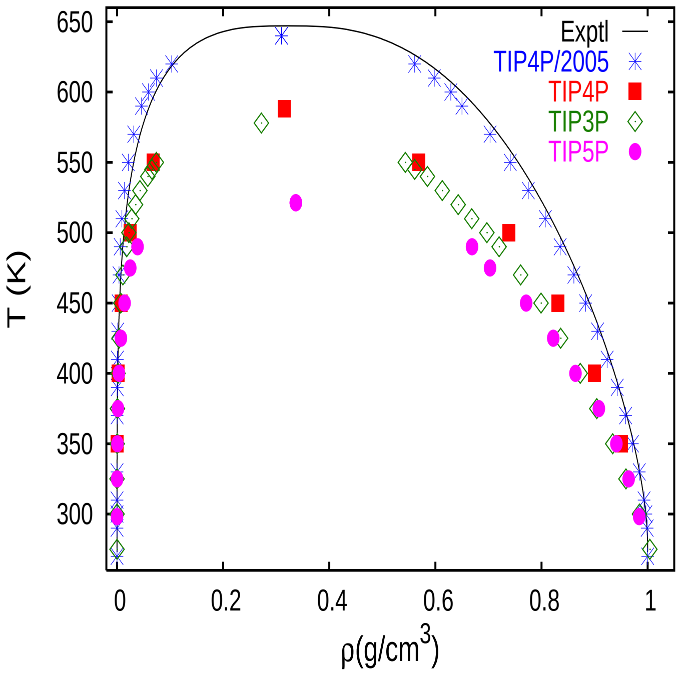
Does such a small change make any difference ?

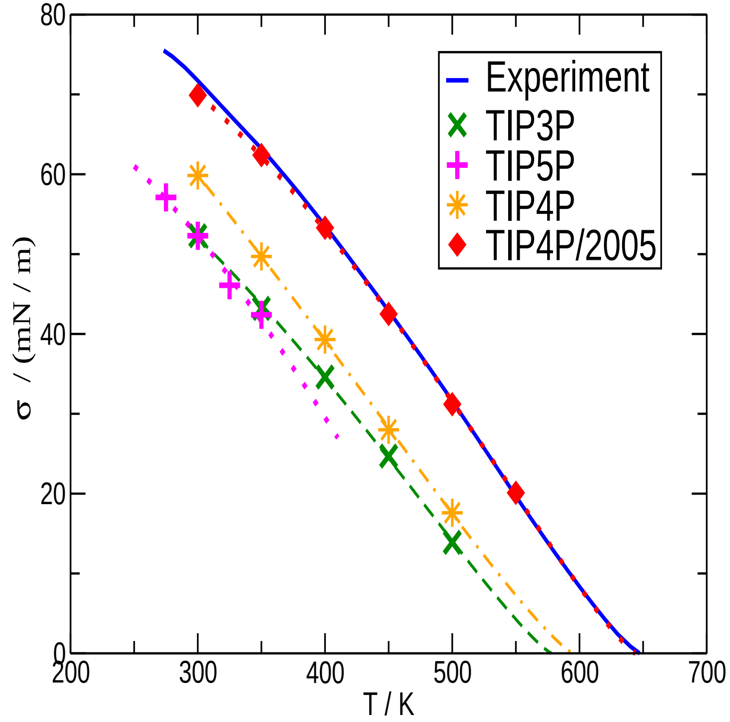
Ten properties to be analyzed

- 1. VLE and critical point.
- 2. Surface tension.
- 3. Densities of the different ice polymorphs.
- 4. Phase diagram calculations.
- 5. Melting temperature.
- 6. TMD. α, and κ_T.
- 7. Structure of water and ice Ih.
- 8. EOS at high pressures.
- 9. Self-diffusion coefficient.
- 10. Dielectric constant.

Award 0 to 3 points for each property (3=best)

Vapour-liquid equilibrium and surface tension



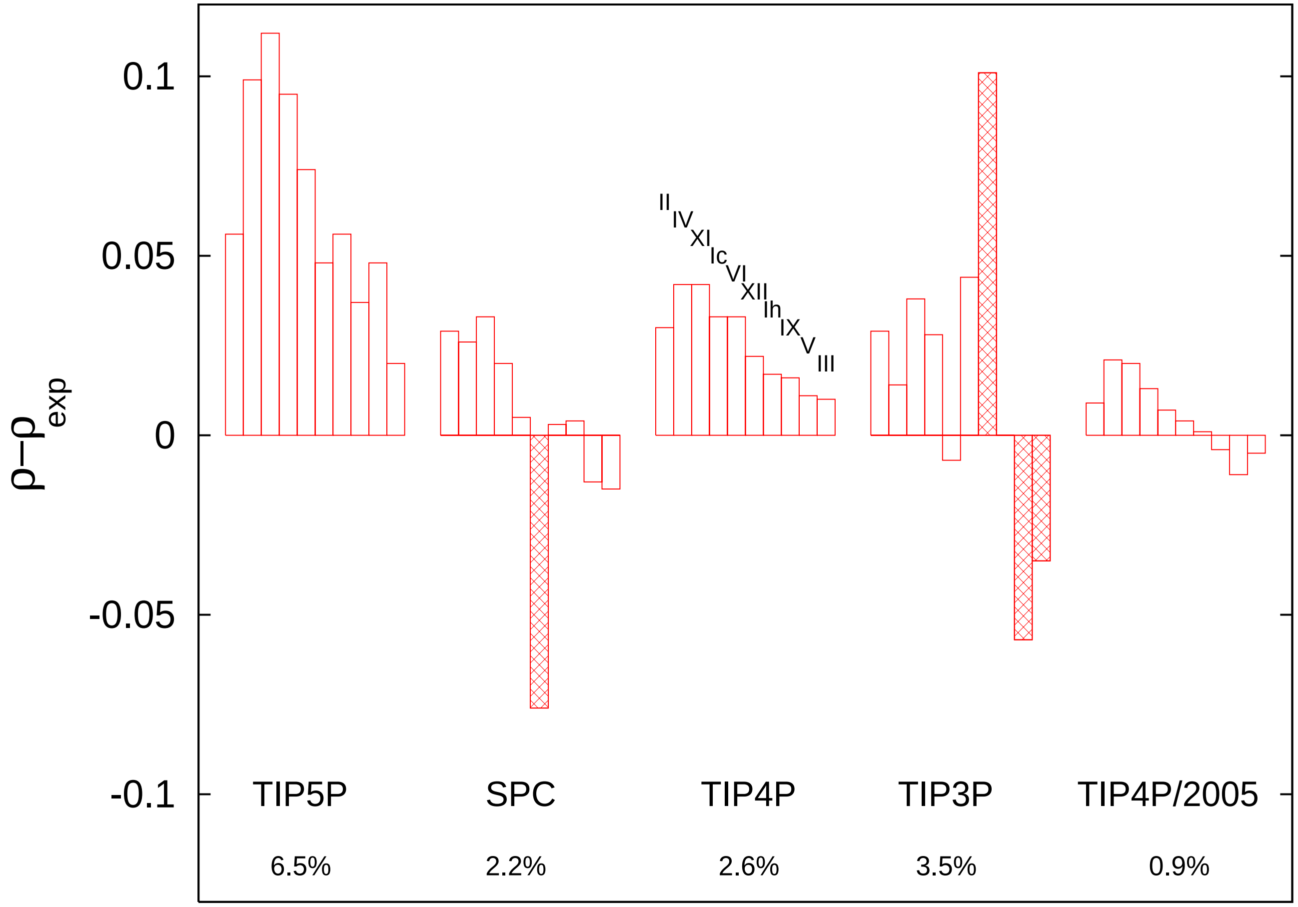


$$\sigma = \frac{L_z}{2}\left[\bar{p}_N - \bar{p}_T\right] \qquad (1)$$

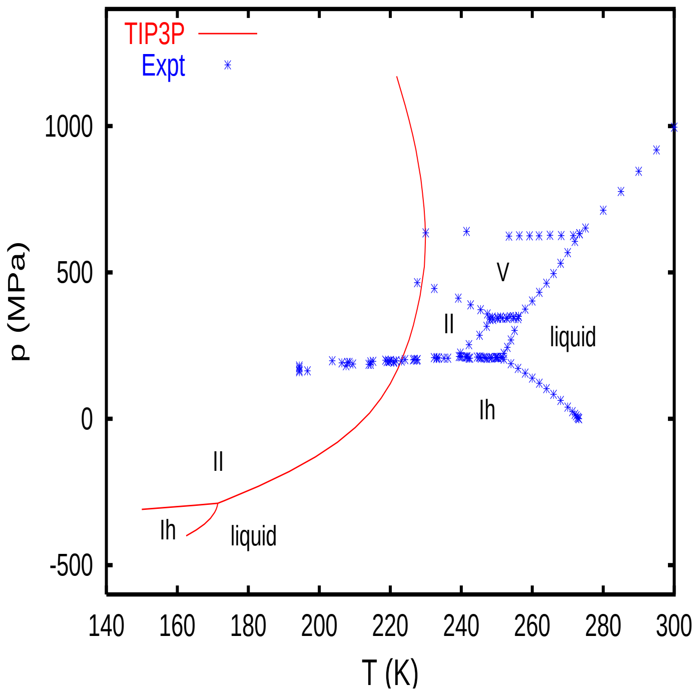
$$\sigma = \lim_{\Delta S \to 0} \frac{-kT}{2\Delta S}\left(\ln\left\langle \exp(-\Delta U^{+}/kT)\right\rangle - \ln\left\langle \exp(-\Delta U^{-}/kT)\right\rangle\right) \qquad (2)$$

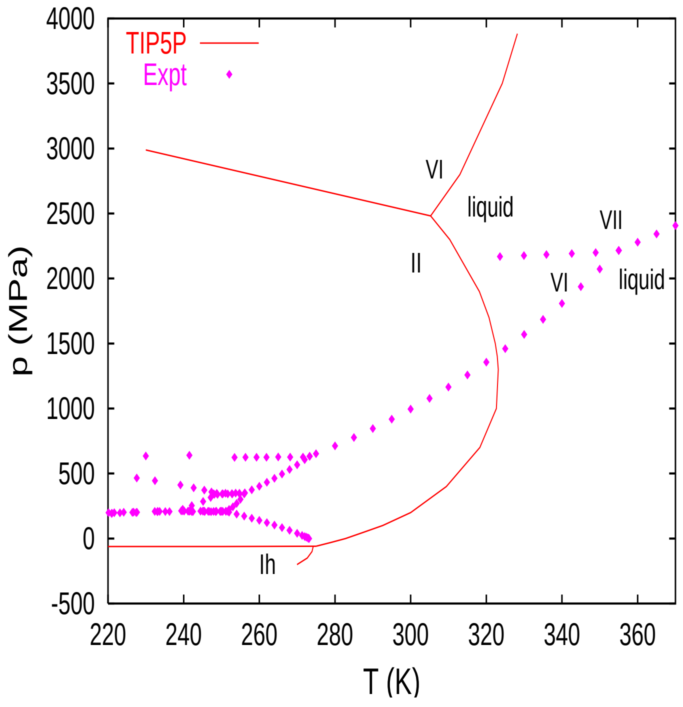
TAM. G. J. Gloor , G. Jackson , F. J. Blas and E. de Miguel, JCP, 123, 134703, (2005)

Density predictions for ices

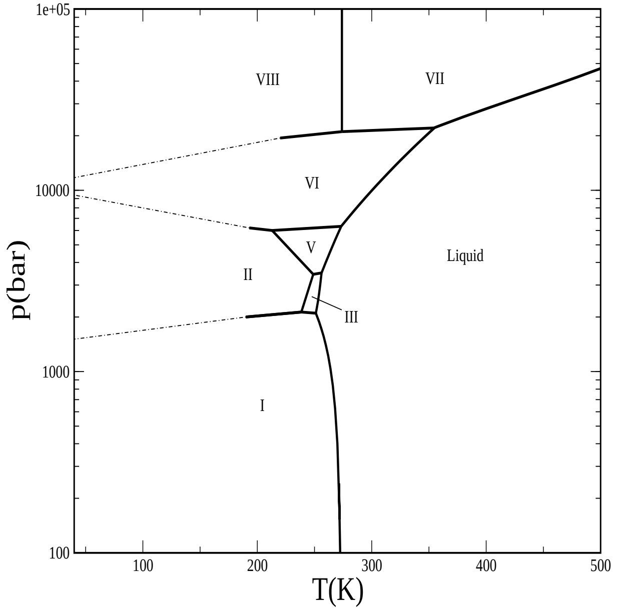


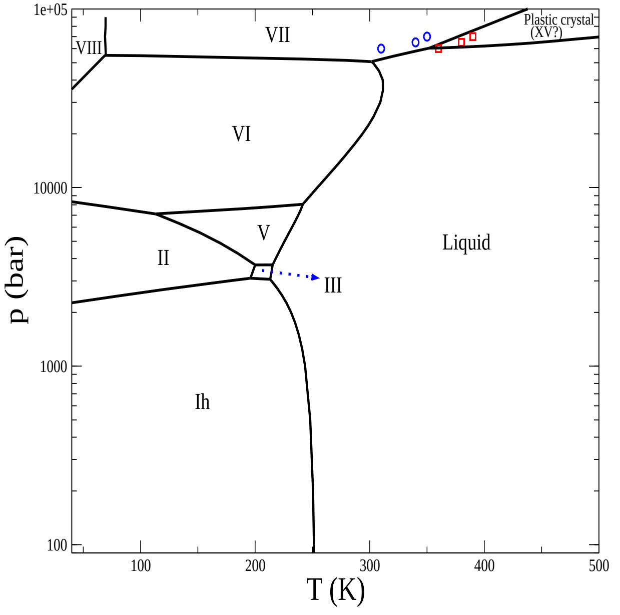
Phase diagram of TIP3P and TIP5P





Phase diagram of TIP4P/2005



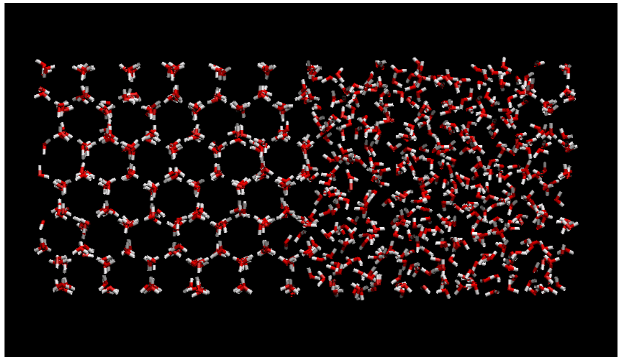


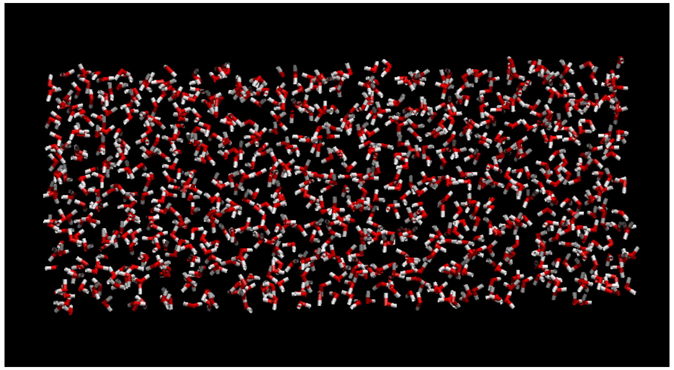
J.L.Aragones,M.M.Conde,E.G.Noya and C.Vega,Phys.Chem.Chem.Phys., in press, 2008.

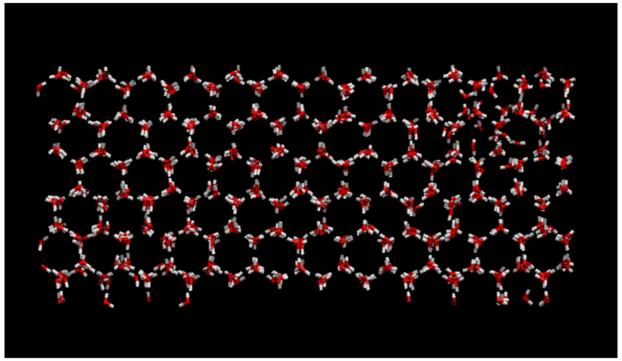
Melting properties of ice Ih

Model	TIP3P	SPC/E	TIP4P	TIP4P/2005	TIP5P	Exptl
T_m(K)	146	215	232	252	274	273.15
ρ_l	1.017	1.011	1.002	0.993	0.987	0.999
ρ_{Ih}	0.947	0.950	0.940	0.921	0.967	0.917
ΔH_m	0.30	0.74	1.05	1.16	1.75	1.44
dp/dT	-66	-126	-160	-135	-708	-137
T_m/T_c	0.25	0.337	0.394	0.394	0.525	0.422

DIRECT DETERMINATION OF THE FLUID-SOLID EQUILIBRIA



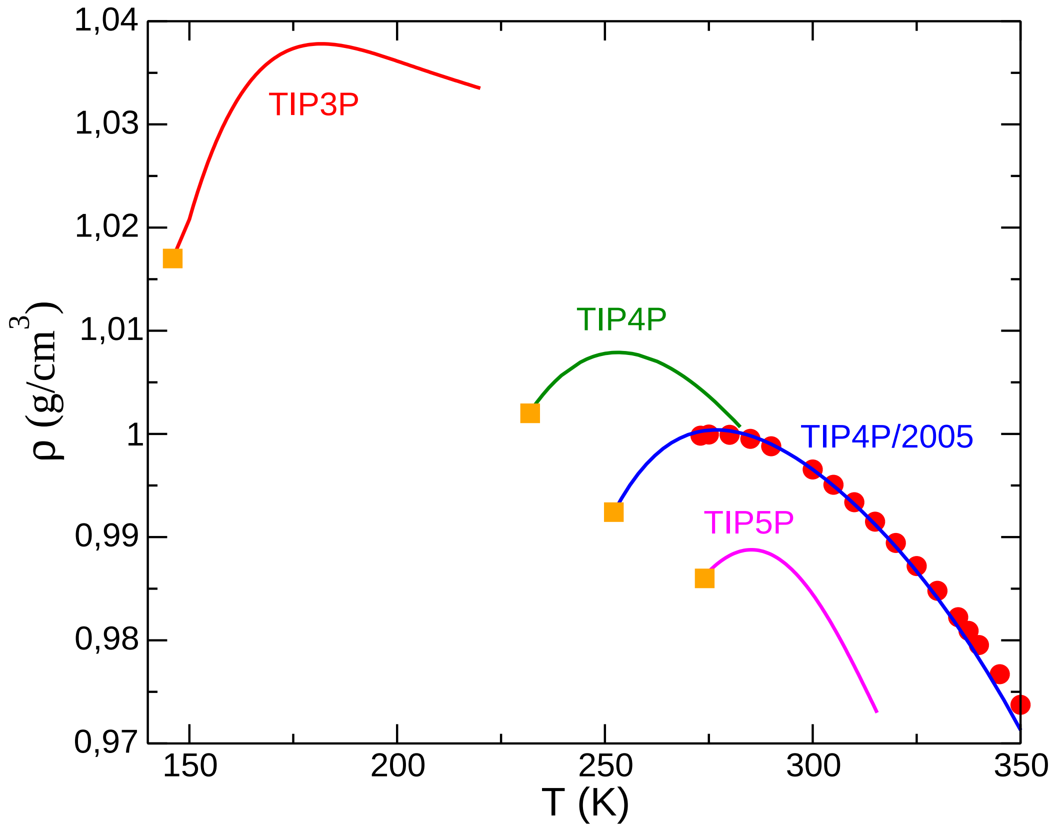




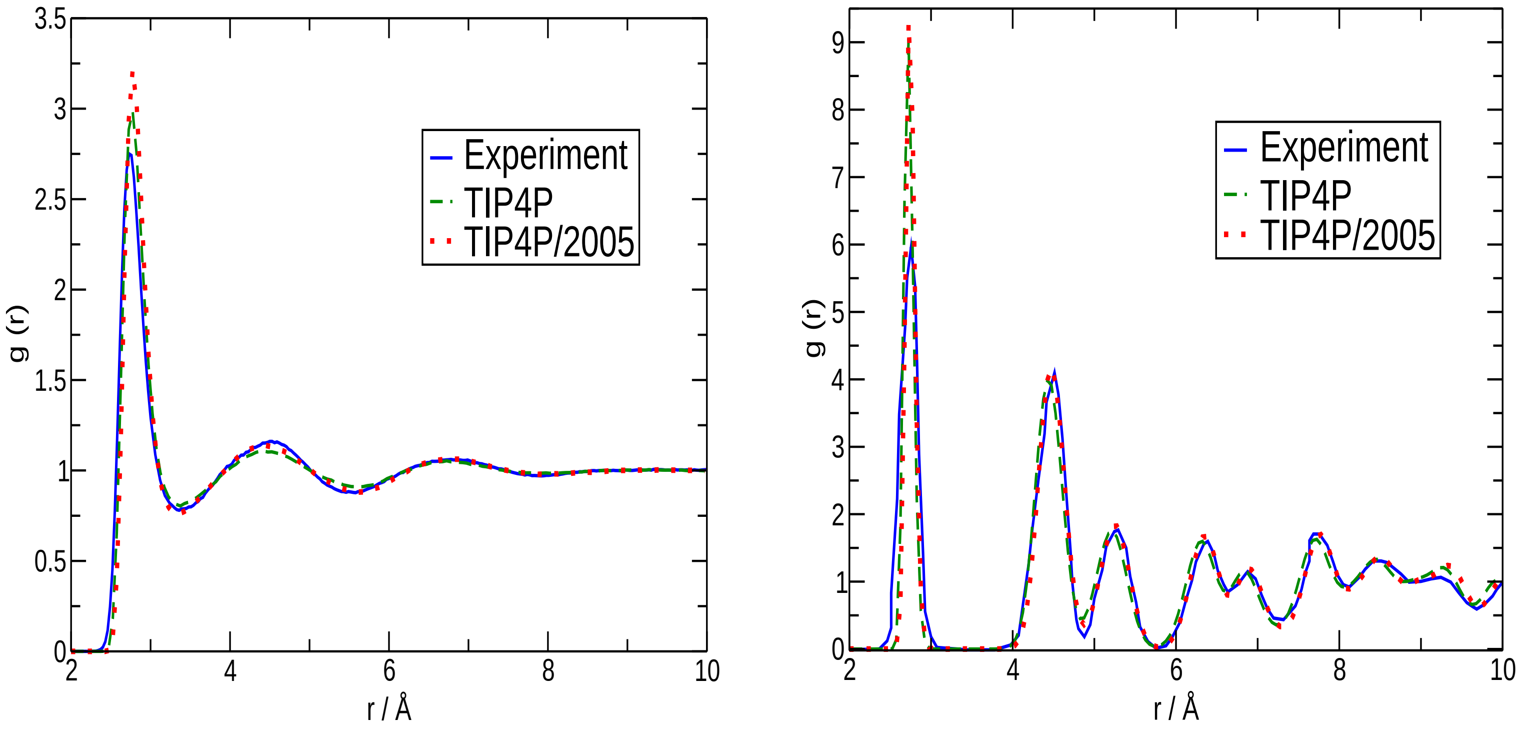
R.G. Fernandez, J.L.F.Abascal and C.Vega, JCP, 124, 144506, (2006)

Melting temperatures obtained by direct coexistence are in agreement with those obtained from free energy calculations

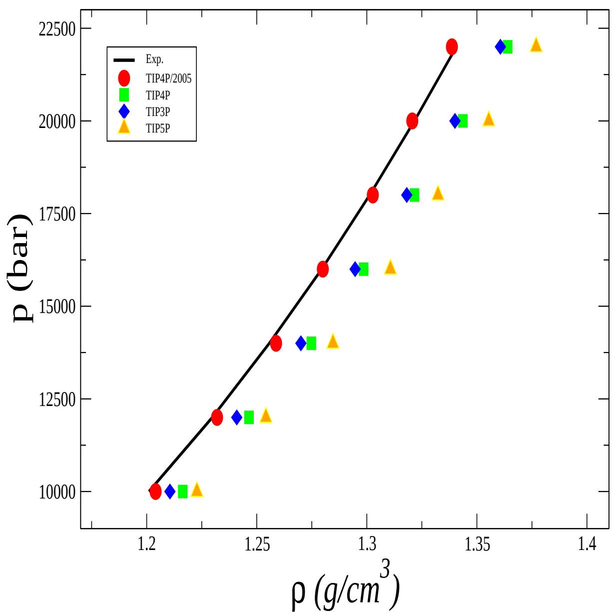
Temperature of maximum density

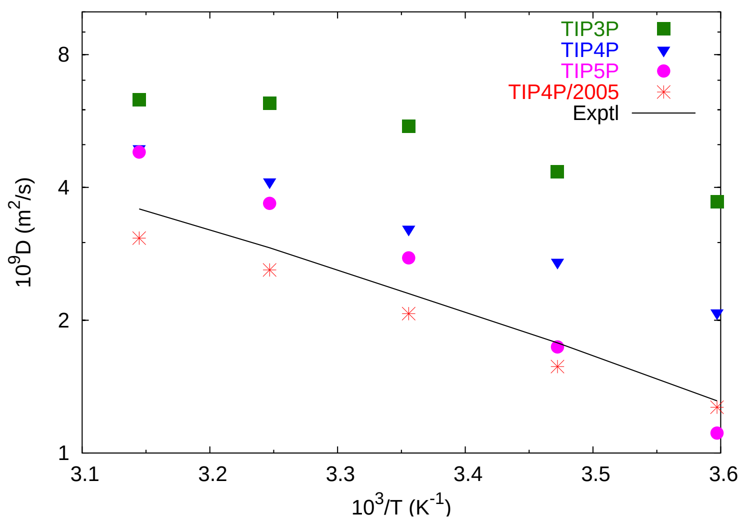


O-O radial distribution function : water and ice Ih



Equation of state and diffusion coefficient of water



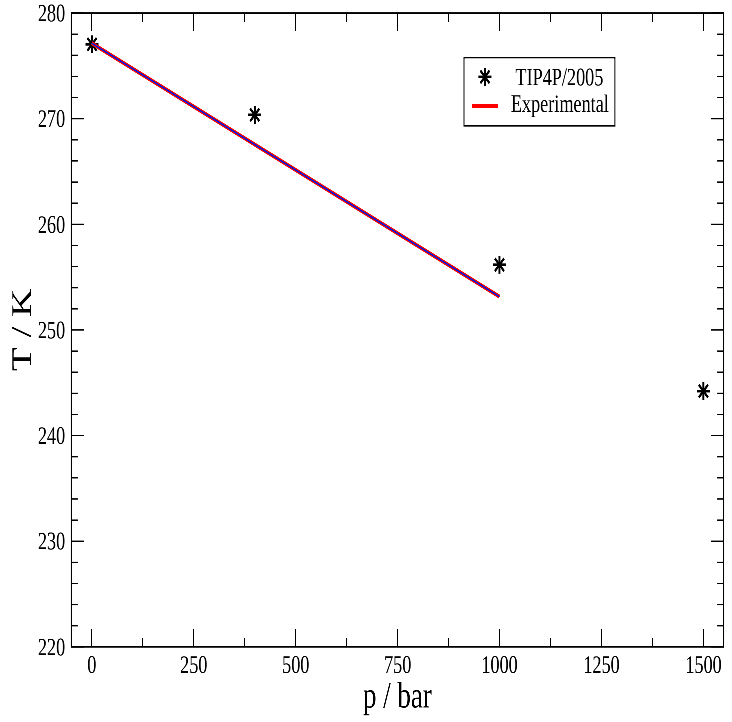


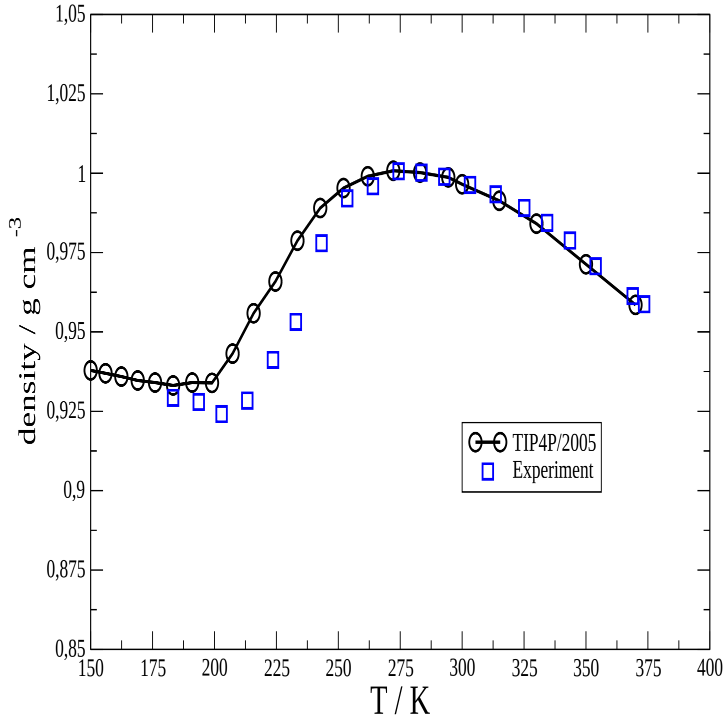
Property	TIP3P	TIP4P	TIP4P/2005	TIP5P
1. VLE, T_c	1	2	3	0
2. Surface tension	1	2	3	0
3. ρ ices	0	2	3	1
4. Phase diagram	0	2	3	1
5. T_m melting prop.	0	1	2.5	2.5
6. T_{TMD}, α, κ_T	0	1	3	2
7. Structure	0	1	2.5	2.5
8. EOS (high p)	2	1	3	0
9. D	0	1	3	2
10. ϵ	2	0	1	3
Total	**6**	**13**	**27**	**14**

Viscosity of water at room T and p

Model	Viscosity (centi Poises)
TIP3P	0,33
SPC/E	0,73
TIP4P/2005	0,86
Experiment	0,89

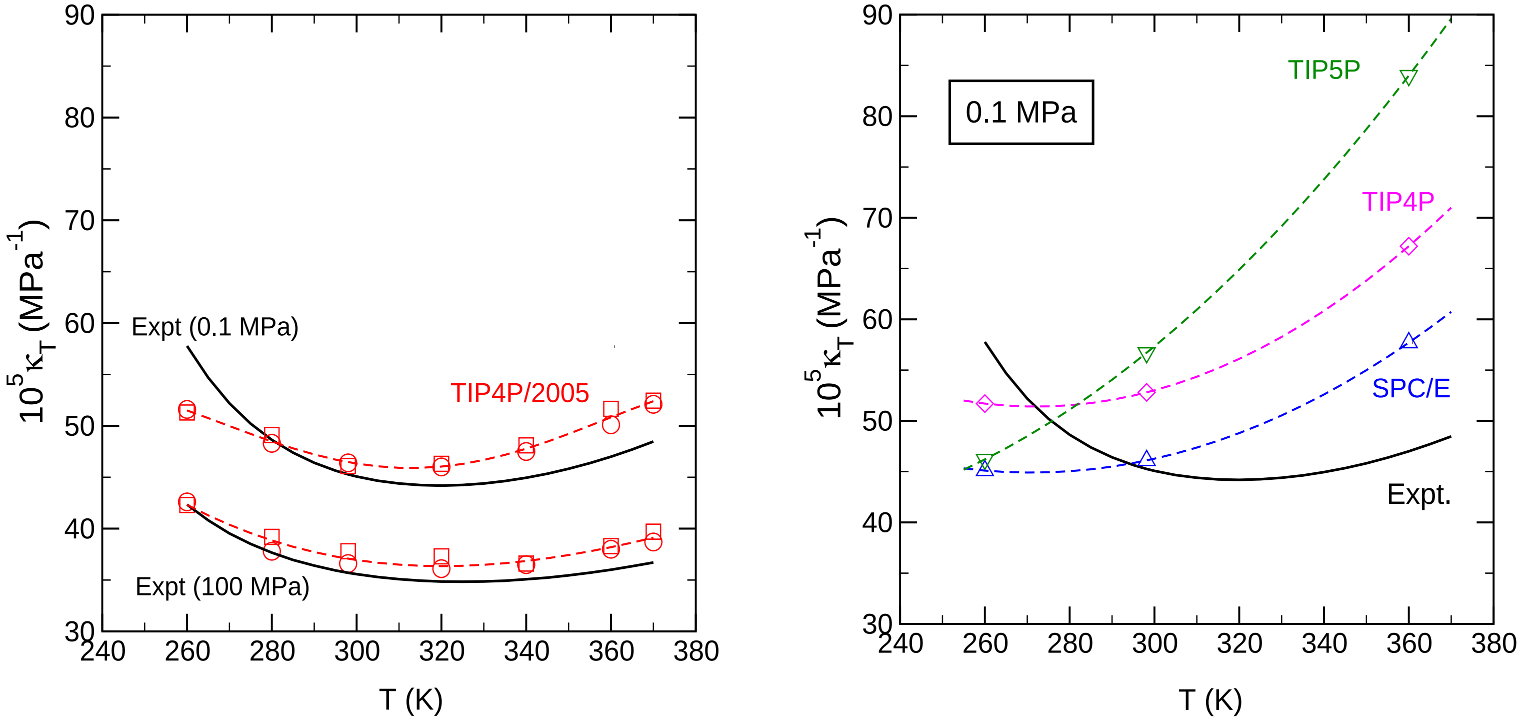
Variation of the TMD with p, and EOS for supercooled water





Experiment (confined water): F. Mallamace et al., PNAS, 104, 18387, (2007)

Calculations: H.L.Pi, C.Vega, et al., Mol.Phys. , submitted (J.J.Weiss special issue)



Isothermal compressibility

Conclusions

- The TIP4P/2005 model (designed to be used with Ewald sums) keeps the geometry of TIP4P, incorporates the polarization correction of Berendsen et al. (as SPC/E) and incorporates the TMD as a target property (as TIP5P)
- Since the model does not include polarizability it fails in describing the dielectric constant of water and the properties of the vapor phase.
- The model provides a quite good description of the phase diagram of water, density of ices, TMD of water , melting point , (by design). The model describes quite well D, EOS at high p, VLE, T_c, σ, η, k_T and TMD(p).
- The model provides an overall improvement (27 points) in the description of water with respect to TIP3P (6 points) , TIP4P (13 points), TIP5P (14 points) and SPC/E (21 points). The model is probably close to the best of what can be achieved by a rigid, non-polarizable model , with a LJ center and three charges.

References.

- The model.

J.L.F.Abascal and C.Vega,J.Chem.Phys., 123, 234505, (2005)

- Free energy calculations and phase diagram determination.

C.Vega, E.Sanz, J.L.F.Abascal and E.G.Noya , Determination of phase diagrams via computer simulation: methodology and applications to water, electrolytes and proteins , J.Phys.Condens.Matter 20, 153101, (2008).

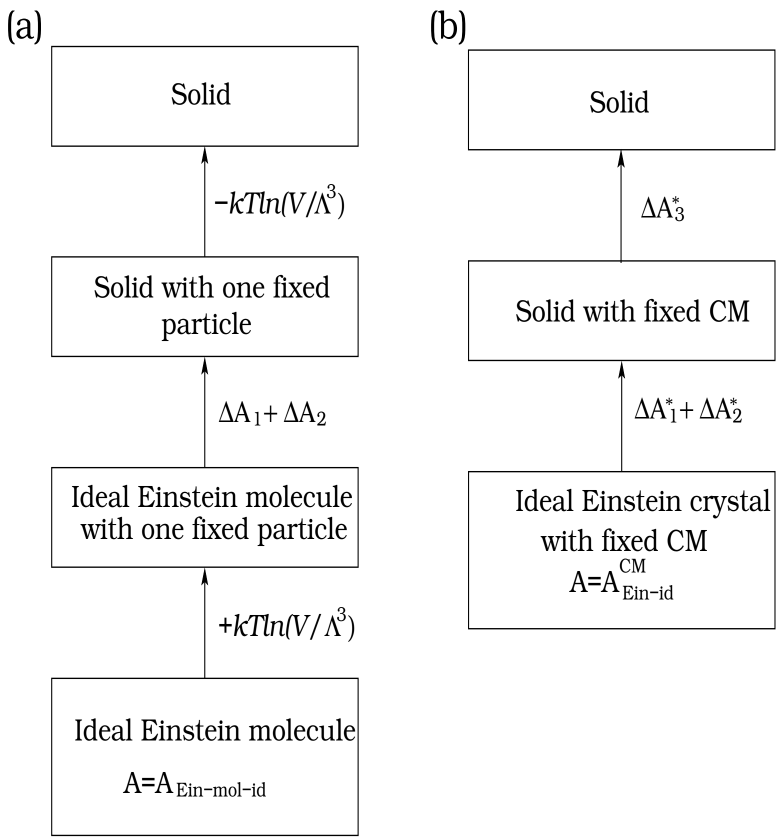
- Comparing TIP4P/2005 with other water models.

C. Vega, J. L. F. Abascal , M. M. Conde and J. L. Aragones What ice can teach us about water interactions: a critical comparison of the performance of different water models, Faraday Discussions, 141, 251, (2009). DOI: 10.1039/b805531a

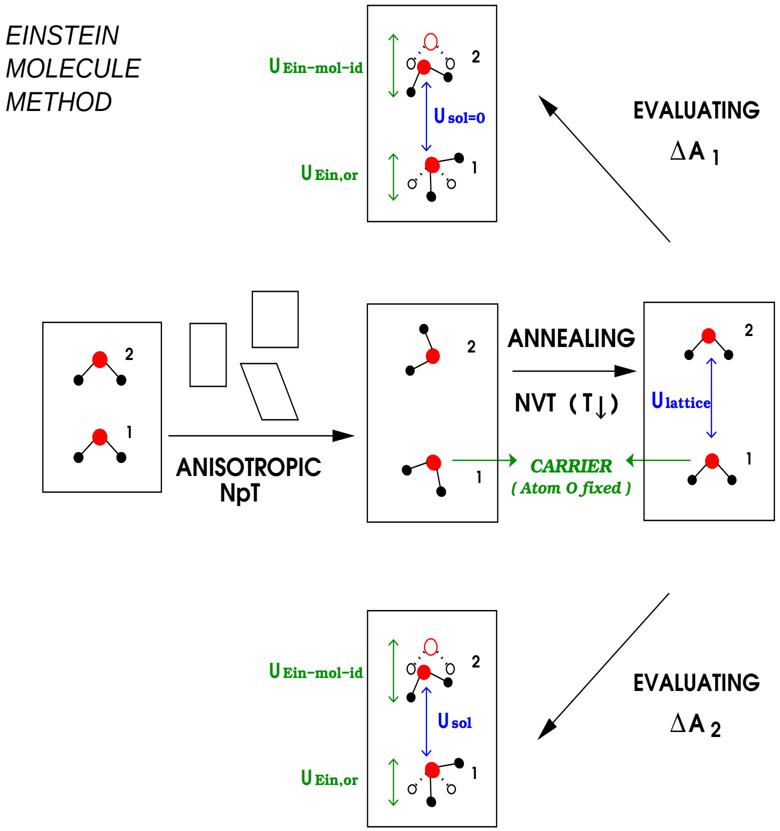
Dipole and quadrupole moments

Model	μ	Q_{xx}	Q_{yy}	Q_{zz}	Q_T	μ/Q_T
SPC	2.27	2.12	-1.82	-0.29	1.97	1.15
SPC/E	2.35	2.19	-1.88	-0.30	2.03	1.15
TIP3P	2.35	1.76	-1.68	-0.08	1.72	1.36
TIP4P	2.18	2.20	-2.09	-0.11	2.15	1.01
TIP4P/2005	2.30	2.36	-2.23	-0.13	2.30	1.00
TIP5P	2.29	1.65	-1.48	-0.17	1.56	1.46
Gas(Expt.)	1.85	2.63	-2.50	-0.13	2.56	0.72

Computing the free energy for solids



The Einstein molecule approach



E.G.Noya, M.M.Conde and C.Vega, J.Chem.Phys., 129, 104704, (2008)