Water models in computer simulations

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Introduction

This lecture is mostly based on

- http://www.lsbu.ac.uk/water/
- Bertrand Guillot *A reappraisal of what we have learnt during three decades of computer simulations on water*, Journal of Molecular Liquids 101:219 (2002)
- Andrew R. Leach *Molecular Modelling 2nd ed.*, Prentice Hall (2001)

Introduction

Essential molecule and most investigated liquid

- environmental science
- geoscience
- medium for biointeractions
- ....

Introduction

What water models are people using?

- SPC (Berendsen et al [1] 1981, book)
- SPC/E (Berendsen et al [2] 1987, cited 2004 times)
- TIP3P (Jorgensen et al [3] 1983, cited 674 times)
- TIP4P (Jorgensen et al [3]1983, cited 674 times)
- TIP5P (Jorgensen and Mahoney [4] 2000, cited 300 times)

History

- 1932 - Spectroscopic proofs of the V-shaped water molecule
- 1933 - Bernal and Fowler [5] propose 1st realistic interaction potential for water
- 1953 - Metropolis et al [6] presents the 1st Monte Carlo sampling scheme
- 1957 - Adler and Wainwright [7] performed 1st MD simulation
- 1967 - Pink Floyds 1st album *the piper at the gates of dawn*
- 1969 - Baker and Watts [8] 1st computer simulations of water
- 1976 - Lie et al [9] 1st pair potential from ab initio calculations for water
- 1981 - Berendsen et al [1] construct the 1st "accurate" and simple pair potential for liquid water
- 1993 - Laasonen et al [10] 1st ab initio calculations for liquid water

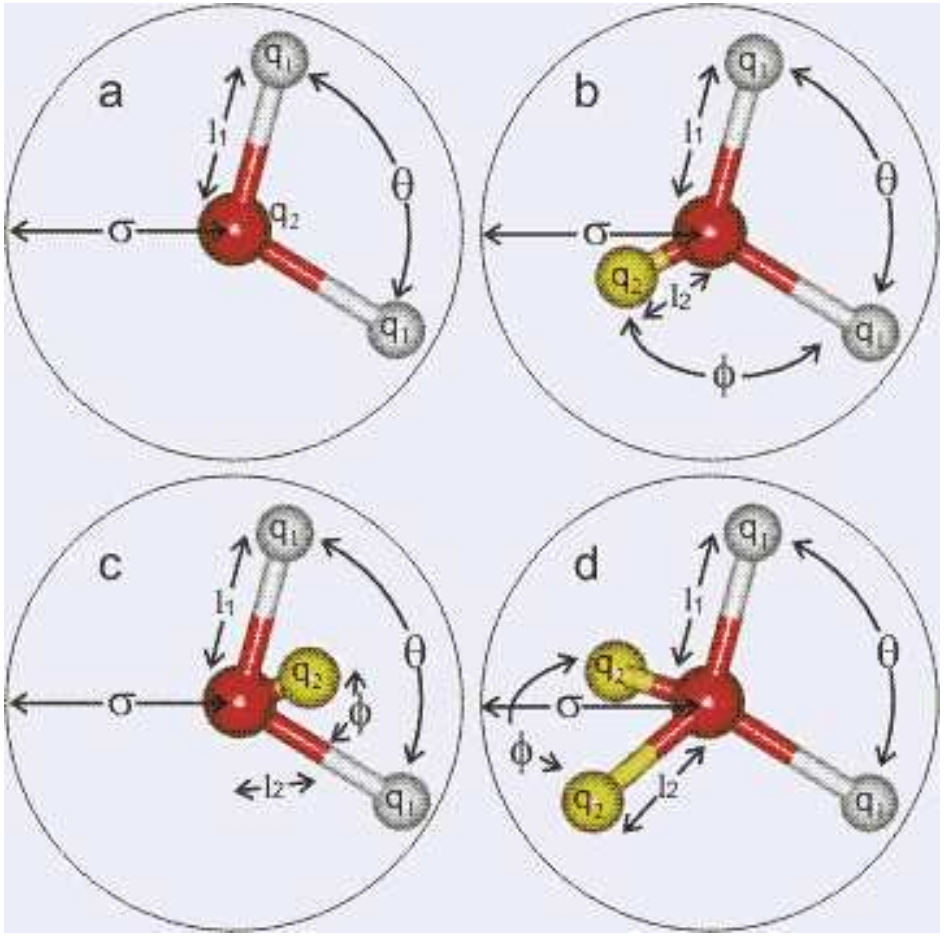
Water models

Three Types:

- Rigid models: Fixed atom positions
- Flexible models: Atoms on "springs"
- Polarizable models: Include explicit polarization term

Water models

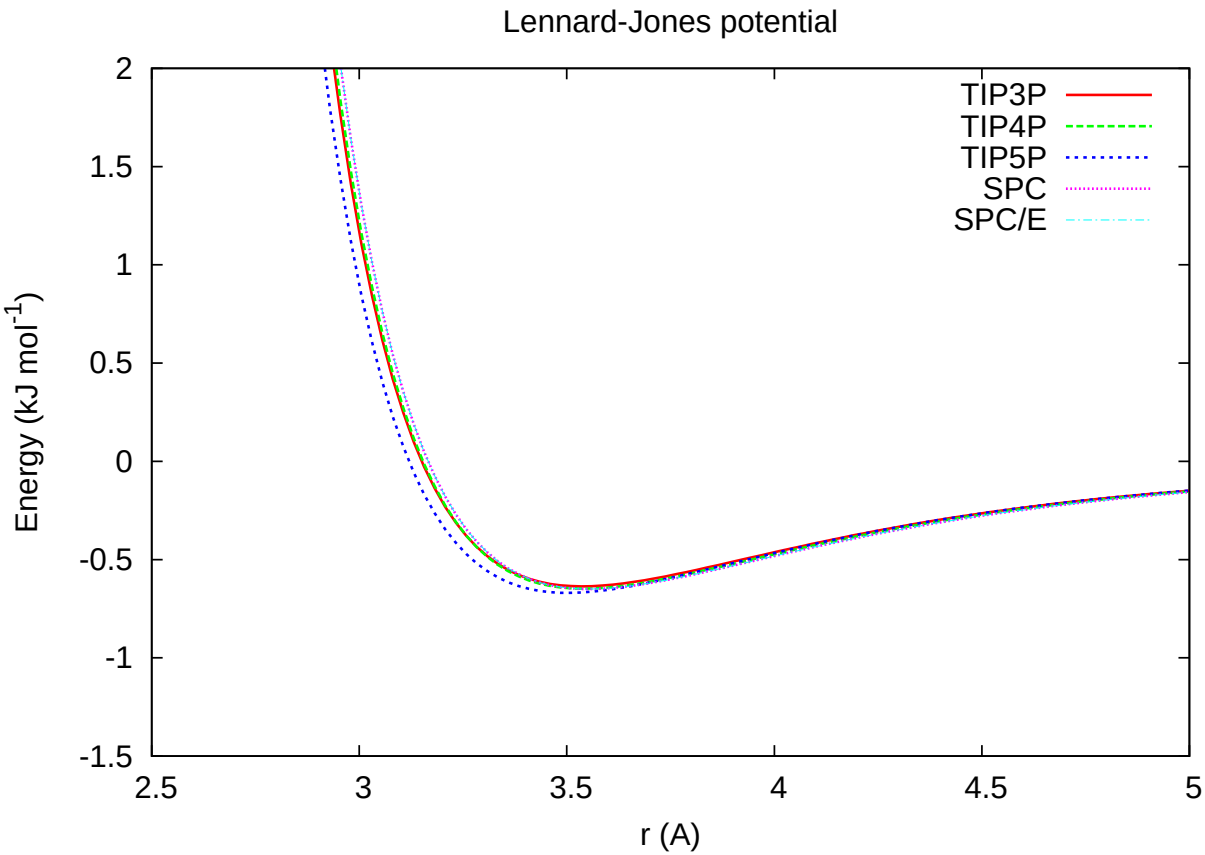
Mainly 4 structures: 3-5 interaction points



Water models

Model	Type	σ Å [6]	ϵ kJ mol^{-1} [6]	l_1 Å	l_2 Å	q_1 (e)	q_2 (e)	θ°	φ°
SSD [511]	- [8]	3.016	15.319	-	-	-	-	109.47	109.47
SPC [94]	a	3.166	0.650	1.0000	-	+0.410	-0.8200	109.47	-
SPC/E [3]	a	3.166	0.650	1.0000	-	+0.4238	-0.8476	109.47	-
SPC/HW (D_2O) [220]	a	3.166	0.650	1.0000	-	+0.4350	-0.8700	109.47	-
SPC/Fw [2] [994]	a	3.166	0.650	1.0120	-	+0.410	-0.8200	113.24	-
TIP3P [180]	a	3.15061	0.6364	0.9572	-	+0.4170	-0.8340	104.52	-
TIP3P/Fw [2] [994]	a	3.1506	0.6368	0.9600	-	+0.4170	-0.8340	104.5	-
PPC [1, 2] [3]	b	3.23400	0.6000	0.9430	0.06	+0.5170	-1.0340	106.00	127.00
TIP4P [180]	c	3.15365	0.6480	0.9572	0.15	+0.5200	-1.0400	104.52	52.26
TIP4P-Ew [649]	c	3.16435	0.680946	0.9572	0.125	+0.52422	-1.04844	104.52	52.26
TIP4P-FQ [197]	c	3.15365	0.6480	0.9572	0.15	+0.63[1]	-1.26[1]	104.52	52.26
TIP4P/Ice [838]	c	3.1668	0.8822	0.9572	0.1577	+0.5897	-1.1794	104.52	52.26
TIP4P/2005 [984]	c	3.1589	0.7749	0.9572	0.1546	+0.5564	-1.1128	104.52	52.26
SWFLEX-AI [2] [201]	c	four terms used		0.968[1]	0.14[1,3]	+0.6213	-1.2459	102.7[1]	51.35[1]
COS/G3 [704] [9]	c	3.17459	0.9445	1.0000	0.15	+0.450672	-0.901344	109.47	-
GCPM [2] [859] [10]	c	3.69 [4,11]	0.9146 [4]	0.9572	0.27	+0.6113	-1.2226	104.52	52.26
SWM4-NDP [2] [13] [933]	c	3.18395	0.88257	0.9572	0.24034	0.55733	-1.11466	104.52	52.26
ST2 [872] [12]	d	3.10000	0.31694	1.0000	0.80	+0.24357	-0.24357	109.47	109.47
TIP5P [180]	d	3.12000	0.6694	0.9572	0.70	+0.2410	-0.2410	104.52	109.47
TIP5P-Ew [619]	d	3.097	0.7448	0.9572	0.70	+0.2410	-0.2410	104.52	109.47
TTM2-F [1027] [14]	c	five parameters used		0.9572	0.70	+0.574	-1.148	104.52	52.26
POL5/TZ [2] [256]	d	2.9837 [4]	[4]	0.9572	0.5	varies [5]	-0.42188	104.52	109.47
Six-site [491]	c/d [7]	3.115_{OO} 0.673_{HH}	0.715_{OO} 0.115_{HH}	0.980	0.8892_{L} 0.230_{M}	+0.477	-0.044_{L} -0.866_{M}	108.00	111.00

Water models



$$V_r^{lj} = 4\varepsilon \left((\frac{\sigma}{r_{ij}})^{12} - (\frac{\sigma}{r_{ij}})^{6} \right) \quad (1)$$

Water models

Potentials

- Ab initio: Potentials determined from calculations of dimers, trimers or higher order clusters. Analytical fit to ab initio results are often problematic. Examples: MCY [11], MCHO [12], NCC [13]
- Empirical: Potentials developed to reproduce experimental values, in gas or liquid phase.

Water models

Flexible water models

- Includes bond stretching and angle bending
- Can reproduce vibration spectra
- Examples: CF [14], MCY [11]

Water models

Polarizable water models

Includes an explicit polarization term, which should enhance the ability to reproduce water in different phases and the interaction between them

- First attempt: PE - Barnes et al [15], Nature (1979)
- Examples: SPC/FQ and TIP4P/FQ - Rick et al [16], reproduces the liquid and gasephase dipole moment well. Computional cost only 1.1 times the corresponding rigid model.

Water models

Force fields

Many water models are developed in a specific force field, and then (sometimes correctly) adopted to other force field. Common models and force fields:

- SPC, SPC/E - gromos
- TIP3P - amber (there is also a modified TIP3P made for charmm)
- TIP4P, TIP5P - opls

Water models

How good are the water models?

Model	Type	μ_{gas} (D)	μ_{liq} (D)	ε	E_{conf} (kJ/mol)
SPC	R	2.27	2.27	65	-41
SPC/E	R	2.35	2.35	71	-41.5
TIP3P	R	2.35	2.35	82	-41.1
TIP4P	R	2.18	2.18	53	-41.8
TIP5P	R	2.29	2.29	81.5	-41.3
SPC/FQ	P	1.85	2.83	115	
TIP4P/FQ	P	1.85	2.62	79	-41.4
Exp.		1.855	2.95 (25°C)	78.4	-41.5

Water models

Can simple models describe the phase diagram?

In the solid phase water exhibits one of the most complex phase diagrams, having 13 different (known) solid structures. Vega et al [17] show that from the simple water models (SPC, SPC/E, TIP3P, TIP4P and TIP5P) only TIP4P provides a qualitatively correct phase diagram on water.

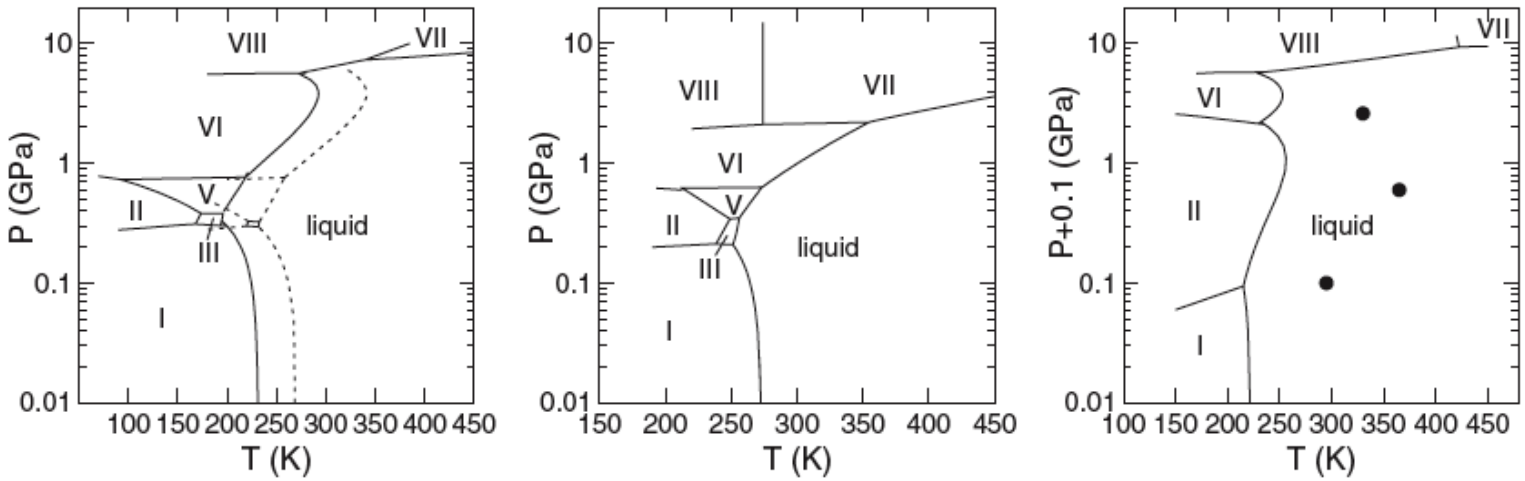


Figure 1. Phase diagram of water as obtained from experiment (centre), for the SPC/E model (right) and for the TIP4P and TIP4P/ice models (left). Left side, solid lines (TIP4P), dashed lines (TIP4P/ice). Right side, lines: coexistence line of SPC/E; symbols: stability limit of the ice phases (note the shift of 0.1 GPa in p for this model).

Water models

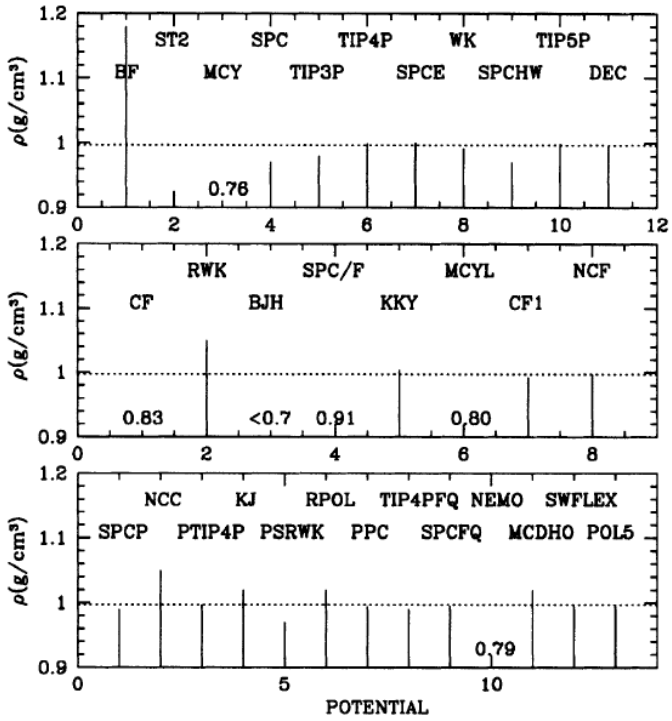
Density

Many potentials are fitted to reproduce the experimental liquid density, which is the case for most of the models that show good agreement. When the density is not used as a fitting parameter,as in the case with ab initio potentials (for example MCY, MCYL and NEMO) the results are rather poor.

Water models

Density

Top panel: rigid models, middle panel: flexible models, bottom panel: polarizable models.



Water models

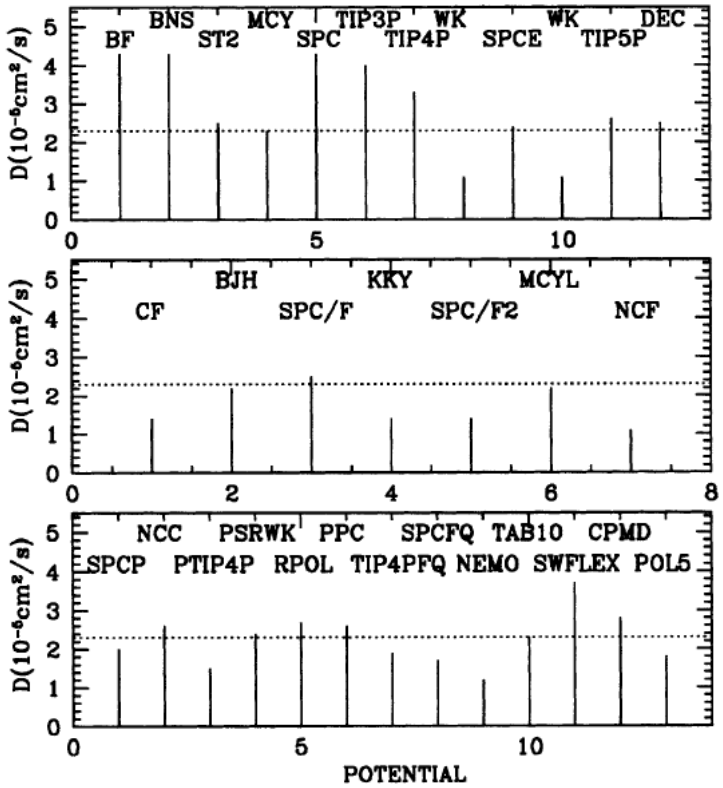
Diffusion coefficient

The mobility is of the water molecules is an indicator of the influence of the hydrogen bonds on the molecular motions. Many of the common rigid models over estimate the diffusivity.

Water models

Diffusion coefficient

Top panel: rigid models, middle panel: flexible models, bottom panel: polarizable models.



Water models

Some models worth mentioning

- F3C - Levitt et al [18] (1997). A water model calibrated for simulation of molecular dynamics of proteins and nucleic acids in solution. Cited 130 times.
- DEC - Guillot and Guissani [19] (2001). A water model that employs diffuse charges, in addition to the usual point charges, on the oxygen and hydrogen atoms, to account for charge penetration effects. Cited 61 times.
- TIP4P/FLEX - Lawrence and Skinner [20] (2003). Model that well describes the absorption spectra for liquid water. Cited 8 times (mostly by them self).

Water models

Some comparing papers

- B. Guillot, J. Mol. Liq. 101:219 (2002). Review article comparing 46 different models: dielectric constant, liquid density, heat of evaporazation, diffusion coefficient, structure, critical parameter and temperature of max density
- D. van der Spoel et al, J. Chem. Phys 101:10220 (1998). Comparing SPC, SPC/E, TIP3P and TIP4P. All systems were simulated at 300 K with and without reaction fields and with two different cutoff radii, in order to study the impact of the cutoff treatment on density, energy, dynamic, and dielectric properties
- B. Hess and N. F. A. van der Vegt, J. Phys. Chem. B 110:17616 (2006). SPC, SPC/E, TIP3P, TIP4P and TIP4P-Ew studied in different force fields: Hydration Thermodynamic Properties of Amino Acid Analogues.

Conclusions

- No water model available is able to reproduce all the water properties with good accuracy. All empirical models are fitted to something and the ab initio models suck....
- It is, never the less, possible to describe the force field of water using simple empirical models, and predict nature in many fields.
- It is worth considering which models to use when performing any simulation including water. Computional cost vs accuracy.

References


H. J. C. Berendsen, J. P. M. Postma, W. F. van Gunsteren, and J. Hermans,
Interaction Models for Water in Relation to Protein Hydration,
in *Intermolecular Forces*, edited by B. Pullman, pp. 331–342, D. Reidel Publishing Company, Dordrecht, 1981.


H. J. C. Berendsen, J. R. Grigera, and T. P. Straatsma,
J. Phys. Chem. **91**, 6269 (1987).


W. L. Jorgensen and J. D. Madura,
J. Am. Chem. Soc. **105**, 1407 (1983).


M. W. Mahoney and W. L. Jorgensen,
J. Chem. Phys. **112**, 8910 (2000).


J. D. Bernal and R. H. Fowler,
J. Chem. Phys. **1**, 515 (1933).


N. Metropolis, A. W. Metropolis, M. N. Rosenbluth, A. H. Teller, and E. Teller,
J. Chem. Phys. **21**, 1087 (1953).


B. J. Adler and T. E. Wainwright,
J. Chem. Phys. **27**, 1208 (1957).


J. A. Baker and R. O. Watts,
Chem. Phys. Lett. **3**, 144 (1969).


G. C. Lie, E. Clementi, and M. Yoishimine,
J. Chem. Phys. **64**, 2314 (1976).


K. Laasonen, M. Sprik, M. Parrinello, and R. Car,
J. Chem. Phys. **99**, 9080 (1993).


O. Matuoka, E. Clementi, and M. Yoshimine,
J. Chem. Phys. **64**, 2314 (1976).


H. Saint-Martin, C. Medianas-Lianos, and I. Ortega-Blake,

J. Chem. Phys. **93**, 6448 (1990).


U. Niesar, G. Corongiu, E. Clementi, G. R. Kneller, and D. K. Bhattacharya,
J. Chem. Phys. **94**, 7949 (1990).


H. L. Lemberg and F. H. Stillinger,
J. Chem. Phys. **62**, 1473 (1975).


P. Barnes, J. L. Finney, J. D. Nicholas, and J. E. Quinn,
Nature **282**, 459 (1979).


S. W. Rick, S. J. Stuart, and B. J. Berne,
J. Chem. Phys. **101**, 6141 (1994).


C. Vega, J. L. F. Abascal, E. Sanz, L. G. MacDowell, and C. McBride,
J. Phys.: Condens. Matter **17**, S3284 (2005).


M. Levitt, M. Hirshberg, R. Sharon, K. E. Laidig, and V. Daggett,

J. Phys. Chem. B **101**, 5051 (1997).


B. J. Guillot and Y. Guissani,
J. Chem. Phys. **114**, 6720 (2001).


C. P. Lawrence and J. L. Skinner,
Chem. Phys. Lett. **369**, 472 (2003).