Explicit Water Models

Shuqiang Wang

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Comparison of simple potential functions for simulating liquid water

William L. Jorgensen, etc

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Topics

I. Introduction
II. Potential Functions
III. Computer Simulation
IV. Results and Discussion
V. Summary

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I. Introduction

- Property of Water
  - ✓ Water is very important
  - ✓ the anomalous properties of water.
  - ✓ 3 phases: ice, liquid, gas.
  - ✓ Water clusters, biowater.
- Fluid mechanics
- Explicit water model

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I. Introduction

Property of Water

✓ Water is very important

water is the most common liquid on our planet, vital to all life forms.

the large heat capacity and high water content in organisms and on earth contribute to thermal regulation and prevent local temperature fluctuations.

the high latent heat of evaporation gives resistance to dehydration and considerable evaporative cooling.

It is the dispersion medium for all biochemical reactions of the living process and takes part in many of these reactions.

Although the water molecule only has 3 atoms, it has a lot of anomalous property.

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I. Introduction

Property of Water

✓ the anomalous properties of water

Forty-one anomalies of water:

1) water has unusually high melting point
2) water has unusually high boiling point
3) water has unusually high critical point
4) water has unusually high surface tension
5) water has unusually high viscosity
6) water has unusually high heat of vaporization
7) water shrinks on melting
8) water has a high density that increases on heating (up to 3.984°C)
9) the number of nearest neighbors increases with melting
10) the number of nearest neighbors increases with temperature
11) pressure reduces its melting point
12) pressure reduces the temperature of maximum density
...

http://www.martin.chaplin.btinternet.co.uk/anmlies.html

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Property of Water

✓ the anomalous properties of water

The chart at the right shows how the volume of water varies with the temperature: the large increase (about 9%) on freezing shows why ice floats on water and why pipes burst when they freeze. The expansion between 4° and 0° is due to the formation of larger clusters. Above 4°, thermal expansion sets in as thermal vibrations of the O—H bonds becomes more vigorous, tending to shove the molecules apart more.

From http://www.chem1.com/acad/sci/aboutwater.html

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Property of Water

✓ 3 phases: ice, liquid, gas

each water molecule is surrounded by four neighboring H2Os. two of these are hydrogen-bonded to the oxygen atom on the central H2O molecule, and each of the two hydrogen atoms is similarly bonded to another neighboring H2O.

the four bonds from each O atom point toward the four corners of a tetrahedron centered on the O atom. This basic assembly repeats itself in three dimensions to build the ice crystal.

From http://www.chem1.com/acad/sci/aboutwater.html

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Property of Water

✓ 3 phases: ice, liquid, gas

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Property of Water

✓ 3 phases: ice, liquid, gas
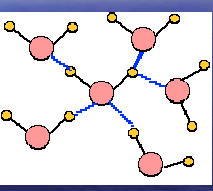
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Property of Water

✓ 3 phases: ice, liquid, gas

When ice melts to form **liquid water**, the uniform three-dimensional tetrahedral organization of the solid breaks down as thermal motions disrupt, distort, and occasionally break hydrogen bonds. The methods used to determine the positions of molecules in a solid do not work with liquids, so there is no unambiguous way of determining the detailed structure of water.

From http://www.chem1.com/acad/sci/aboutwater.html

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Property of Water

✓ Water clusters, Biowater

Since the 1930s, chemists have described water as an "associated" liquid, meaning that hydrogen-bonding attractions between H2O create loosely-linked aggregates. Because the strength of a hydrogen bond is comparable to the average thermal energy at ordinary temperatures, these bonds are disrupted by thermal motions almost as quickly as they form. Theoretical studies have shown that certain specific cyclic arrangements **("clusters")** of 3, 4, and 5 H2O molecules are especially stable, as is a three-dimensional hexamer (6 molecules) that has a cage-like form. But even the most stable of these clusters will flicker out of existence after only about 10 picoseconds (10^-12) . It must be emphasized that no clustered unit or arrangement has ever been isolated or identified in pure bulk liquid water.

From http://www.chem1.com/acad/sci/aboutwater.html

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I. Introduction
Property of Water

✓ Water clusters, Biowater

Water can hydrogen-bond not only to itself, but also to any other molecules that have -OH or -NH2 units hanging off of them. This includes simple molecules such as alcohols, surfaces such as glass, and macromolecules such as proteins. The biological activity of proteins (of which enzymes are an important subset) is critically dependent not only on their composition but also on the way these huge molecules are folded; this folding involves hydrogen-bonded interactions with water, and also between different parts of the molecule itself. Anything that disrupts these intramolecular hydrogen bonds will denature the protein and destroy its biological activity.

From http://www.chem1.com/acad/sci/aboutwater.html   13

I. Introduction
Property of Water

✓ Water clusters, Biowater

It is now known that the intracellular water very close to any membrane or organelle (sometimes called *vicinal water*) is organized very differently from bulk water, and that this structured water plays a significant role in governing the shape (and thus biological activity) of large folded biopolymers. It is important to bear in mind, however, that the structure of the water in these regions is imposed solely by the geometry of the surrounding hydrogen bonding sites.

From http://www.chem1.com/acad/sci/aboutwater.html   14

I. Introduction
Property of Water

The following facts are well established:
- H_2O molecules attract each other through the special type of dipole-dipole interaction known as hydrogen bonding
- a hydrogen-bonded cluster in which four H_2Os are located at the corners of an imaginary tetrahedron is an especially favorable (low-potential energy) configuration, *but…*
- the molecules undergo rapid thermal motions on a time scale of picoseconds (10–12 second), so the lifetime of any specific clustered configuration will be fleetingly brief.
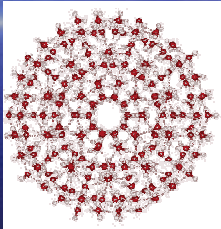
From http://www.chem1.com/acad/sci/aboutwater.html   15

Property of Water

Prof. Martin Chapin of the London South Bank University has recently proposed an **icosahedra clustering model** in which twenty 14-molecule tetrahedral units form an icosohedron (a polyhedron having 20 faces) containing a total of 280 H2O units. This model is consistent with X-ray diffraction data and is able to explain all of the unusual properties of water.

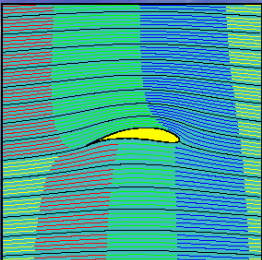From http://www.chem1.com/acad/sci/aboutwater.html

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Fluid mechanics

- Rou(density), P(pressure), U(velocity), E(energy), T.
- Assumption: material is continuous.
  Crudely speaking, matter is taken to occupy every point of the space of interest, regardless of how closely we examine the material.
- the conservation of mass, momentum, and energy. Plus Constitutive equation such as Rou = Rou(P,T).
- Navier-Stokes Equations (Euler)
- Problem:
  weather forecast, pollution control, airplane design.

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Fluid mechanics

Flow around airfoil.

From internet?

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Explicit water model

"The main goal in physics and chemistry of water is first, to reproduce and to understand quantitatively the evolution of water properties over a large range of thermodynamic conditions and next, to ensure the transferability of this description to various environments (aqueous solution, interfaces,...). So the purposes of many studies published in the literature during the last thirty years is the quest of a microscopic model for water susceptible to fulfill the above task." [2]

[2] Bertrand Guillot, A reappraisal of what we have learnt during three decades of computer simulations on water.

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Explicit water model

some milestones about water research:

1932 – Spectroscopic proofs of the V-shaped geometry of H2O.

1933 – Bernal and Fowler propose the first realistic interaction potential for water.

--------------------end of the pre-computer era-----------------------

1953 – Metropolis, Rosenbluth and Teller present the Monte Carlo sampling scheme.

1957 – Alder and Wainwright perform the first molecular dynamics simulation.

1967, 1971 – Barker and Watts, Rahman and Stillinger publish the first computer simulations of liquid water.

1976 – Clementi et al. derive a pair potential for water from ab initio calculations.

1981, 1983 – Determination of accurate and simple (ready to use) pair potentials for liquid water.

1993 – First ab-initio calculation of liquid water.

[2] Bertrand Guillot, A reappraisal of what we have learnt during three decades of computer simulations on water.

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II. Potential Functions

For a given system of N particles without force coming from outside this system, a potential function U could be used to give

$$F = -\nabla U$$

$$ma = F$$

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Potential Functions

$$U(\vec{R}) = \sum_{bonds} K_b(b-b_0)^2 + \sum_{angles} K_\theta(\theta-\theta_0)^2$$
$$+ \sum_{dihedral} K_\chi(1+\cos(n\chi-\delta)) + \sum_{impropers} K_{imp}(\varphi-\varphi_0)^2$$
$$+ \sum_{nonbond} (\varepsilon[(\frac{R\min_{ij}}{r_{ij}})^{12} - (\frac{R\min_{ij}}{r_{ij}})^6]) + \frac{q_i q_j}{\varepsilon r_{ij}}$$

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Potential Functions for water

$$\varepsilon_{mn} = \sum_i^{on(m)} \sum^{on(n)} \frac{q_i q_j e^2}{r_{ij}} + \frac{A}{r_{oo}^{12}} - \frac{C}{r_{oo}^6}$$

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Potential Functions for water

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Potential Functions for water

The methods which have been used to calculate interaction potentials may be broadly classified into three groups:

• The first type of model is completely empirical

    all parameters are chosen to fit experimental data.

• A second group consists of the ab initio models

    these potential functions are completely determined from quantum mechanical calculations. Such calculations are long and difficult and, except for the simplest systems, are not very accurate.

• The final type of model, the semi-empirical model, is a combination of the previous two.

    those parts of the potential for which the form is known accurately from quantum calculation are retained, whilst empirical corrections are used to describe the remainder of the potential.

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Potential Functions for water

A recent review listed 46 distinct models [1], 1-23:

Acronym (date)	Reference	Status	Type	Sites	$\mu_g(D)$	$\mu_l(D)$
BF (1933)	7	empirical	R	4	2.0	2.0
R (1951)	21	empirical	R	5	1.84	1.84
BNS (1971)	22	empirical	R	5	2.17	2.17
ST2 (1973,1993)	23	empirical	R	5	2.35	2.35
CF (1975,1978,1995)	24	empirical	F	3	1.86	1.98
MCY (1976)	25	ab initio	R	4	2.19	2.19
DCF (1978,1980,1993)	26	empirical	F,D,P	3	1.855	-
PE (1979)	27	empirical	P	1	1.855	2.50
SPC (1981)	14	empirical	R	3	2.27	2.27
TIP3P (1981,1983)	15	empirical	R	3	2.35	2.35
RWK (1982)	28	empirical	F	4	1.85	1.89
TIP4P (1983)	15	empirical	R	4	2.18	2.18
BJH (1983)	29	empirical	F	3	1.87	1.99
SPC/F (1985)	30	empirical	F	3	2.27	2.42
MCYL (1986)	31	ab initio	F	4	2.19	2.26
SPC/E (1987)	32	empirical	R	3	2.35	2.35
WK (1989)	33	empirical	R	4	2.60	2.60
SPCP (1989)	34	empirical	P	3	1.85	2.90
CKL (1990)	35	empirical	F,P	4	1.88	2.20
MCHO (1990)	36	ab initio	P	6	2.12	=3.0
NCC (1990)	37	ab initio	P	6	1.85	2.80
NEMO (1990,1995)	38	ab initio	P	5	2.04	2.89
PTIP4P (1991)	39	empirical	P	4	1.85	2.80

R stands for rigid, F for flexible, D for dissociable and P for polarizable, mu are the dipole moment in gaseous/liquid phase

[1] B.Guillot, A reappraisal of what we have learnt during three decades of computer simulations on water, *J. Mol. Liquids,* **101** (2002) 219-260.

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Potential Functions for water
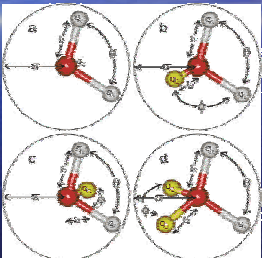
A recent review listed 46 distinct models [1], 24-46:

Acronym (date)	Reference	Status	Type	Sites	$\mu_g(D)$	$\mu_l(D)$
SPC/FP (1991)	40	empirical	F,P	3	1.85	2.44
PSRWK (1991)	41	empirical	P	4	1.88	2.63
KJ (1992)	42	empirical	P	4	1.85	-
NCCvib (1992)	37b	ab initio	F,P	6	1.85	3.11
ASP-W (1992,1998)	43	ab initio	P	3	1.85	2.90
RPOL (1992)	44	empirical	P	3	2.02	2.62
CPMD (1993,1999)	45	DFT+CP	F,D,P	nucl.+el.	1.87	2.95
PPC (1994)	46	ab initio	P	4	2.14	2.51
SPC/FQ (1994)	47	empirical	P	3	1.85	2.83
TIP4P/FQ (1994)	47	empirical	P	4	1.85	2.62
KKY (1994)	48	empirical	F,D	3	2.38	2.21
SQPM (1995)	49	valence bond	P	4	1.85	2.62
SCPDP (1996)	50	empirical	P	4	1.85	2.87
TAB/10D (1998)	51	SCF+MD	P	5	1.85	2.65
NSPCE (1998)	52	empirical	R	3	2.18	2.18
NCF (1998)	53	empirical	F	3	1.85	1.90
MCDHO (2000)	54	ab initio	F, P	4	1.85	3.01
TIP5P (2000)	55	empirical	R	5	2.29	2.29
SPC/HW (2001)	56	empirical	R	3	2.41	2.41
DEC (2001)	57	empirical	R	3	1.85	1.85
SWFLEX (2001)	58	empirical	P	4	1.85	2.59
POLARFLEX (2001)	59	valence bond	F,P	3	1.85	2.55
POL5 (2001)	60	ab initio	P	5	1.85	2.71

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[1] B.Guillot, A reappraisal of what we have learnt during three decades of computer simulations on water, *J. Mol. Liquids,* **101** (2002) 219-260.

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II. Potential Functions

Potential Functions for water

More than 46 distinct models [1], indirectly indicates their lack of success in reproducing the properties of real water. Some of the more successful simple models are given.

Models types **a**, **b** and **c** are all planar whereas type **d** is almost tetrahedral

[1] B.Guillot, A reappraisal of what we have learnt during three decades of computer simulations on water, *J. Mol. Liquids* **101** (2002) 219-260.
http://www.martin.chaplin.btinternet.co.uk/intro.html
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II. Potential Functions

Potential Functions for water

Model	Type	σ Å [6]	ε kJ mol[-1][6]	l_1 Å	l_2 Å	q_1	q_2	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	-
TIP3P [180]	a	3.15061	0.6364	0.9572	-	+0.4170	-0.8340	104.52	-
PPC 1, 2 [3]	b	3.23400	0.6000	0.9430	0.06	+0.5170	-1.0340	106.00	127.00
TIP4P [180] 10	c	3.15365	0.6480	0.9572	0.15	+0.5200	-1.0400	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
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]
TIP5P [180]	d	3.12000[9]	0.6694[9]	0.9572	0.70	+0.2410	-0.2410	104.52	109.47
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 / 0.573 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

[1] B.Guillot, A reappraisal of what we have learnt during three decades of computer simulations on water, *J. Mol. Liquids* **101** (2002) 219-260.
http://www.martin.chaplin.btinternet.co.uk/intro.html
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II. Potential Functions

Explicit water models

- SPC,   Simple Point Charge Model
- ST2,   Frank H. Stillinger & Aneesur Rahman
- BF,   Bernal-Fowler
- TIPS2,   Transferable Intermolecular Potential Functions
- TIP3P,   TIP 3-point model
- TIP4P,   TIP 4-point model

- TIP5P,   TIP 5-point model

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Explicit water models

- SPC,   a
- ST2,   d
- BF,   c
- TIPS2,   c
- TIP3P,   a
- TIP4P,   c

- TIP5P,   d

Models types **a**, **b** and **c** are all planar whereas type **d** is almost tetrahedral

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TABLE I. Monomer geometry and parameters for potential functions.

	SPC	TIP3P	BF	TIPS2	TIP4P
$r(OH)$, Å	1.0	0.9572	0.96	0.9572	0.9572
$\angle HOH$, deg	109.47	104.52	105.7	104.52	104.52
$A \times 10^{-3}$, kcal Å^{12}/mol	629.4	582.0	560.4	695.0	600.0
C, kcal Å^6/mol	625.5	595.0	837.0	600.0	610.0
$q(O)$	−0.82	−0.834	0.0	0.0	0.0
$q(H)$	0.41	0.417	0.49	0.535	0.52
$q(M)$	0.0	0.0	−0.98	−1.07	−1.04
$r(OM)$, Å	0.0	0.0	0.15	0.15	0.15

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3-site model (SPC, TIP3P)

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4-site model (BF, TIPS2 & TIP4P)

	BF	TIPS2	TIP4P
r(OH), Å	0.96	0.9572	0.9572
∠HOH, deg	105.7	104.52	104.52
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r(OM), Å	0.15	0.15	0.15

$$\varepsilon_{mn} = \sum_{i}^{on(m)} \sum^{on(n)} \frac{q_i q_j e^2}{r_{ij}} + \frac{A}{r_{oo}^{12}} - \frac{C}{r_{oo}^{6}}$$

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5-site model (ST2, TIP5P)

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III. Computer Simulations

- Monte Carlo method

  in NPT ensemble at 25 º C and 1 atm.
  using cubic samples of 125 monomers.
  periodic boundary conditions.
  Metropolis sampling.
  Spherical cutoffs at 7.5 Å.

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IV. Results and Discussion

A. Thermodynamics
B. Self-diffusion coefficients
C. Structure
D. Energy and hydrogen bonding
   distributions

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A. Thermodynamics

TABLE III. Calculated and experimental properties for liquid water at 25°C and 1 atm. [a]

	SPC	TIP3P	BF	TIPS2	TIP4P	ST2	Expt. [b]
$d(\text{g/cm}^3)$	0.971	0.982	1.181	0.927	0.999	0.925	0.997
$-E_i$ (kcal/mol)	10.18	9.86	10.49	9.88	10.07	10.37	9.92[c]
ΔH_{vap} (kcal/mol)	10.77	10.45	11.08	10.47	10.66	10.96	10.51
C_p (cal/mol deg)	23.4	16.8	16.0	18.9	19.3	22.2	17.99
$10^5 \alpha$ (deg^{-1})	68	41	59	88	94	-69	25.7
$10^6 \kappa$ (atm^{-1})	27	18	18	56	35	63	45.8

[a]No cutoff corrections have been made to the computed properties.
[b]See Refs. 4 and 12.
[c]See the text.

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A. Thermodynamics

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C_p (cal/mol deg)	23.4	18.8	16.0	18.9	19.3	22.2	17.99
$10^5 \alpha$ (deg^{-1})	58	41	59	88	94	−69	25.7
$10^6 \kappa$ (atm^{-1})	27	18	18	56	35	63	45.8

[a]No cutoff corrections have been made to the computed properties.
[b]See Refs. 4 and 12.
[c]See the text.

d: density. Overall, the computed densities with or without cutoff corrections are in reasonable accord with experiment except for the BF potential.

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[b]See Refs. 4 and 12.
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$-E_i$: intermolecular energy.

ΔH_{vap} : heat of vaporization. The energy required to change a gram of a liquid into the gaseous state at the boiling point is called the "heat of vaporization".

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TABLE III.   Calculated and experimental properties for liquid water at 25°C and 1 atm.[a]

	SPC	TIP3P	BF	TIPS2	TIP4P	ST2	Expt.[b]
d(g/cm^3)	0.971	0.982	1.181	0.927	0.999	0.925	0.997
$-E_i$ (kcal/mol)	10.18	9.86	10.49	9.88	10.07	10.37	9.92[c]
ΔH_{vap} (kcal/mol)	10.77	10.45	11.08	10.47	10.66	10.96	10.51
C_p (cal/mol deg)	23.4	18.8	16.0	18.9	19.3	22.2	17.99
$10^5 \alpha$ (deg^{-1})	58	41	59	88	94	−69	25.7
$10^6 \kappa$ (atm^{-1})	27	18	18	56	35	63	45.8

[a]No cutoff corrections have been made to the computed properties.
[b]See Refs. 4 and 12.
[c]See the text.

Cp: isobaric heat capacity.

α : coefficient of thermal expansion.

K : isothermal compressibility.

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IV. Results and Discussion

B. Self-diffusion coefficients

- Diffusion is the term used to describe the mixing of gases.

- These models all yield significant overestimates of D with the least error occurring with the ST2 potential.
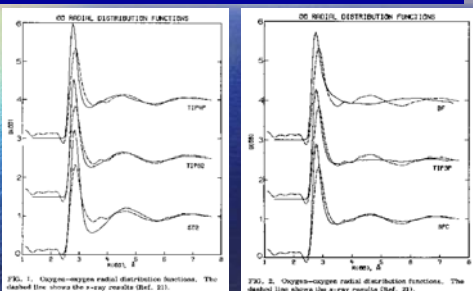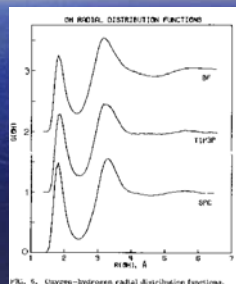
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IV. Results and Discussion

C. Structure

- radial distribution functions
- Partial structure function

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IV. Results and Discussion
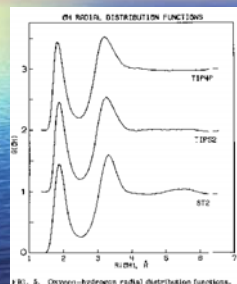
C. Structure

- radial distribution functions

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IV. Results and Discussion

C. Structure

- radial distribution functions

FIG. 5. Oxygen–hydrogen radial distribution functions.

FIG. 6. Oxygen–hydrogen radial distribution functions.

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IV. Results and Discussion

C. Structure

- radial distribution functions

FIG. 9. Hydrogen–hydrogen radial distribution functions.

FIG. 10. Hydrogen–hydrogen radial distribution functions.
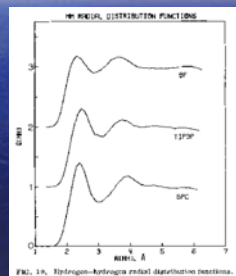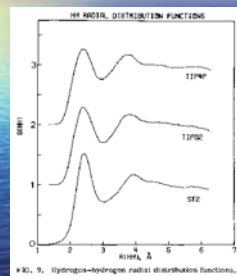
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IV. Results and Discussion

D. Energy/hydrogen bonding distributions
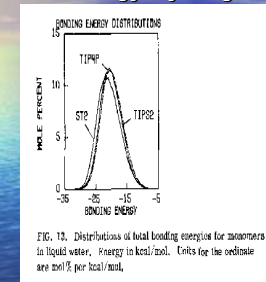
FIG. 13. Distributions of total bonding energies for monomers in liquid water. Energy in kcal/mol. Units for the ordinate are mol% per kcal/mol.
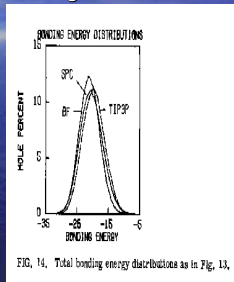
FIG. 14. Total bonding energy distributions as in Fig. 13.

Bonding energy distributions for water monomers

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IV. Results and Discussion
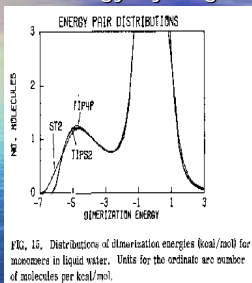
D. Energy/hydrogen bonding distributions

FIG. 15. Distributions of dimerization energies (kcal/mol) for monomers in liquid water. Units for the ordinate are number of molecules per kcal/mol.
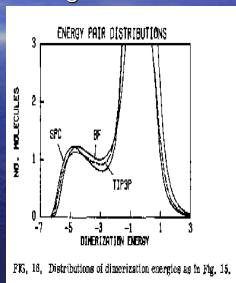
FIG. 18. Distributions of dimerization energies as in Fig. 15.

dimerization energy distributions for water monomers

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V. Conclusion

- The six models in this paper are all rigid models.
- They are simple and able to reproduce with accuracy some of the water properties.

- Besides these, there are lots of works concerning the modeling of water.
- But none of the water models is able to reproduce with a great accuracy all the water properties.
- Despite many efforts to improve this situation, very few significant progress can be asserted.

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