The Computational Statistical Mechanics of Simple Models of Liquid Water

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Thanks to:
W. L. Jorgensen, Julian Tirado-Rives, and John Tully
and to:
NSF and NIH

Given a water model, one can study many things.

We will focus on: how the **defining properties** of **simple models** of liquid water affect the ability of those models to reproduce the **structural** and **thermodynamic properties** of liquid water at a **range of thermodynamic state points**.

- **defining properties**: geometry, parameters, etc.
- **simple models**: interaction-site potential functions
- **structural properties**: radial distribution functions
- **thermodynamic properties**: E, ρ, and their fluctuations
- **range of thermodynamic state points**: vary T, P

Reproducing the structure and thermodynamics:

- provides a good merit function for the applications in which people are interested
- reproduces the *size* and *shape* of molecules and the *strength* of intermolecular interactions

The most difficult test: $\rho(T)$

Some Unusual Properties of Water

1. Contraction upon melting.

2. Density maximum in the stable liquid.

3. Numerous ice polymorphs.

4. High melting, boiling and critical temperatures.

5. Compressibility minimum.

6. Large dielectric constant.

7. Negative pressure coefficient of viscosity.

8. High molar heat capacity.

9. Non-Arrhenius dynamics.

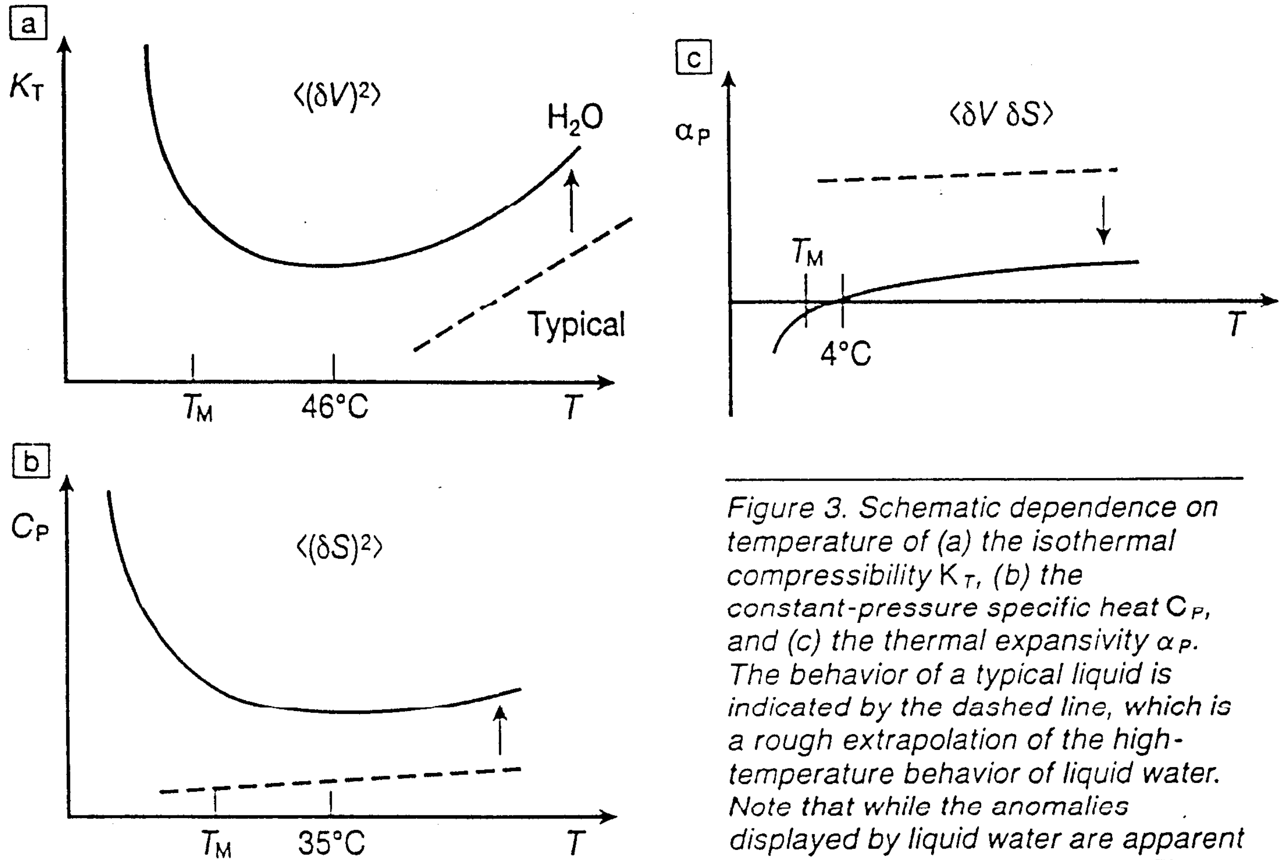


Figure 3. Schematic dependence on temperature of (a) the isothermal compressibility K_T, (b) the constant-pressure specific heat C_P, and (c) the thermal expansivity α_P. The behavior of a typical liquid is indicated by the dashed line, which is a rough extrapolation of the high-temperature behavior of liquid water. Note that while the anomalies displayed by liquid water are apparent above the melting temperature T_M, they become more striking as one supercools below T_M. Courtesy of F.W. Starr.

Potential Energy Function

$$\mathrm{U}_{\mathrm{Total}} = \mathrm{U}_{bonds} + \mathrm{U}_{angles} + \mathrm{U}_{dihedrals} + \mathrm{U}_{non-bonded}$$

$$\mathrm{U}_{bonds} = \sum_{bonds} \mathrm{K}_{\mathrm{r}}(\mathrm{r} - \mathrm{r}_{eq})^2$$

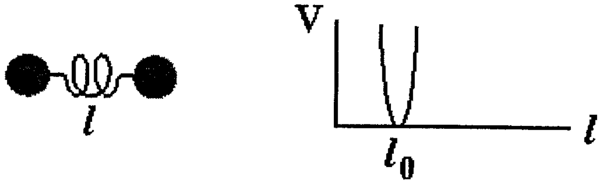
$$\mathrm{U}_{angles} = \sum_{angles} \mathrm{K}_{\theta}(\theta - \theta_{eq})^2$$

$$\mathrm{U}_{dihedrals} = \sum_{dihedrals} \frac{\mathrm{V}_n}{2}(1 \pm cos\mathrm{n}\phi - \gamma)$$

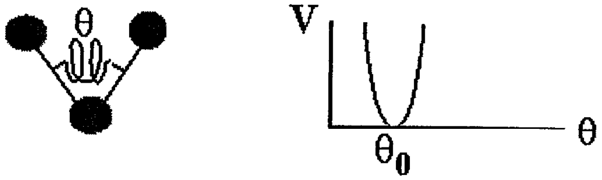
$$\mathrm{U}_{non\text{-}bonded} = \sum_{i<j}^{>1,4} \left\{ \frac{q_i q_j e^2}{r_{ij}} + 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right]\right\}$$

Empirical Potential Energy Function

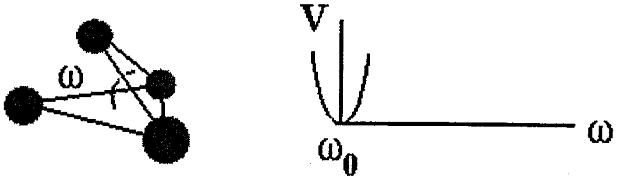
Bonds



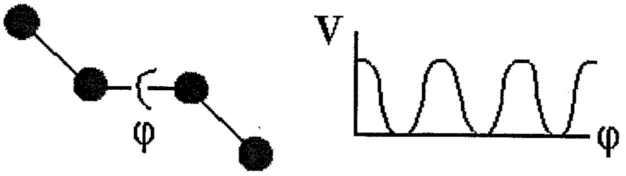
Angles



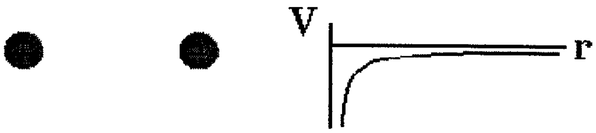
Improper Dihedrals



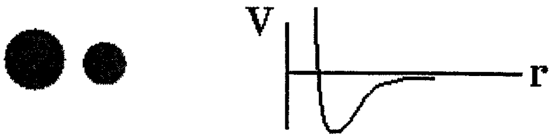
Torsions



Electrostatics



van der Waals



Classical statistical mechanics of rigid nonpolarizable liquid water

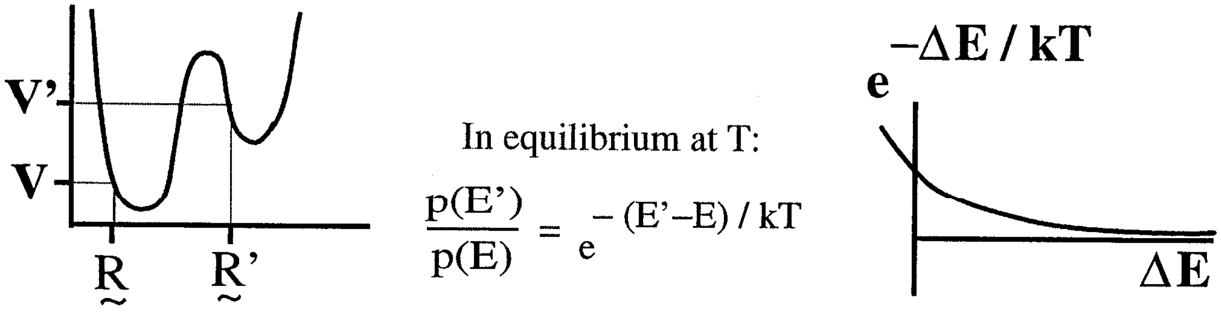
$$E\left(\vec{r}^{\,3N}\right)=\sum\nolimits_{ab} E_{ab}$$

$$E_{ab} = \sum_{ij} \frac{q_i q_j e^2}{r_{ij}} + 4\varepsilon_O \left[\left(\frac{\sigma_O}{r_{OO}}\right)^{12} - \left(\frac{\sigma_O}{r_{OO}}\right)^{6}\right]$$

$$Z_{NPT} = \int dV \exp\left(-PV/k_BT\right)\int d^{3N}\vec{r}\, \exp\left(-E\left(\vec{r}^{\,3N}\right)/k_BT\right)$$

Density	$\rho = M/(0.6022 * V/N)$	
Heat of vaporization	$\Delta H_{vap} \approx -E_{liq}/N + RT$	
Heat capacity	$C_P = \left(\frac{\partial H}{\partial T}\right)_P$	$C_P = \frac{1}{k_B T^2}\left\langle \delta(E+PV)^2 \right\rangle_{NPT}$
	$C_P^{TOT} \approx C_P + 3R$	
Isothermal compressibility	$\kappa = \frac{-1}{V}\left(\frac{\partial V}{\partial P}\right)_T$	$\kappa = \frac{1}{V k_B T}\left\langle \delta V^2 \right\rangle_{NPT}$
Coefficient of thermal expansion	$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$	$\alpha = \frac{1}{k_B T^2 V}\left\langle \delta V \delta(E+PV) \right\rangle_{NPT}$

MC compares energies. No forces calculated.



In equilibrium at T:

$$\frac{p(E')}{p(E)} = e^{-(E'-E)/kT}$$

Figure 9: Monte Carlo makes use of Boltzmann probabilities, not forces.

Monte Carlo Algorithm

```
Generate initial structure $\underset{\sim}{R}$. Calculate V($\underset{\sim}{R}$).
→ Modify structure to $\underset{\sim}{R}'$. Calculate V'=V($\underset{\sim}{R}'$).
  If V' < V then
     $\underset{\sim}{R} \leftarrow \underset{\sim}{R}'$,   $V \leftarrow V'$
  else
     Generate random number RAND:
     If $e^{-(V'-V)/kT}$ > RAND
        $\underset{\sim}{R} \leftarrow \underset{\sim}{R}'$,   $V \leftarrow V'$
     End if
  End if
← Repeat for N steps.
```

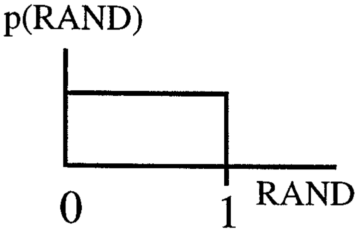
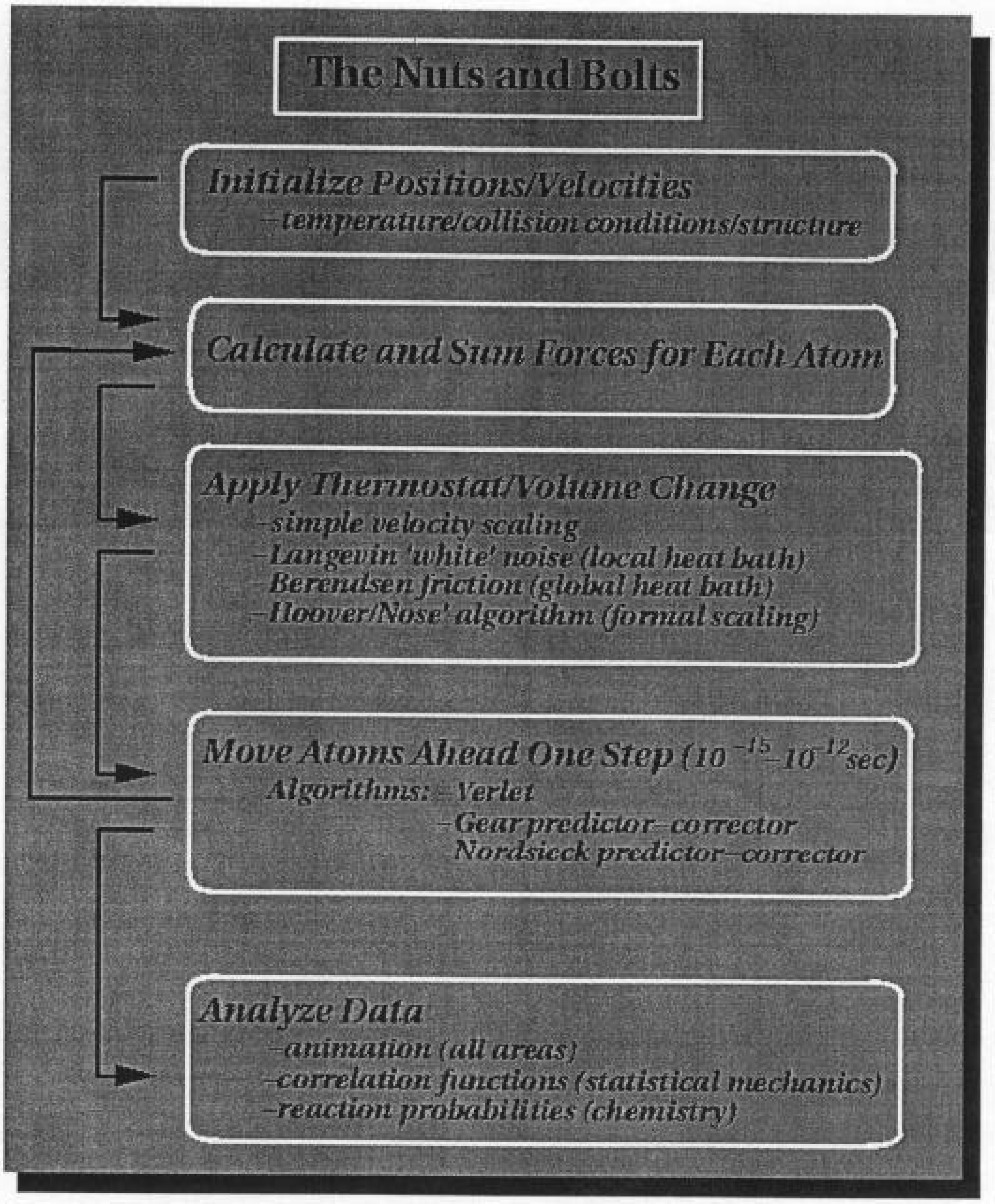


Figure 10: Metropolis Monte Carlo.



The Nuts and Bolts

Initialize Positions/Velocities
–temperature/collision conditions/structure

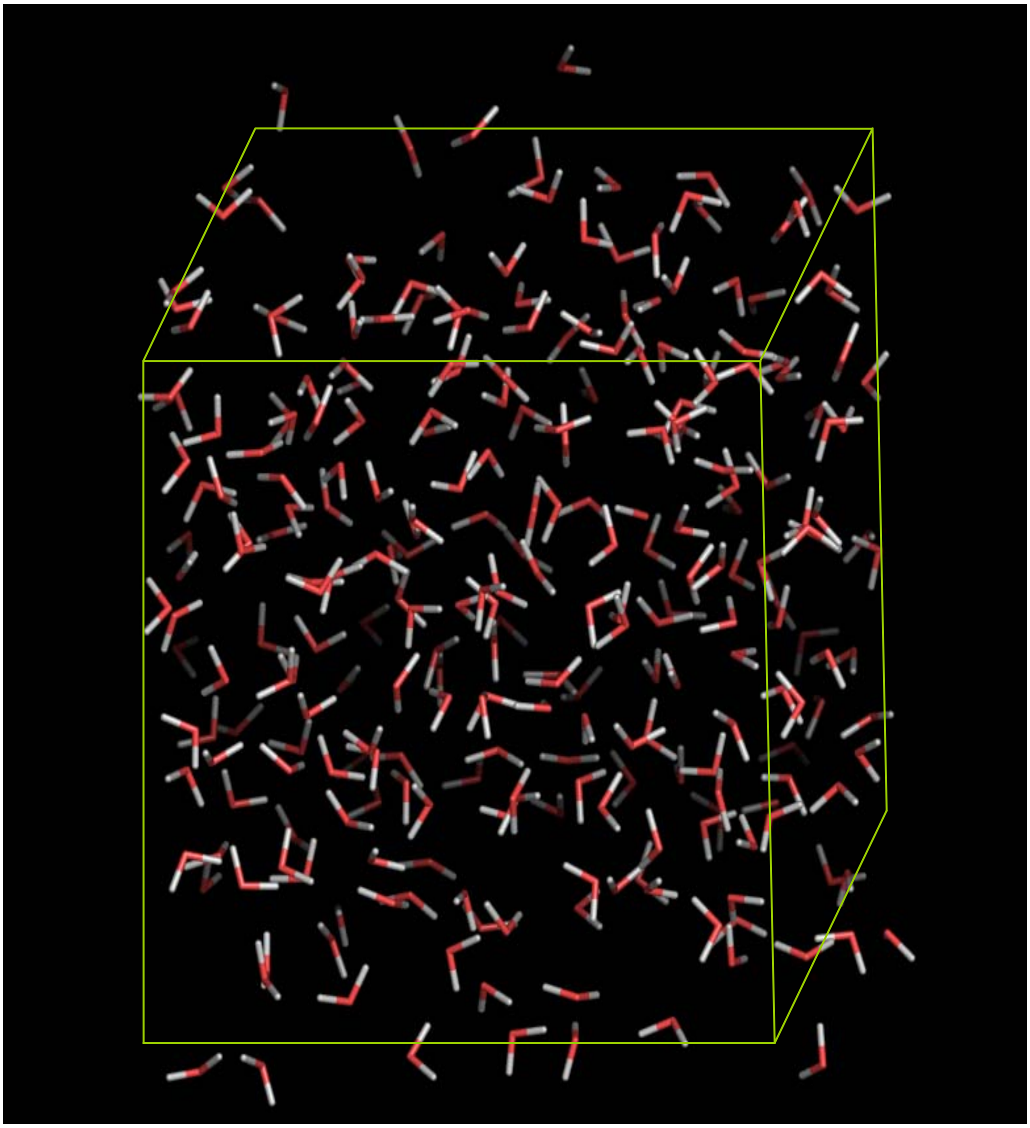
Calculate and Sum Forces for Each Atom

Apply Thermostat/Volume Change
–simple velocity scaling
–Langevin 'white' noise (local heat bath)
Berendsen friction (global heat bath)
–Hoover/Nose' algorithm (formal scaling)

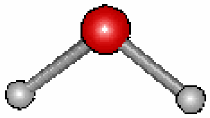
Move Atoms Ahead One Step (10^{-15}–10^{-12}sec)
Algorithms: –Verlet
–Gear predictor–corrector
Nordsieck predictor–corrector

Analyze Data
–animation (all areas)
–correlation functions (statistical mechanics)
–reaction probabilities (chemistry)

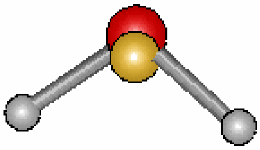
< back forward>



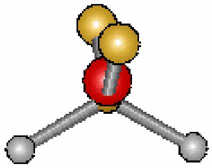
Nmol = 267
T = 298.15, P = 1 atm
20 Å box of P.B.C.
Nconfig. = 10m. – 1b.



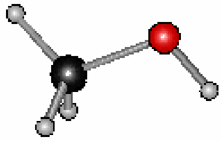
TIP3P
Water



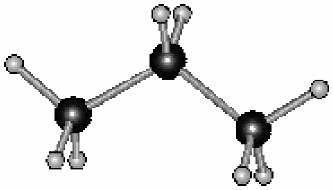
TIP4P
Water



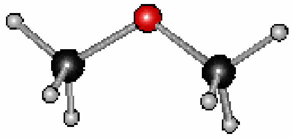
TIP5P
Water



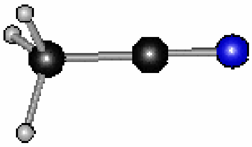
CH3OH
(Methanol)



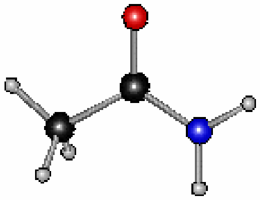
CH3CH2CH3
(Propane)



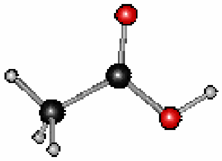
CH3OCH3
(Ether)



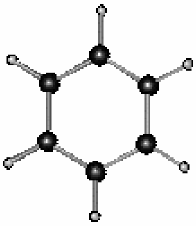
CH3CN
(Nitrile)



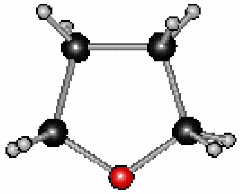
CH3CONH2
(Acetamide)



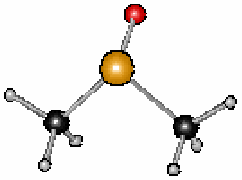
CH3COOH
(Acetic acid)



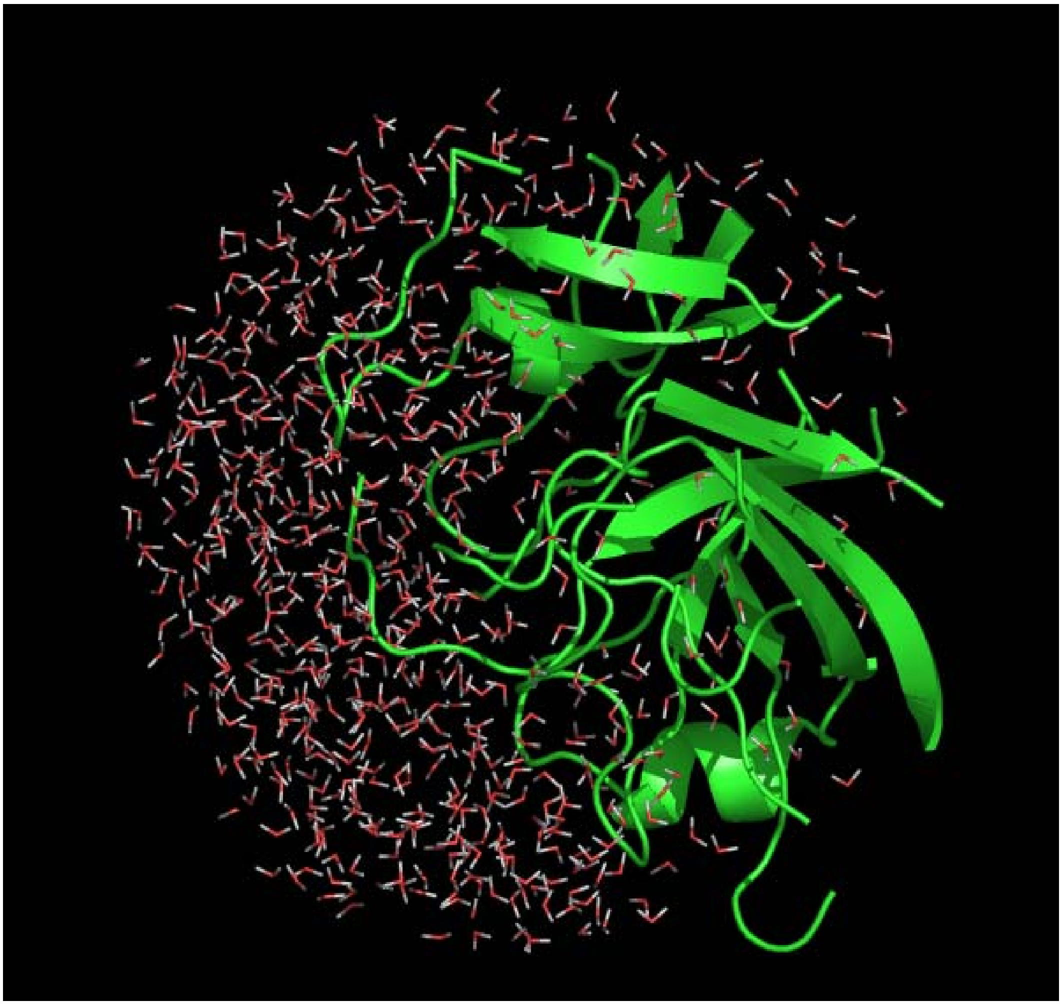
C6H6
(Benzene)



THF



DMSO



Thrombin surrounded by H2O
164 amino acids; 667 TIP5P H2O
22 Å shell of water around active site

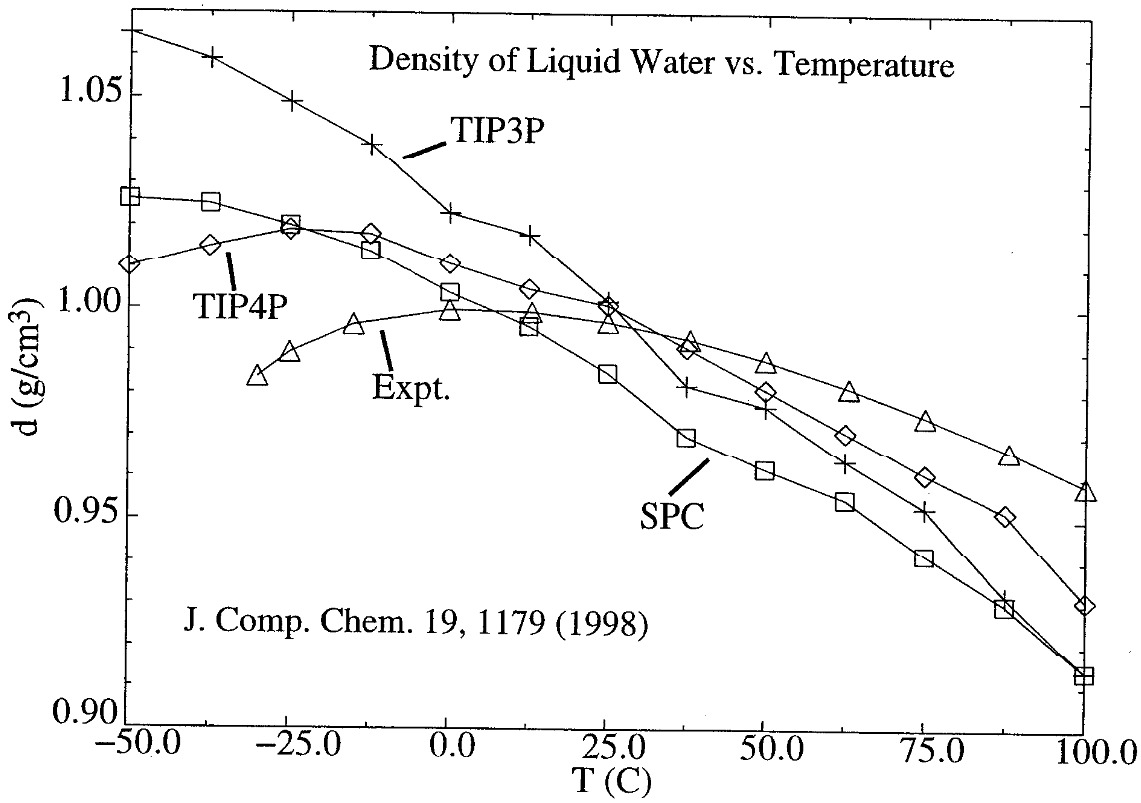
Chronology of Water Models

				1998 Citations
Fixed-Charge Models:				
1933	Bernal & Fowler		JCP *1*, 515	42
1951	Rowlinson		TFS *47*, 120	4
1969	Rowlinson -	Barker & Watts	CPL *3*, 144	17
1971	BNS -	Rahman & Stillinger	JCP *55*, 3336	33
1974	ST2 -	Rahman & Stillinger	JCP *60*, 1545	36
1975	CF1 -	Lemberg & Stillinger	JCP *62*, 1677	8
1976	MCY -	Matsuoka et al.	JCP *64*, 1351	29
1981	TIPS -	Jorgensen	JACS *103*, 335	40
1981	SPC -	Berendsen et al.	IF, Reidel, 331	109
1982	TIPS2 -	Jorgensen	JCP *77*, 4156	19
1983	TIP3P & TIP4P -	Jorgensen et al.	JCP *79*, 926	303
1987	SPC/E -	Berendsen et al.	JPC *91*, 6269	104
Polarizable Models:				
1988	Fluc. P -	Sprik & Klein	JCP *89*, 7556	22
1989	WK -	Watanabe & Klein	CP *131*, 157	17
1990	POL1 -	Caldwell, Dang, Kollman	JACS *112*, 9144	14
1994	Fluc. q -	Rick, Stuart, Berne	JCP *101*, 6141	30

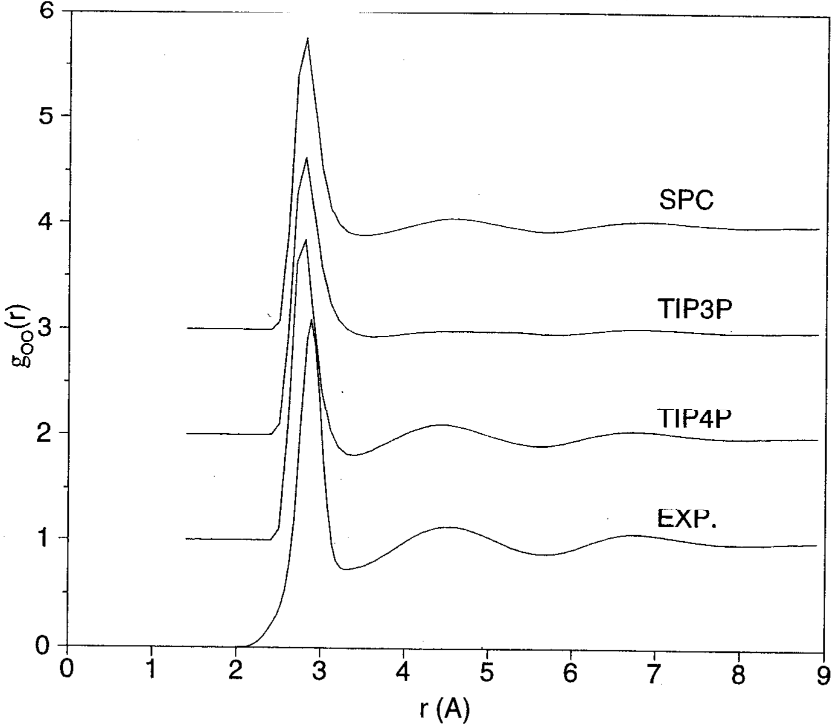
Parameterization

Liquid Phase

"Computation of condensed–phase properties is necessary in the development of force fields for condensed–phase simulations."



OO Radial Distribution Functions for Liquid Water



Consider:

Number of Interaction Sites

Intramolecular Flexibility

Form of the Repulsive Potential

Explicit Polarization

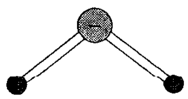
Require:

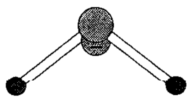
No Loss of Accuracy at 25 C, 1 atm

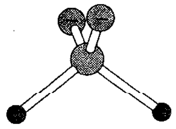
Efficient Evaluation

No Parameters Depending on T, P

Rigid Water Models







	TIP3P	TIP4P	TIP5P
q_H	0.417	0.520	0.241
σ_O	3.15061	3.15365	3.12
ε_O	0.1521	0.1550	0.16
r_{OH}	0.9572	0.9572	0.9572
θ_{HOH}	104.52	104.52	104.52
r_{OL}		0.15	0.70
θ_{LOL}			109.47
μ,D	2.35	2.18	2.29

TABLE VI. Dipole[a] and quadrupole[b] moments for the water monomer.

	μ	Q_{xx}	Q_{yy}	Q_{zz}
Expt.[c]	1.85	2.63	-2.50	-0.13
TIP3P	2.35	1.76	-1.68	-0.08
TIP4P	2.18	2.20	-2.09	-0.11
TIP5P	2.29	1.65	-1.48	-0.17

[a] Units are 10^{-18} esu-cm.

[b] Units are 10^{-26} esu-cm^2.

[c] Refs. 41d and 41e.

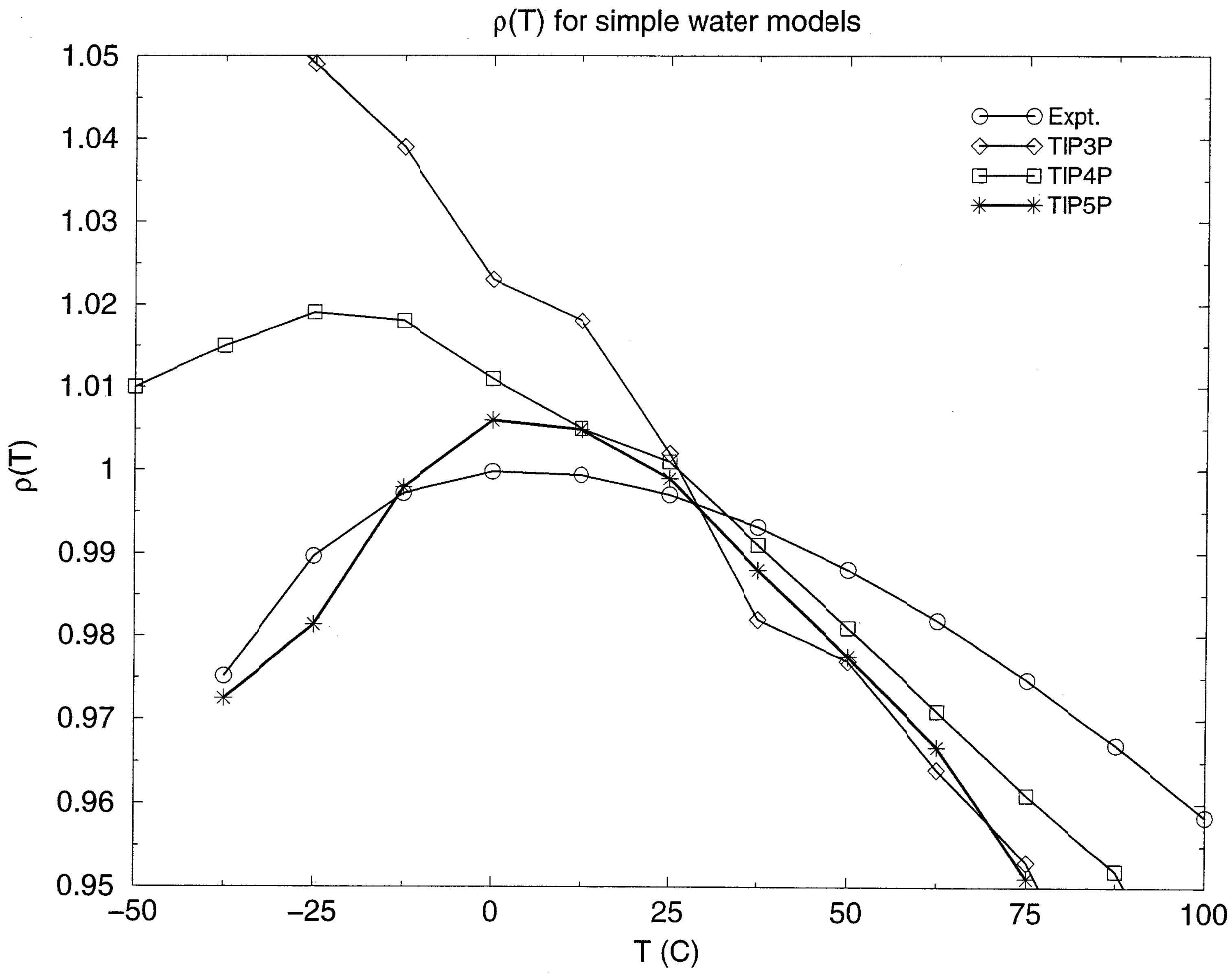
TABLE IIa. Lengths of Monte Carlo simulations with 512 molecules for TIP5P water at 1 atm.

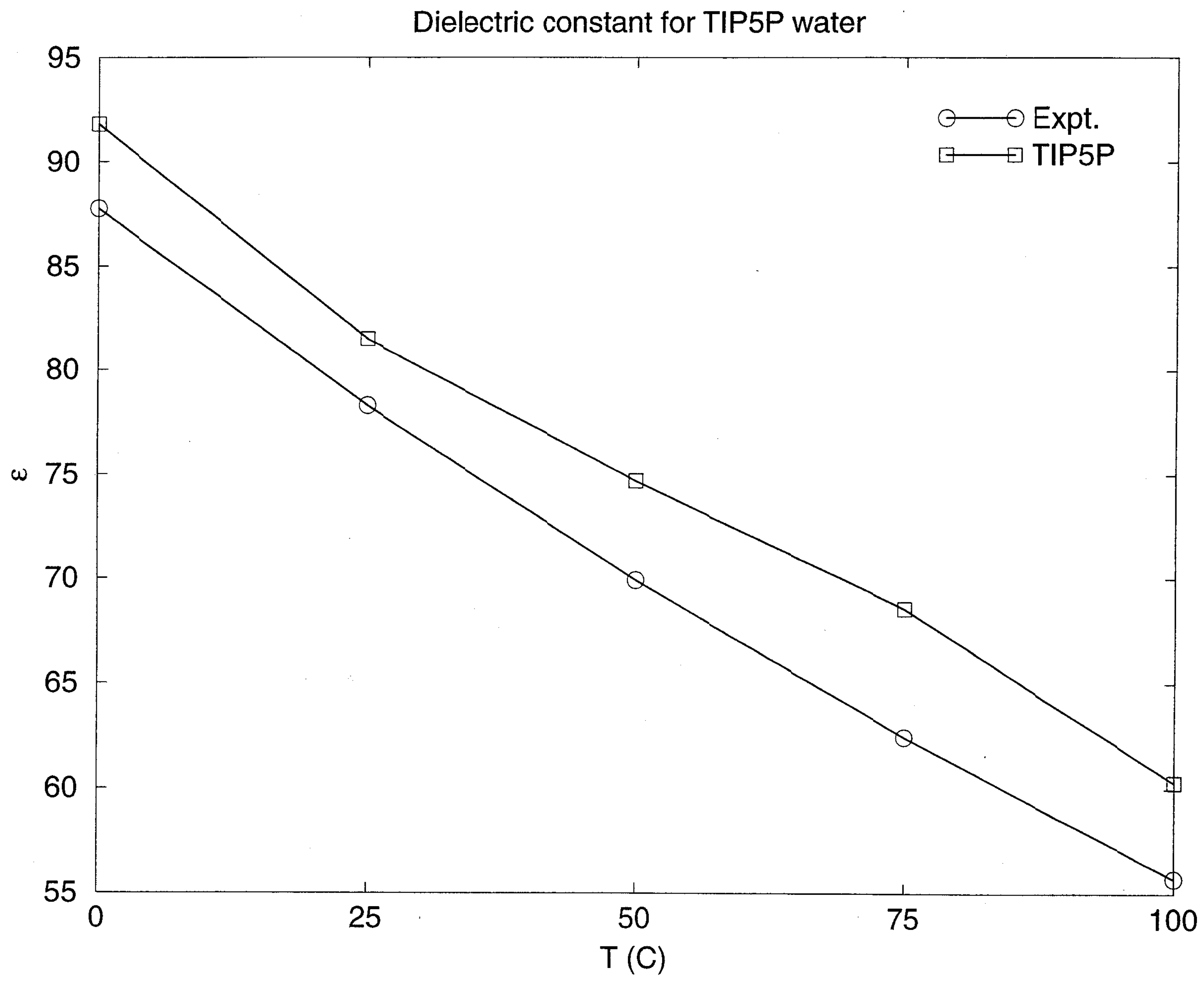
T (°C)	Equil.[a]	Averag.[a]
-37.5	400	1000
-25.0	300	1000
-12.5	300	1000
0.0	100	500
12.5	100	400
25.0	50	250
37.5	50	200
50.0	50	150
62.5	50	150
75.0	50	150

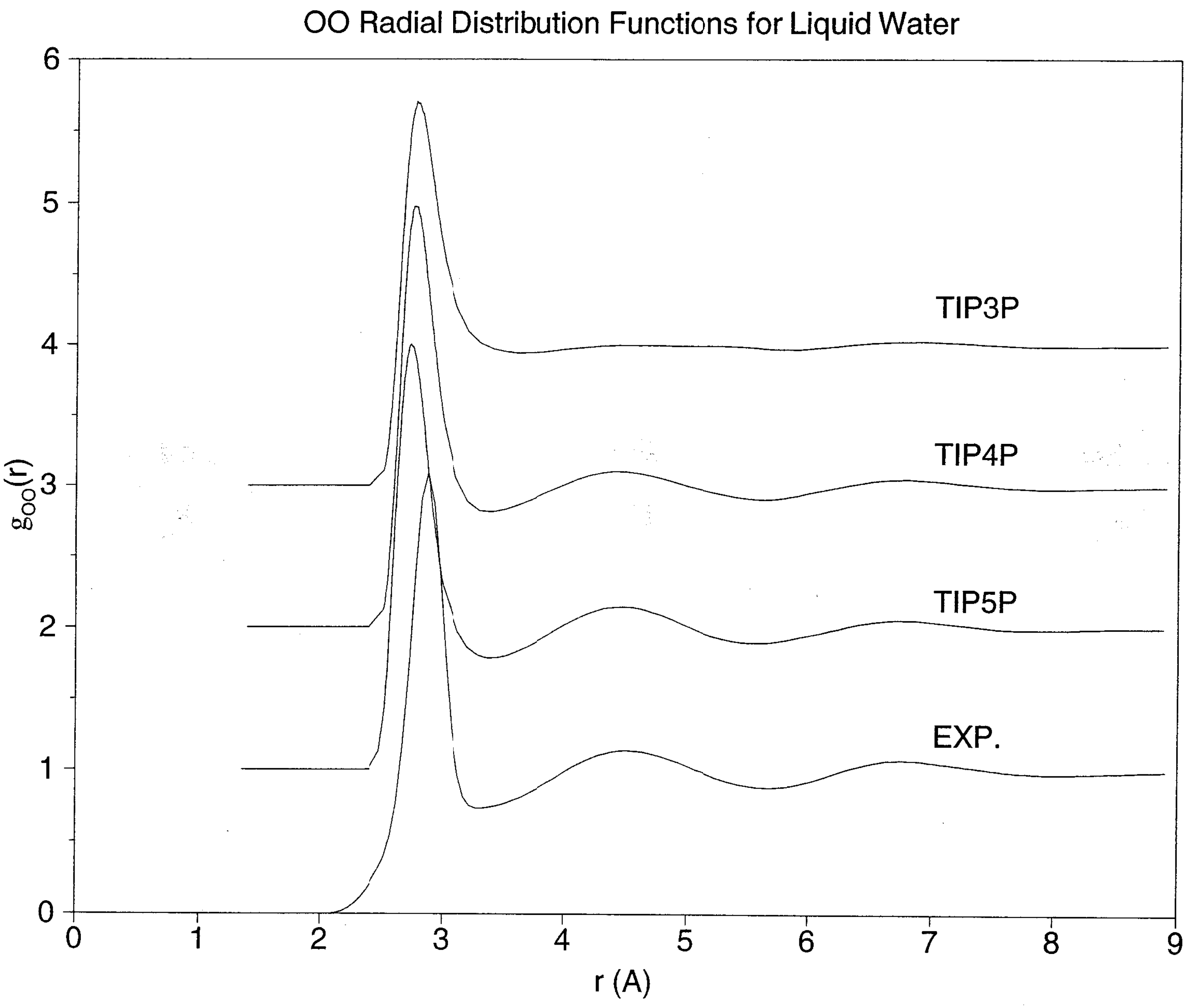
[a] Millions of MC steps.

Computed and Experimental Properties of Water (25 C, 1 atm)

Property	TIP3P	TIP4P	TIP5P	Expt.
d (g cm^{-3})	1.002 ± 0.001	1.001 ± 0.001	0.999 ± 0.001	0.997
ΔH_{vap} (kcal/mol)	10.41 ± 0.01	10.65 ± 0.01	10.46 ± 0.01	10.51
C_p (cal/mol-K)	20.0 ± 0.6	20.4 ± 0.7	29.1 ± 0.8	18.0
$10^6\ \kappa$ (atm^{-1})	64 ± 5	60 ± 5	41 ± 2	45.8
$10^5\ \alpha$ (deg^{-1})	92 ± 8	44 ± 8	72 ± 6	25.7
ε		53, 61, 72	82 ± 2	78


ρ(T) for simple water models
Expt.
TIP3P
TIP4P
TIP5P
ρ(T)
1.05
1.04
1.03
1.02
1.01
1
0.99
0.98
0.97
0.96
0.95
−50
−25
0
25
50
75
100
T (C)


Dielectric constant for TIP5P water
Expt.
TIP5P
ε
95
90
85
80
75
70
65
60
55
0
25
50
75
100
T (C)


OO Radial Distribution Functions for Liquid Water
$g_{OO}(r)$
r (A)
TIP3P
TIP4P
TIP5P
EXP.
0
1
2
3
4
5
6
0
1
2
3
4
5
6
7
8
9

/

Reviewer of the TIP5P paper (*J. Chem. Phys.* 112, 8910-8922 (2000))
December 1999

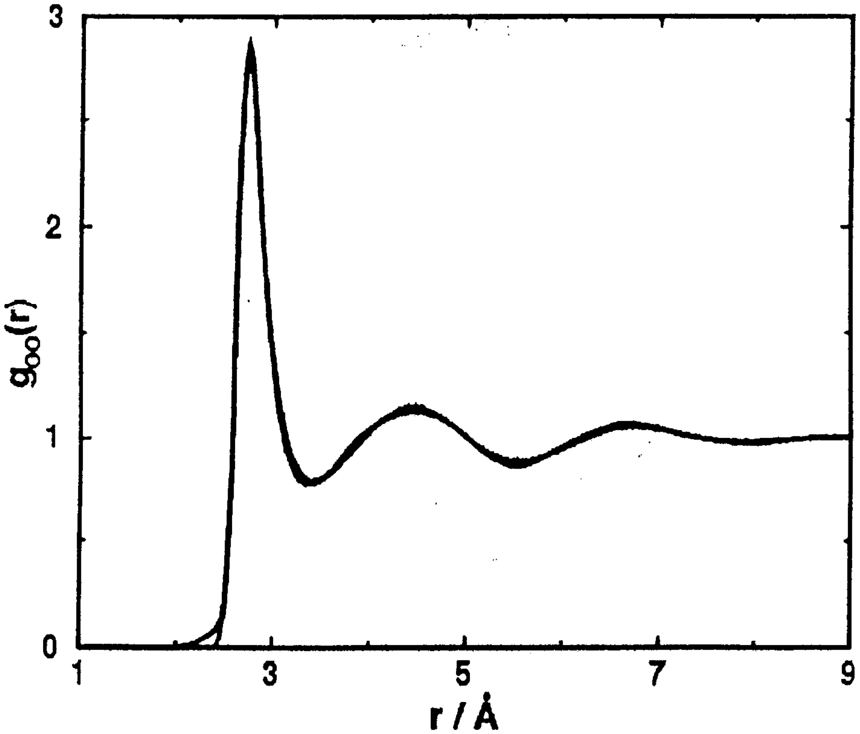
"From Fig. 4 I gather that the TIP5P potential performs much worse than TIP4P (and presumably than many other models) in reproducing the first maximum of the oxygen-oxygen radial distribution function, failing one of the most crucial experimental tests of water models.

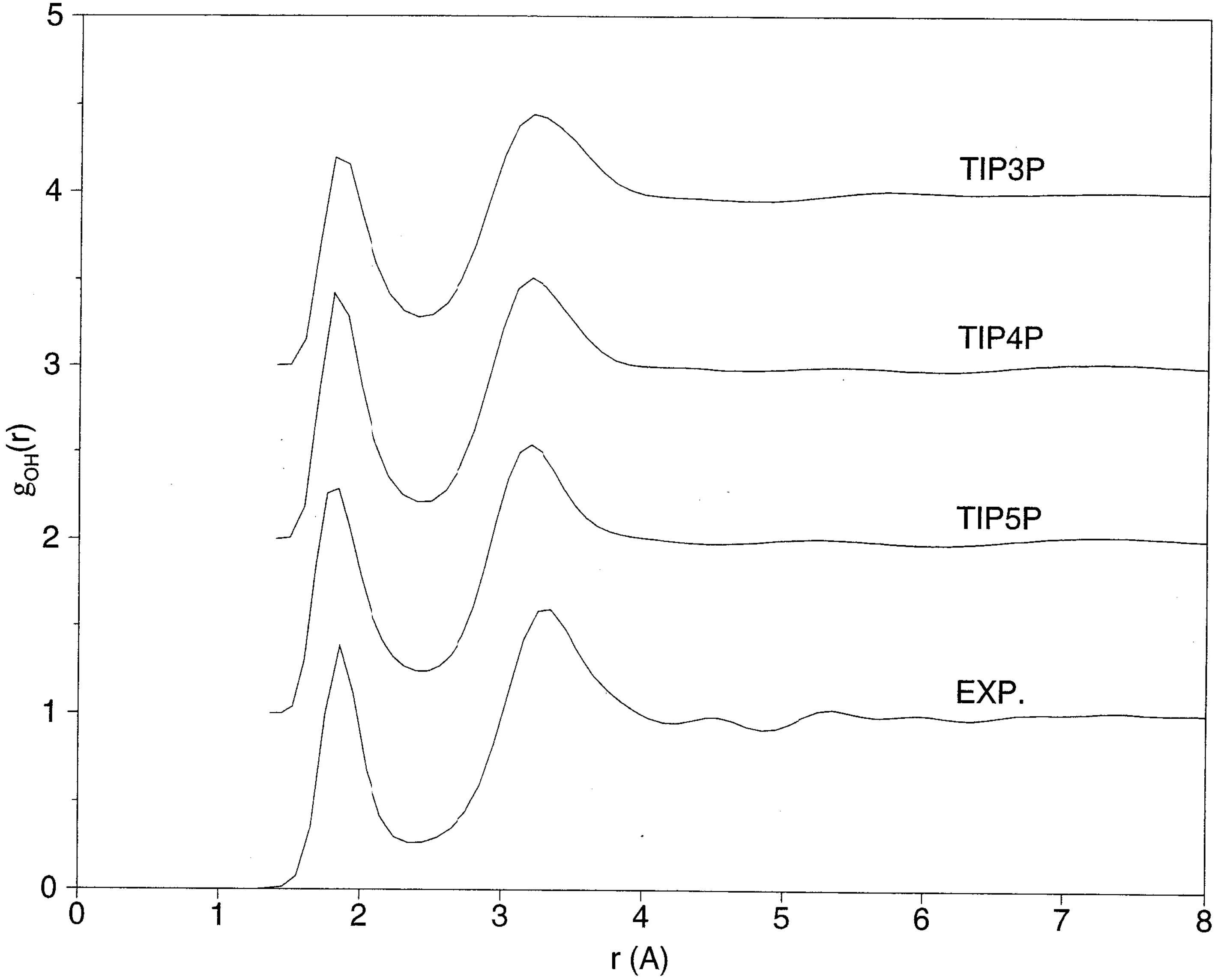
The paper can not be published in its current form."

Preprint of New ALS X-ray Results, T. Head-Gordon et al.
May 2000

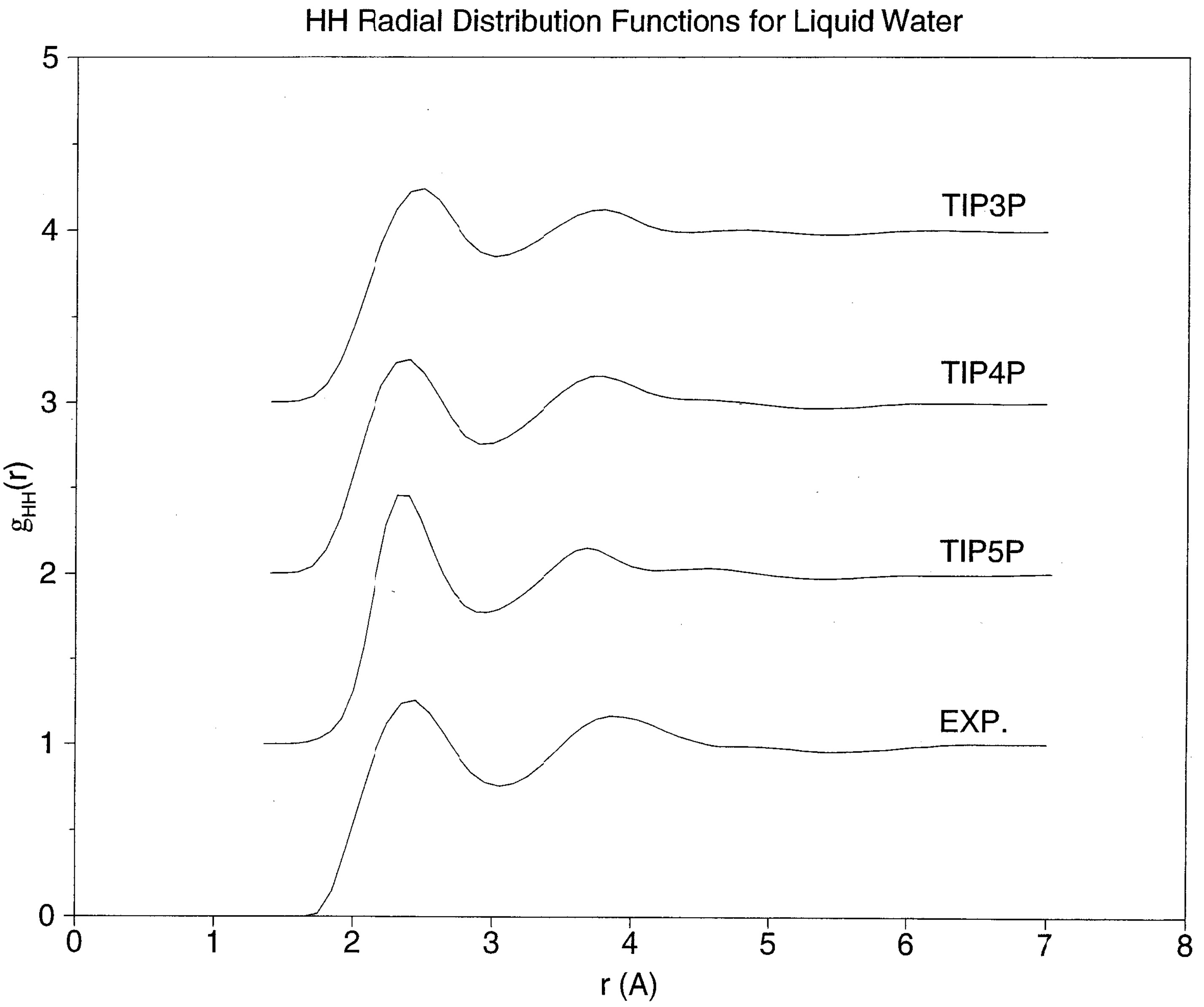
"The agreement of the TIP5P simulation with the ALS data is remarkable, and as far as $g_{OO}(r)$ is concerned is a noteworthy improvement over TIP4P."

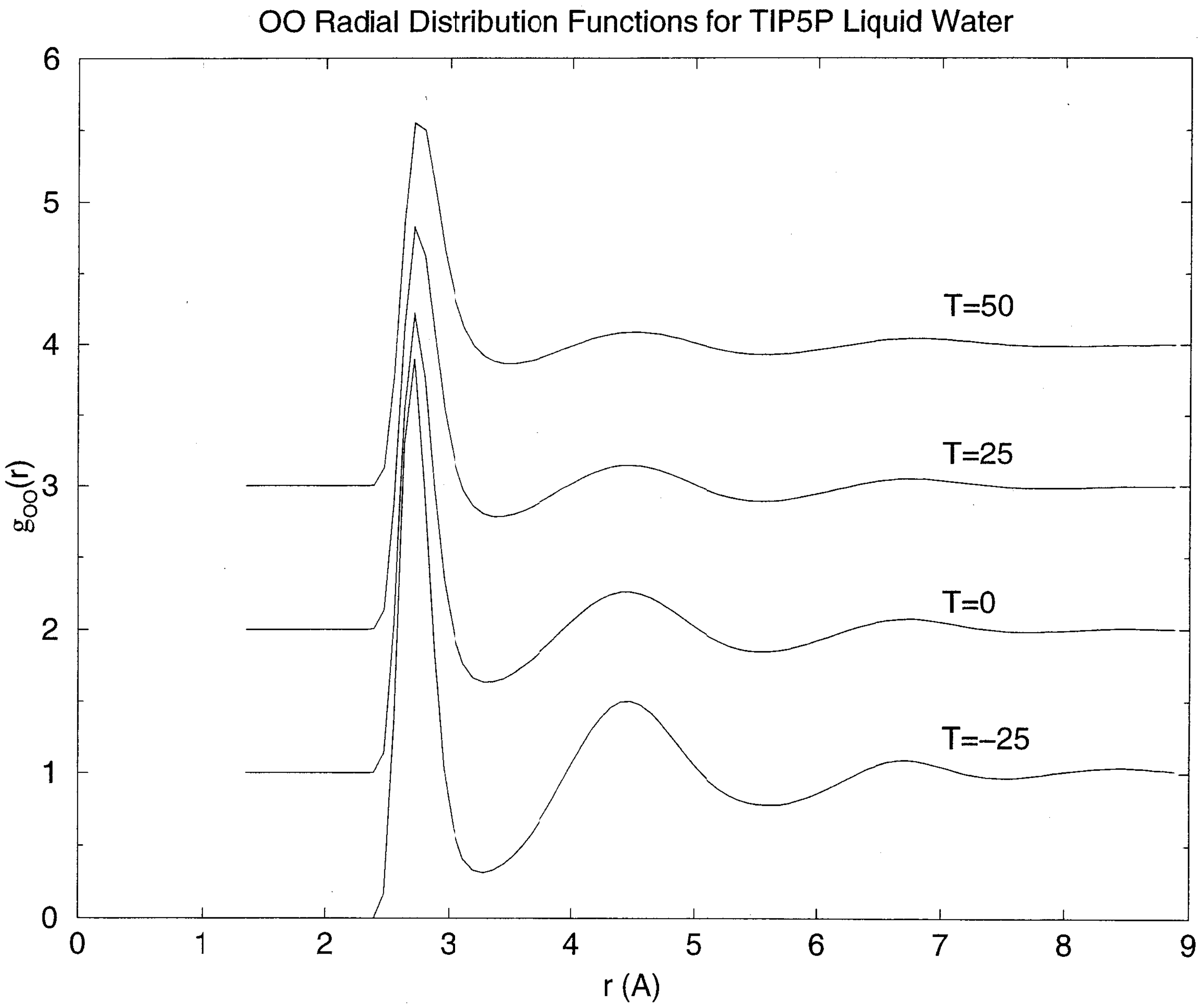
Figure 7(b)

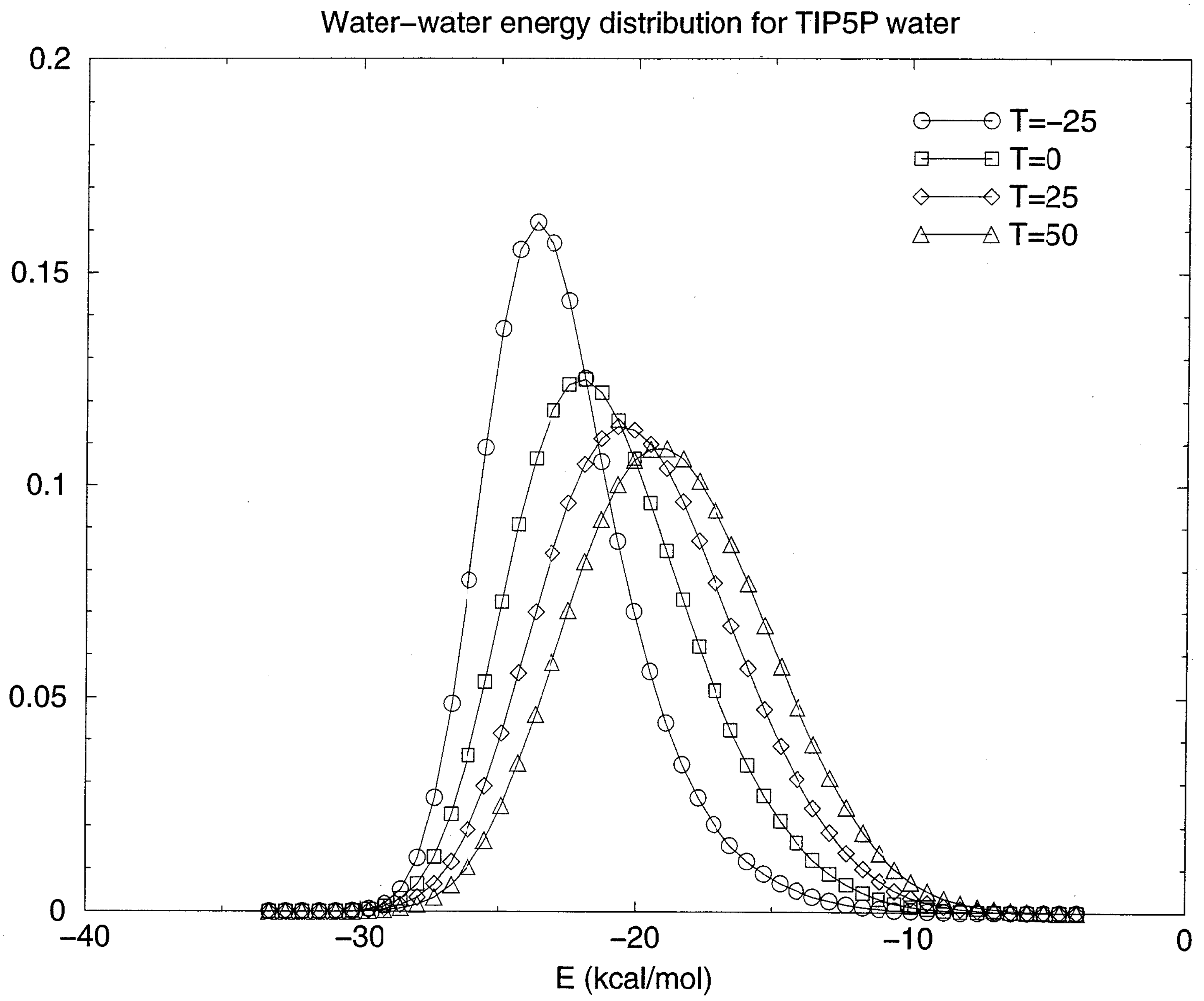




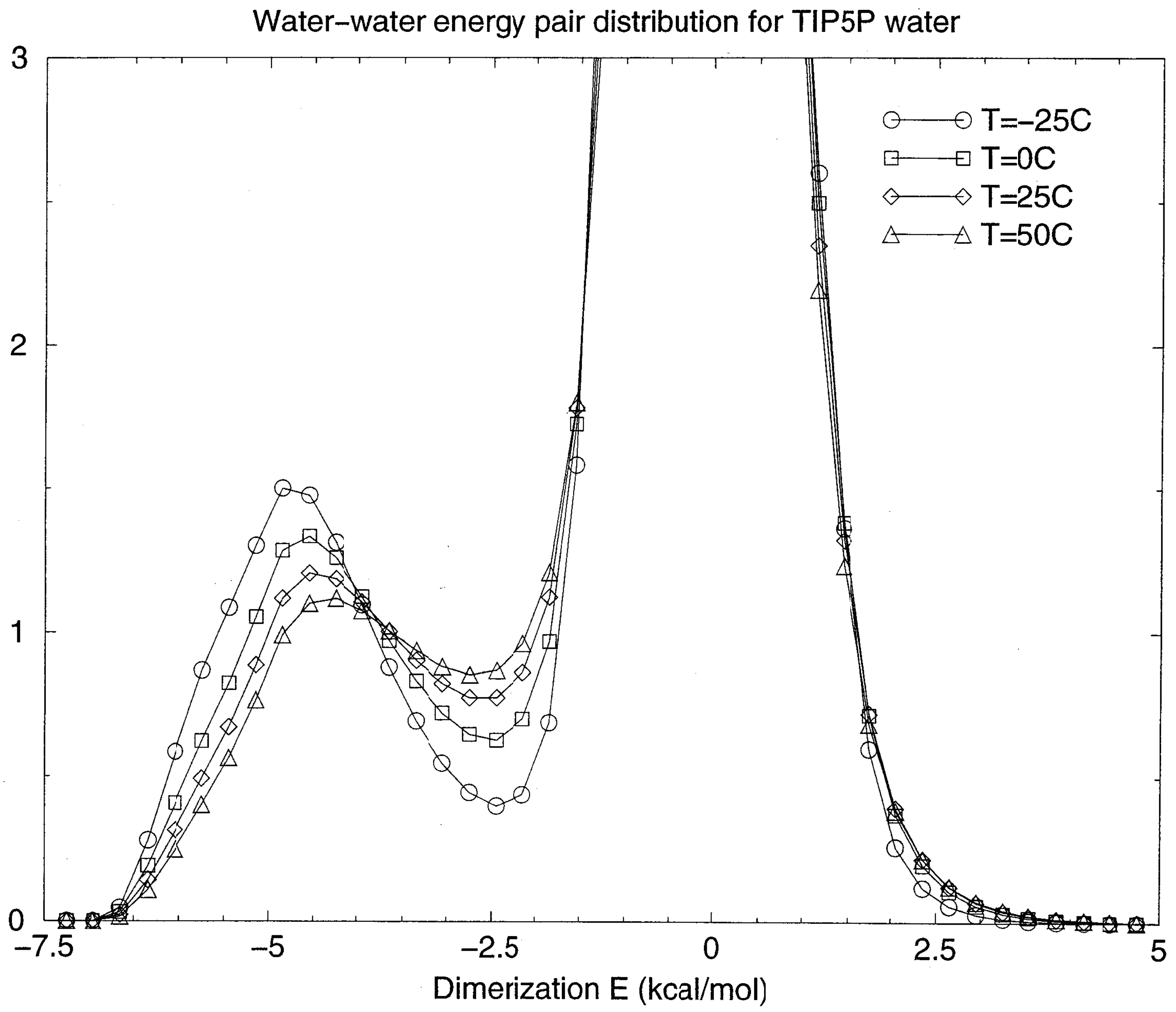
OH Radial Distribution Functions for Liquid Water

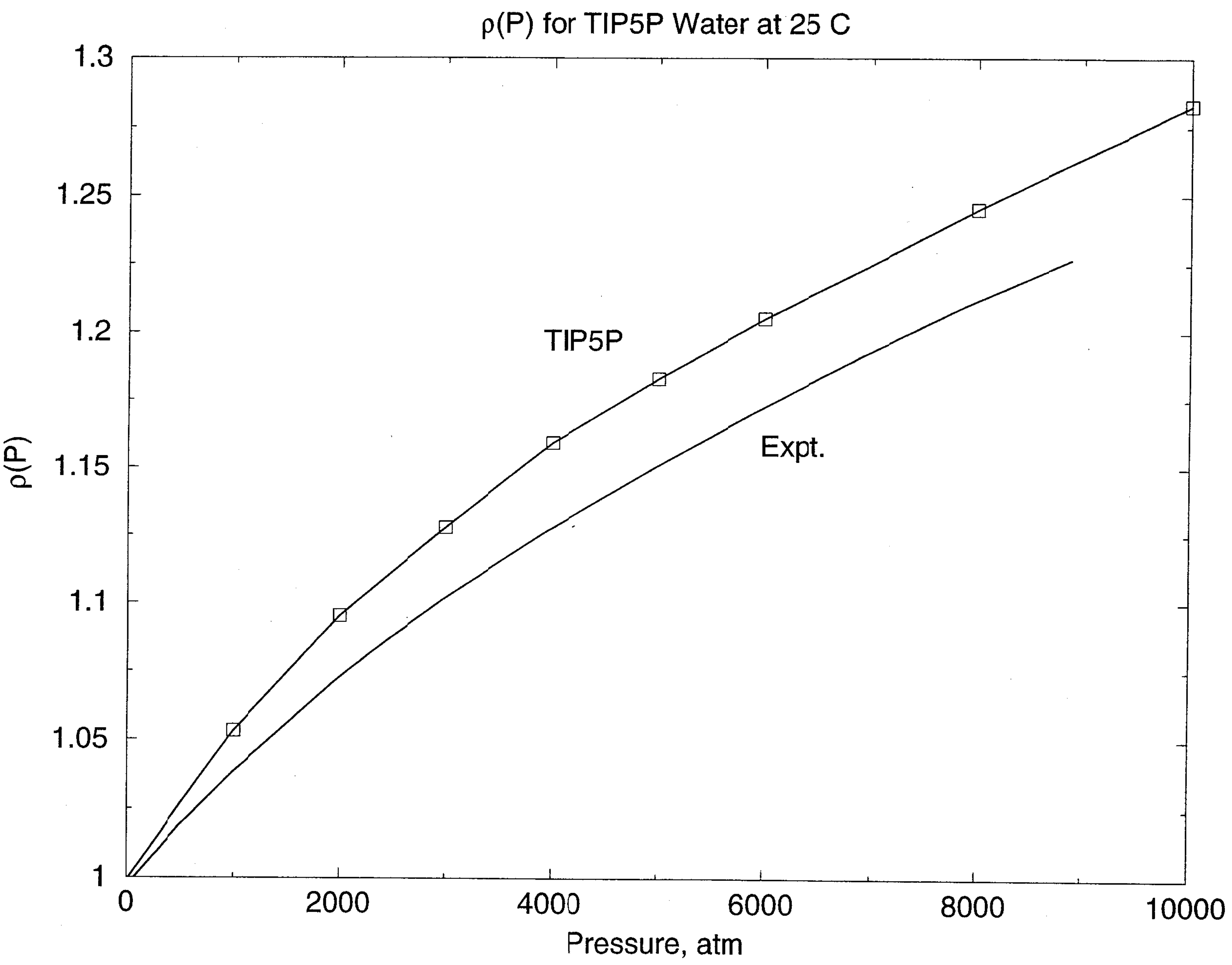

HH Radial Distribution Functions for Liquid Water
$g_{HH}(r)$
r (A)
0
1
2
3
4
5
6
7
8
TIP3P
TIP4P
TIP5P
EXP.

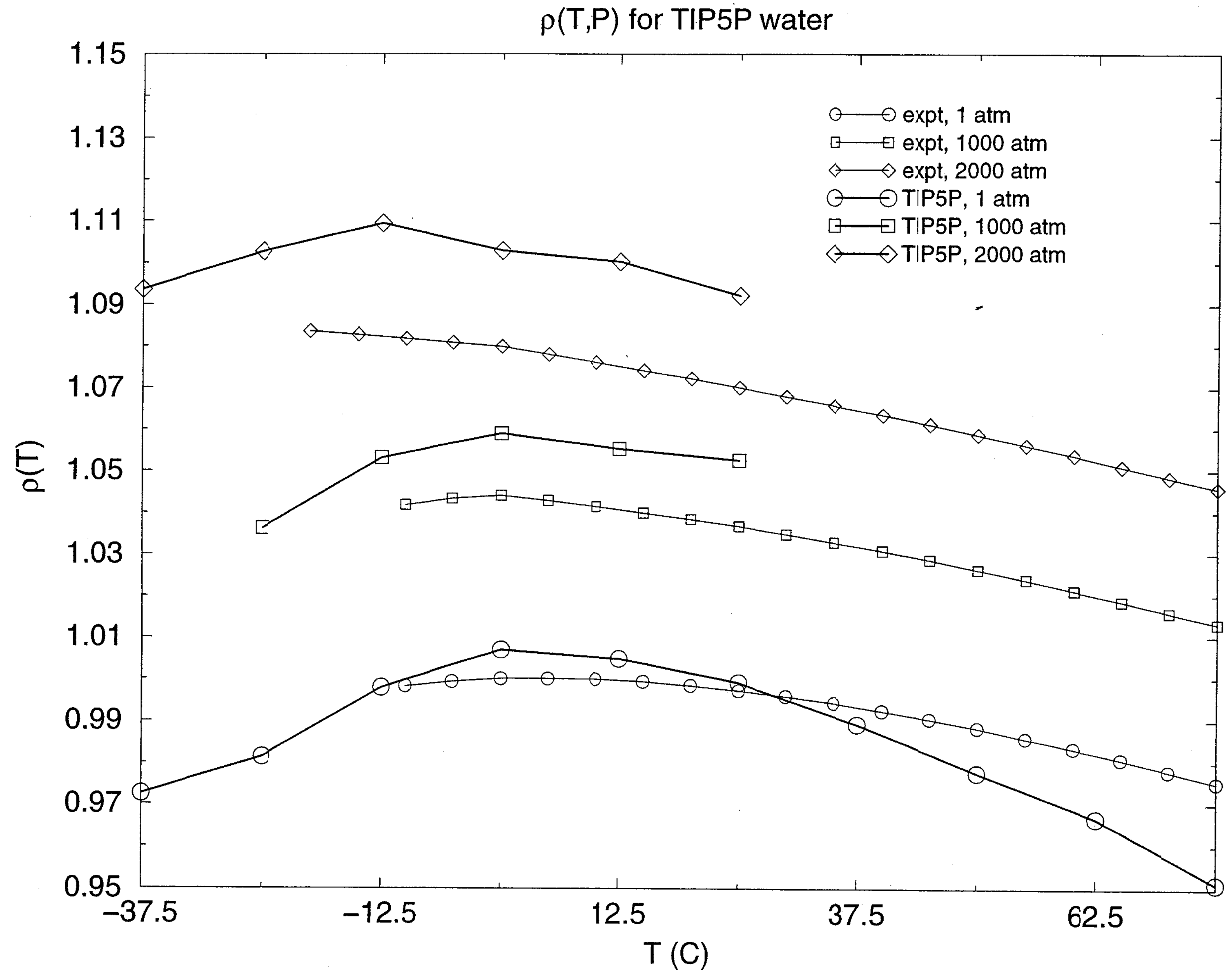

OO Radial Distribution Functions for TIP5P Liquid Water
$g_{OO}(r)$
0
1
2
3
4
5
6
r (A)
0
1
2
3
4
5
6
7
8
9
T=50
T=25
T=0
T=−25

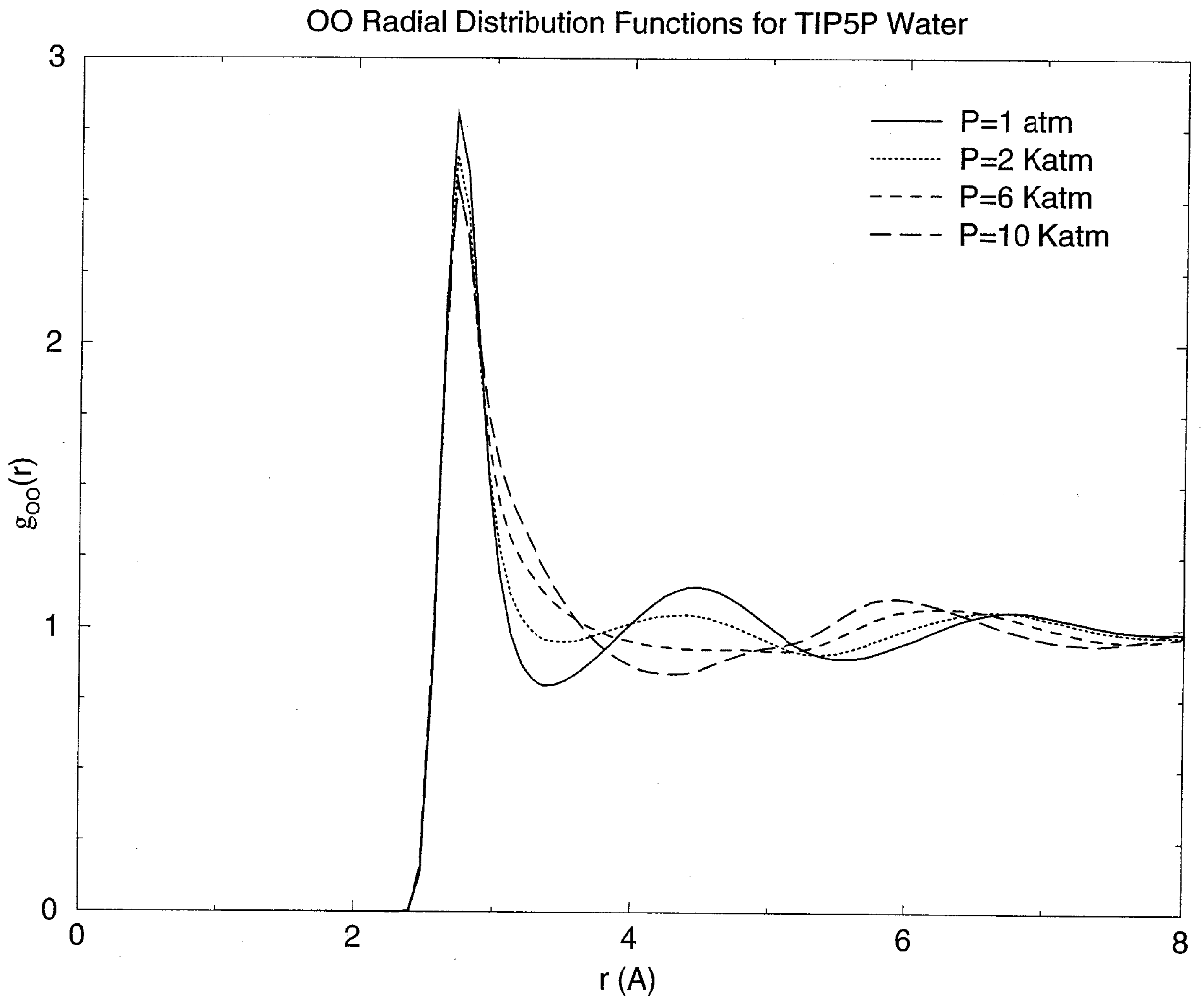


Water–water energy distribution for TIP5P water


Water-water energy pair distribution for TIP5P water
T=-25C
T=0C
T=25C
T=50C
3
2
1
0
-7.5
-5
-2.5
0
2.5
5
Dimerization E (kcal/mol)


ρ(P) for TIP5P Water at 25 C
ρ(P)
1.3
1.25
1.2
1.15
1.1
1.05
1
0
2000
4000
6000
8000
10000
Pressure, atm
TIP5P
Expt.


ρ(T,P) for TIP5P water
expt, 1 atm
expt, 1000 atm
expt, 2000 atm
TIP5P, 1 atm
TIP5P, 1000 atm
TIP5P, 2000 atm
ρ(T)
1.15
1.13
1.11
1.09
1.07
1.05
1.03
1.01
0.99
0.97
0.95
−37.5
−12.5
12.5
37.5
62.5
T (C)



OO Radial Distribution Functions for TIP5P Water

Density Weighted OO Radial Distribution Functions for TIP5P Liquid Water

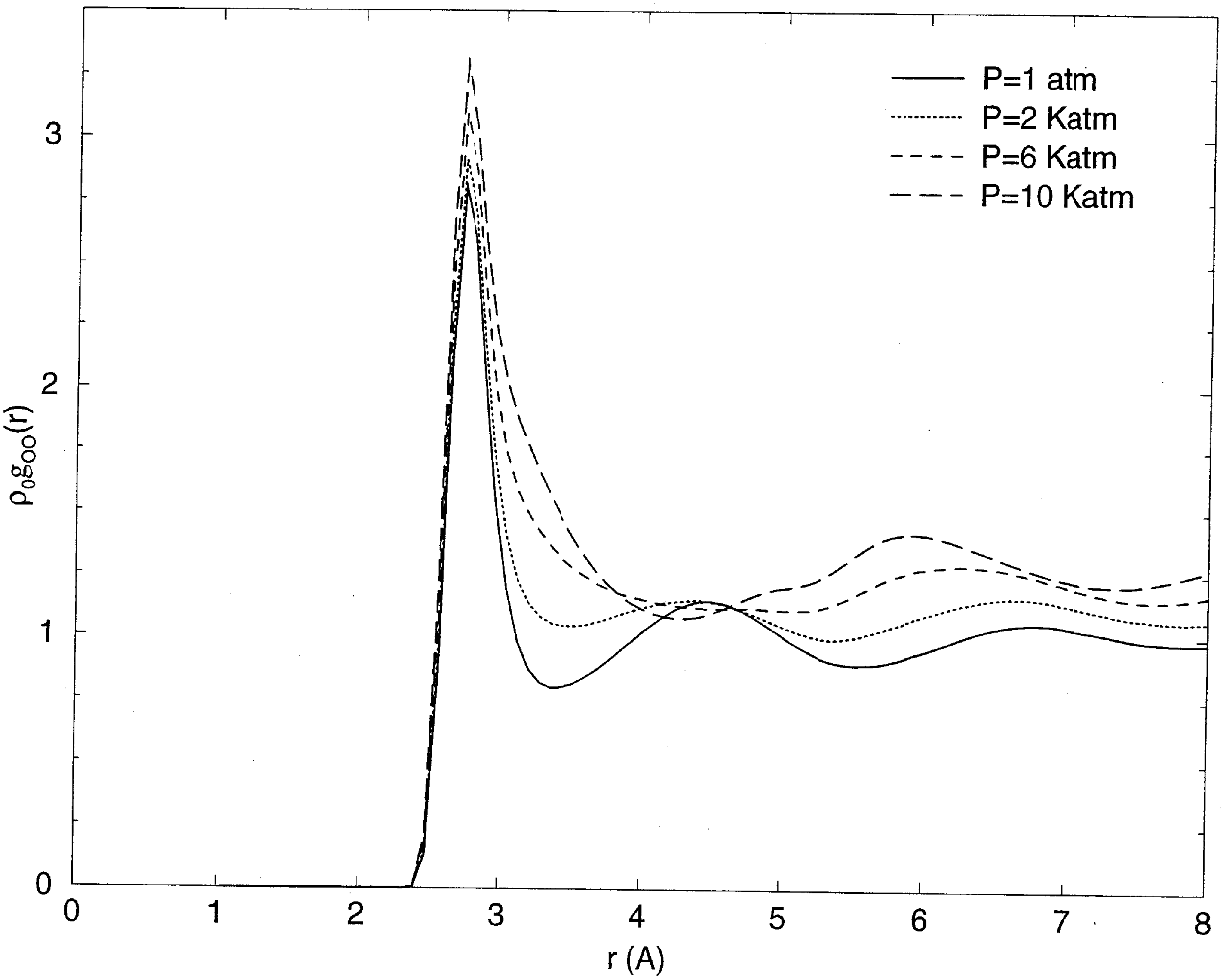


TABLE VIII. Optimized geometry and dimerization energy for the linear water dimer.

	TIP3P	TIP4P	TIP5P	Expt.[a]
$r(OO)$, Å	2.74	2.75	2.68	2.98 ± 0.02
τ, deg	27	46	51	57 ± 10
$-\Delta E$, kcal/mol	6.50	6.24	6.78	5.4 ± 0.5

[a] Ref. 58 for $(D_2O)_2$.

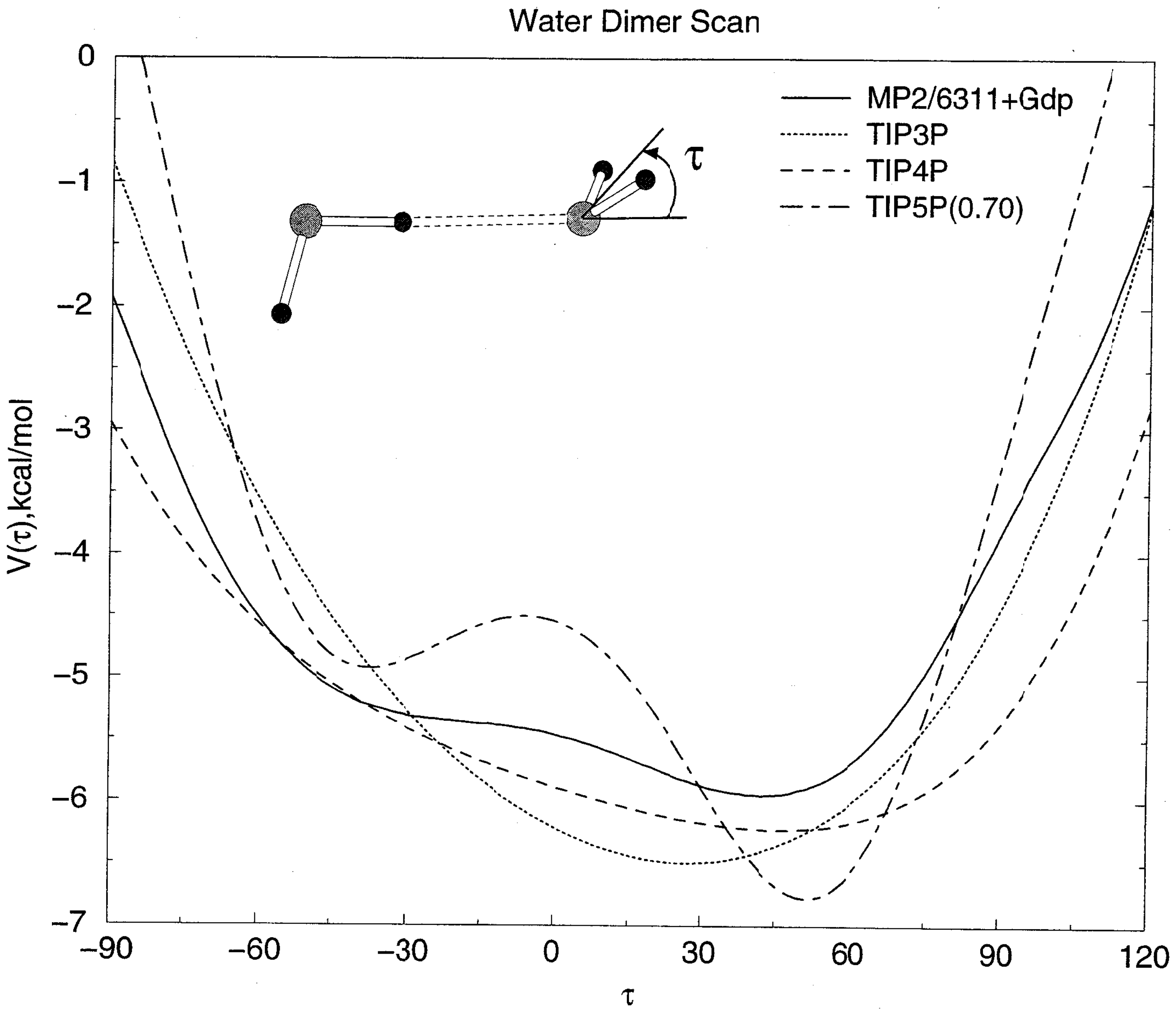

Water Dimer Scan
MP2/6311+Gdp
TIP3P
TIP4P
TIP5P(0.70)
τ
V(τ),kcal/mol
0
−1
−2
−3
−4
−5
−6
−7
−90
−60
−30
0
30
60
90
120
τ

TABLE IX. Five point models examined to reproduce ρ(T) for liquid water.[a]

	TIP5P(0.4875)	TIP5P(0.60)	TIP5P(0.65)	TIP5P(0.70)
σ_O (Å)	3.140	3.145	3.133	3.120
ε_O (kcal/mol)	0.16	0.16	0.16	0.16
r_{OL} (Å)	0.4875	0.60	0.65	0.70
q_L (e)	-0.290	-0.266	-0.254	-0.241

[a] In all cases, r_{OH} = 0.9572 Å, θ_{HOH} = 104.52°, and θ_{LOL} = 109.47°.

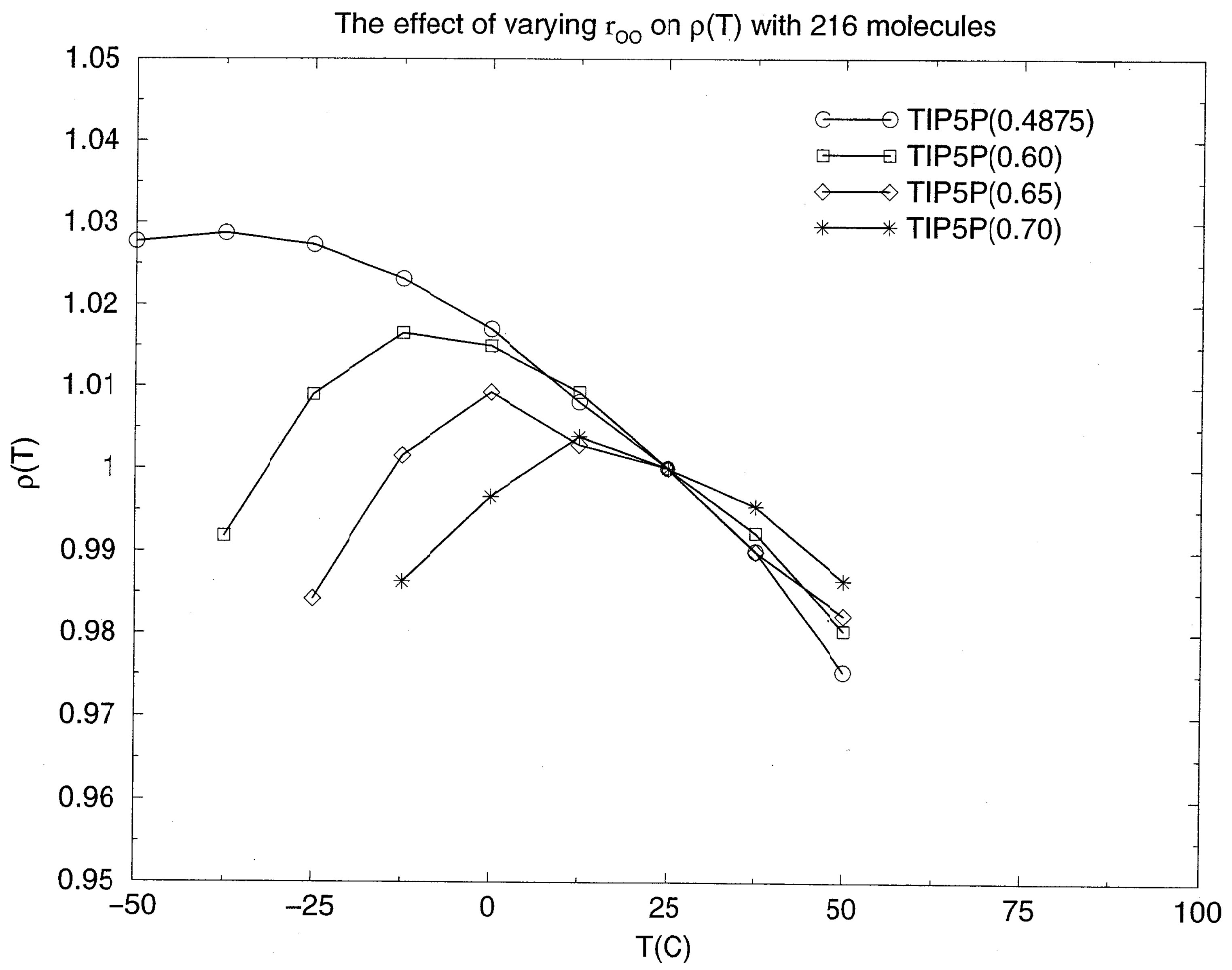

The effect of varying r_{OO} on $\rho(T)$ with 216 molecules
$\rho(T)$
1.05
1.04
1.03
1.02
1.01
1
0.99
0.98
0.97
0.96
0.95
−50
−25
0
25
50
75
100
T(C)
TIP5P(0.4875)
TIP5P(0.60)
TIP5P(0.65)
TIP5P(0.70)

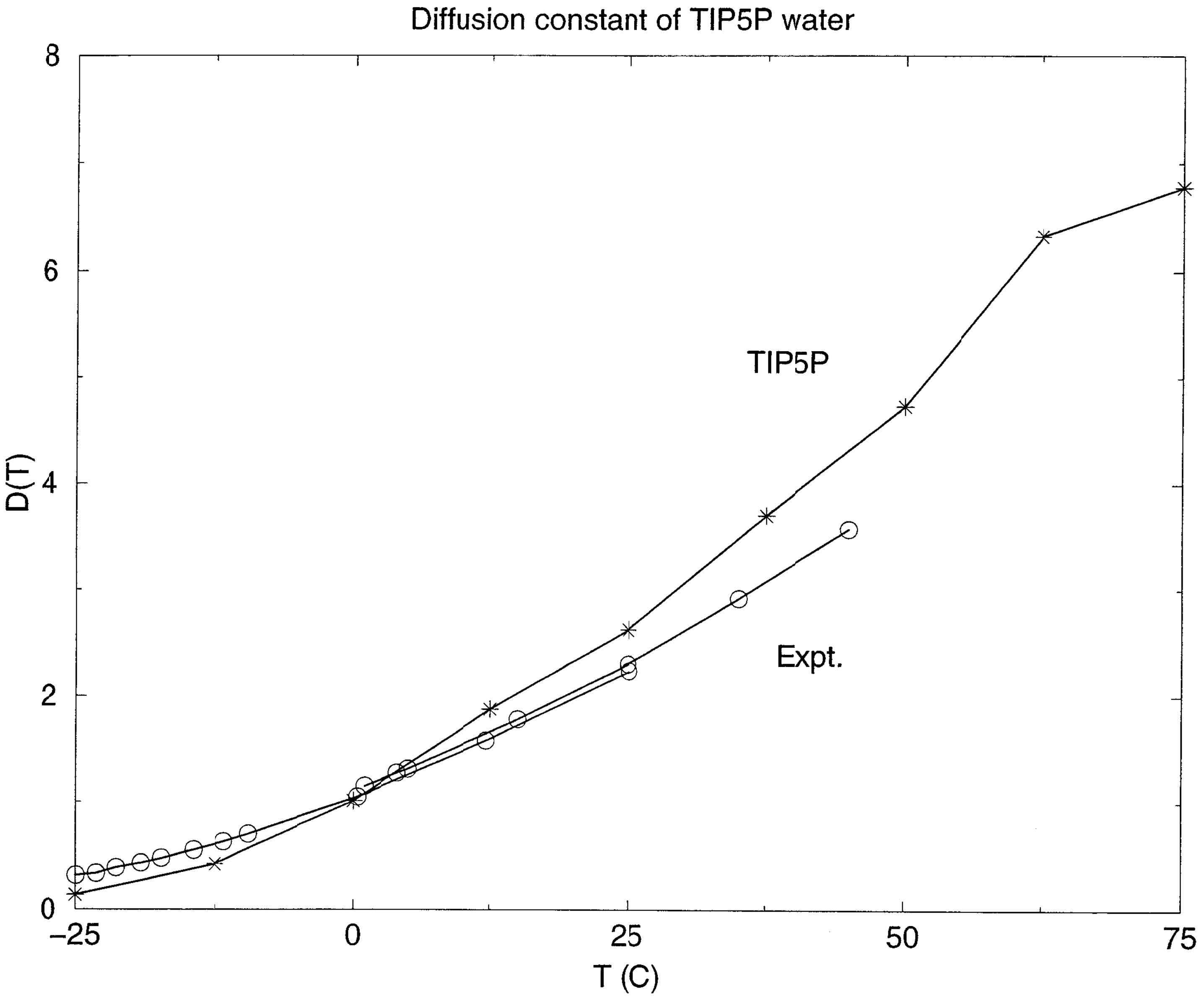
TABLE I. The diffusion constant for simple water models

	Ensemble	T (C)	P (atm)	Density[a]	D[b]
SPC	NPT	25	1		3.85 ± 0.09
SPC/E	NPT	25	1		2.49 ± 0.05
TIP3P	NPT	25	1		5.19 ± 0.08
TIP4P	NPT	25	1		3.31 ± 0.08
TIP3P	NVT	25		0.993	5.06 ± 0.09
TIP4P	NVT	25		0.990	3.29 ± 0.05
TIP5P	NVT	25		0.999	2.62 ± 0.04
Expt.[c]		25	1	0.997	2.30

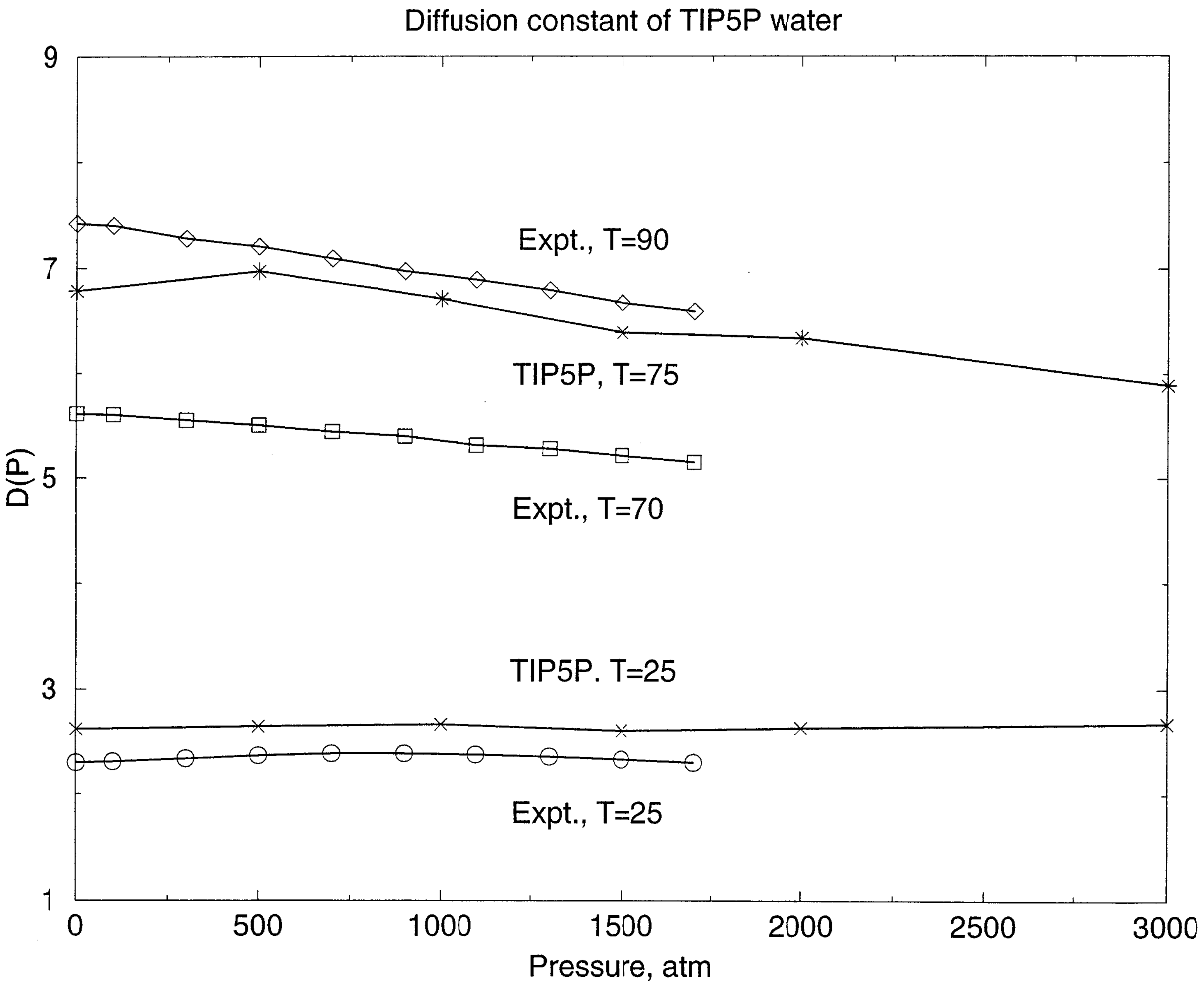
[a] Units are g/cm^3.

[b] Units are 10^{-5} cm^2/s.

[c] See Ref. 2.

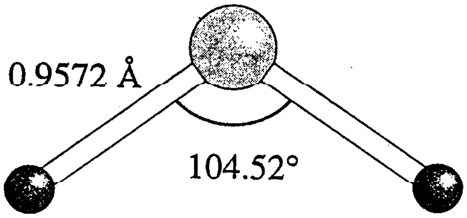


Diffusion constant of TIP5P water

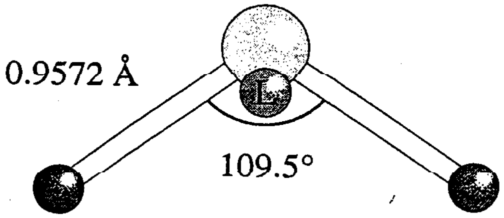

Diffusion constant of TIP5P water
D(P)
9
7
5
3
1
0
500
1000
1500
2000
2500
3000
Pressure, atm
Expt., T=90
TIP5P, T=75
Expt., T=70
TIP5P. T=25
Expt., T=25

Flexible Water Models

TIP3F



TIP4F



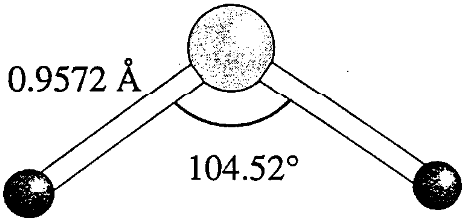
0.411	q_H	0.511
3.176	σ_O	3.270
0.150	ε_O	0.100
529.6*	k_{OH}	600.0
34.05*	k_{HOH}	75.00
38.25*	k_{HH}	—
—	k_{OL}	900.00
—	k_{HOL}	50.00
—	r_{OL}	0.175
2.35	μ (gas)	1.85
1594, 3656, 3755	ν_i (gas)	2371, 3837, 3958

* *J. Phys. Chem.* **1987**,*91*, 3349

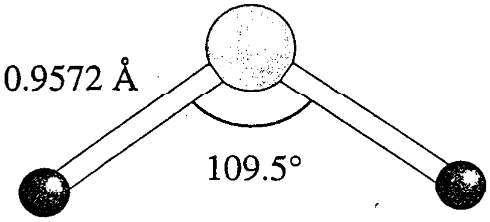
Flexible Water Models – Average Geometries

TIP3F **TIP4F**

Gas Phase at 0 K

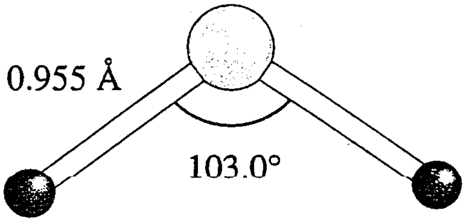


$\mu = 2.35$ D

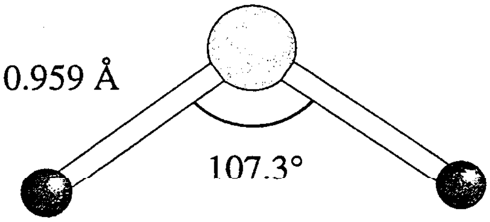


$\mu = 1.85$ D

Gas Phase at 25 C

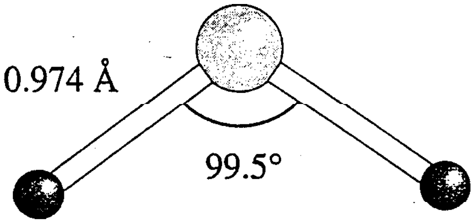


$\mu = 2.31$ D

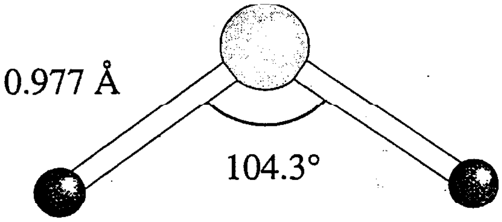


$\mu = 1.93$ D

Liquid at 25 C

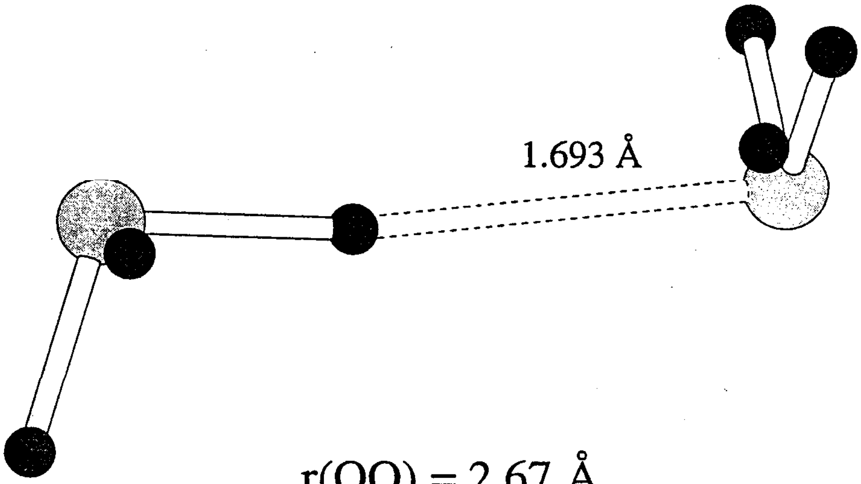


$\mu = 2.48$ D



$\mu = 2.32$ D

TIP4F Dimer



r(OO) = 2.67 Å

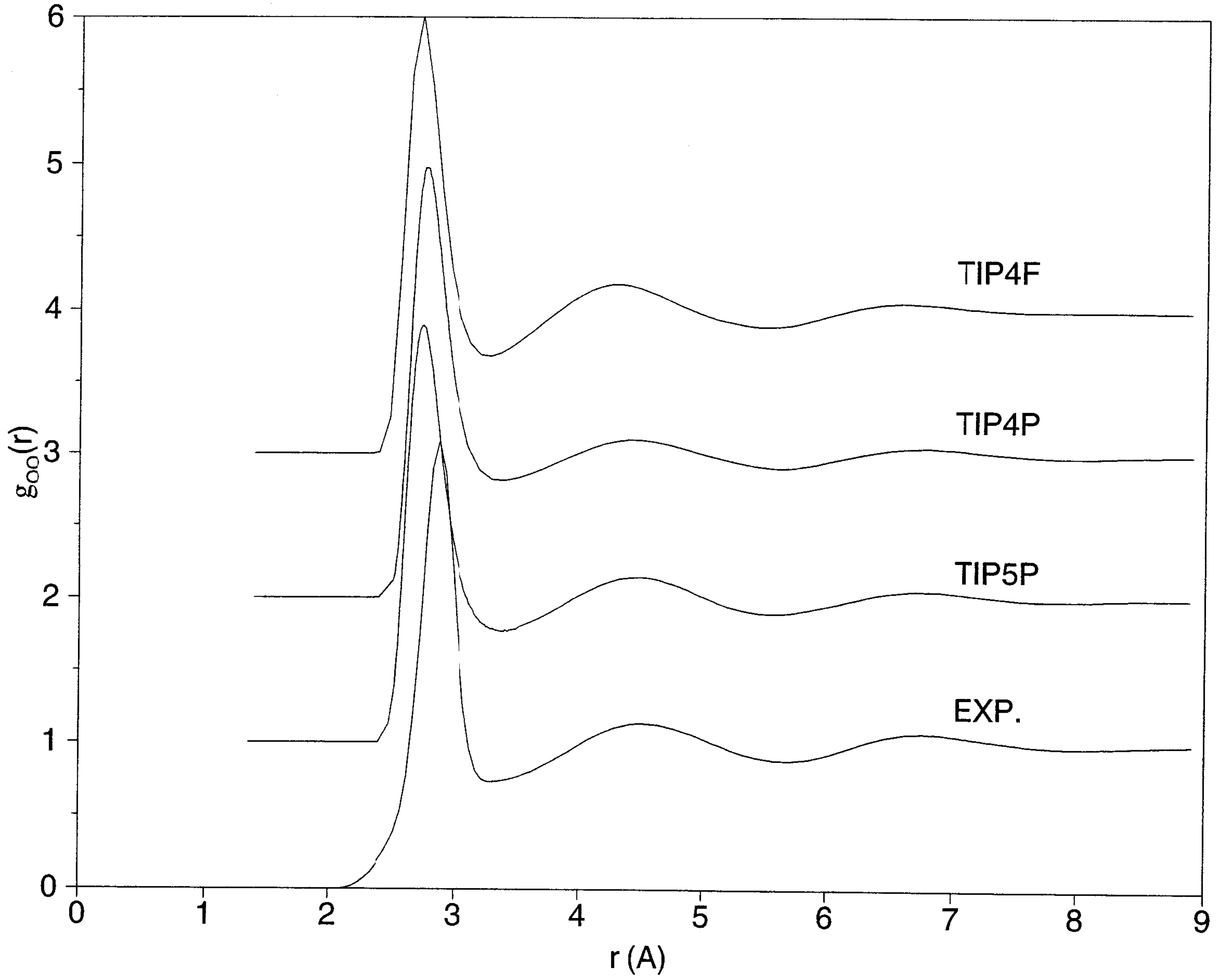
μ = 1.72 D

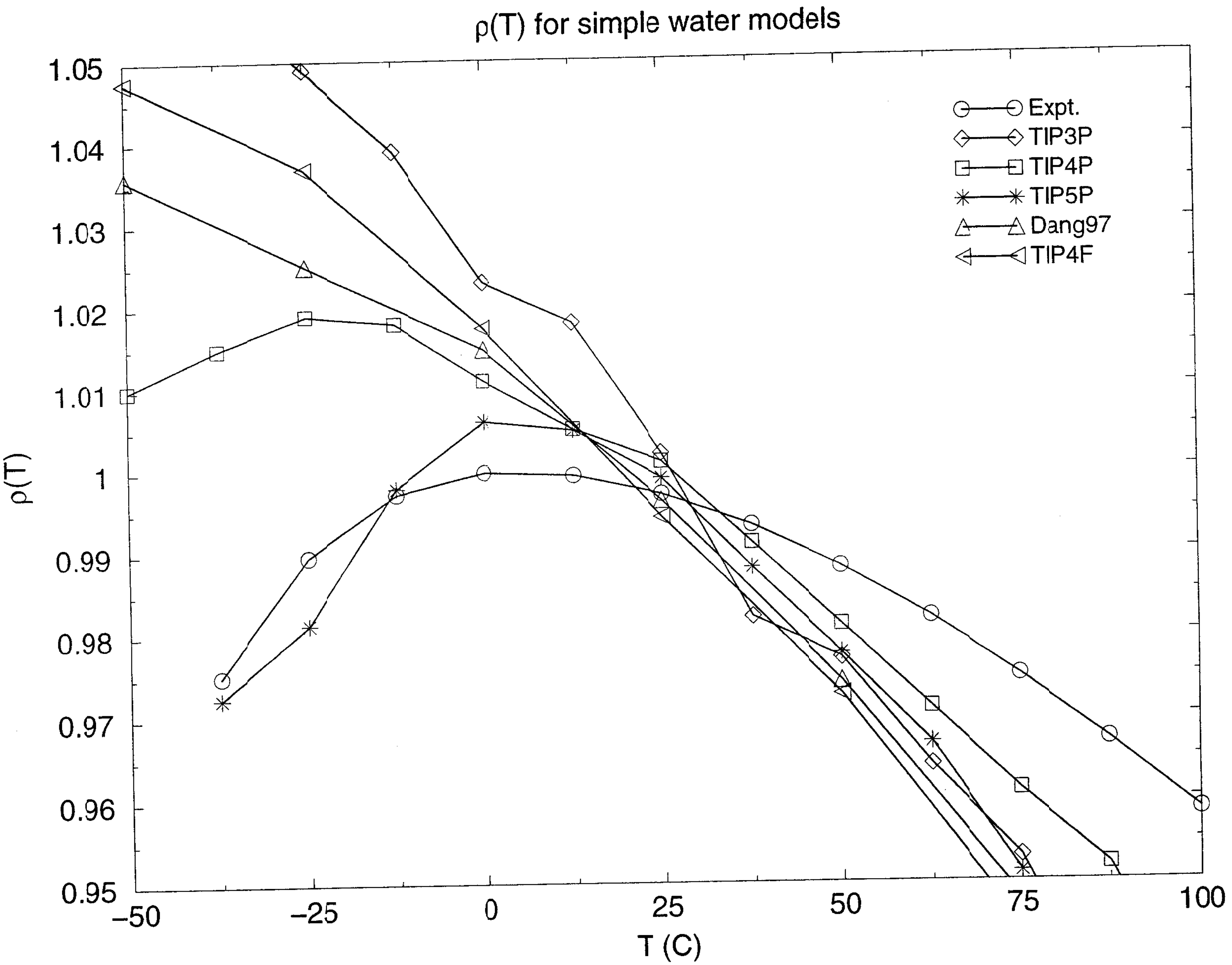
ΔE = –6.36 kcal/mol

Computed and Experimental Properties of Water (25 C, 1 atm)

Property	TIP3F	TIP4P	TIP4F	Exptl
d (g cm^{-3})	1.003 ± 0.001	1.001 ± 0.001	0.998 ± 0.001	0.997
ΔH_{vap} (kcal/mol)	10.58 ± 0.01	10.65 ± 0.01	10.78 ± 0.01	10.51
C_p (cal/mol-K)	25.4 ± 0.6	20.4 ± 0.7	32.4 ± 0.6	18.0
10^6 κ (atm^{-1})	33 ± 5	60 ± 5	41 ± 3	45.8
10^5 α (deg^{-1})	75 ± 10	60 ± 8	82 ± 10	25.7
ε		53, 61, 72	78	
μ, gas (D)	2.35	2.18	1.85	1.85
μ, liquid (D)	2.48	2.18	2.32	~2.4

OO Radial Distribution Functions for Liquid Water




ρ(T) for simple water models

Feynman path integrals and path integral Monte Carlo(PIMC) and molecular dynamics(PIMD)

The quantum partition function Q

$$Q = Tre^{-\beta H} = \int dX \langle X | e^{-\beta H} | X \rangle$$

can be rewritten as:

$$Q = \int dx_1 \cdots \int dx_P \langle x_1 | e^{-\varepsilon H} | x_2 \rangle \langle x_2 | e^{-\varepsilon H} | x_3 \rangle \cdots \langle x_2 | e^{-\varepsilon H} | x_3 \rangle ,$$

with $\varepsilon = \beta / P$ and $\beta = 1 / kT$.

Feynman showed that for large P,

$$Q = \left(\frac{m}{2 \pi \varepsilon \hbar^2} \right)^2 \int dx_1 \cdots \int dx_P e^{-\beta V_{eff}(X)} ,$$

where

$$V_{eff}(X) = \sum_{k=1}^{P} \left[\frac{mP}{2 \beta \hbar^2} (x_k - x_{k+1})^2 + \frac{1}{P} V(x_i) \right]$$

- For fixed P, this has the form of a classical partition function. Thus, quantum particles can be treated classically with many classical-like "pseudo particles"

The Visualization of Path Integral Monte Carlo Results

At extremely low temperatures, the behavior of particles such as hydrogen ions can be described using techniques from quantum mechanics. One way of numerically simulating such particles is through a technique known as Path Integral Monte Carlo (PIMC). At Visualization '94, we presented a new approach to analyzing the results from PIMC simulations based on alpha shapes. Alpha shapes are a geometric techique for describing the shape of a point set, where a global real parameter alpha can be used to specify the level of detail displayed by the shape.

A Few Pictures

Computational physicists have a few standard methods for visualizing the results from PIMC simulations. On technique, illustrated in figure 1, is to draw line segments connecting the brownian motion path of each particle. Note that the simulation was conducted under periodic boundary conditions, with the box outlined by the red dashed line representing the fundamental domain.

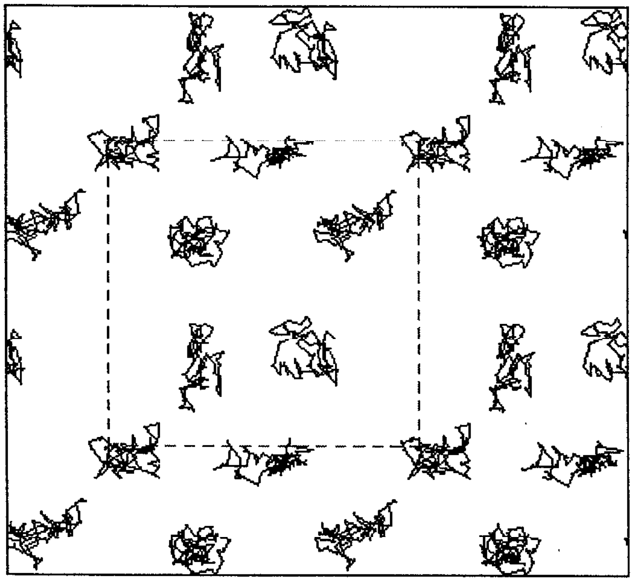
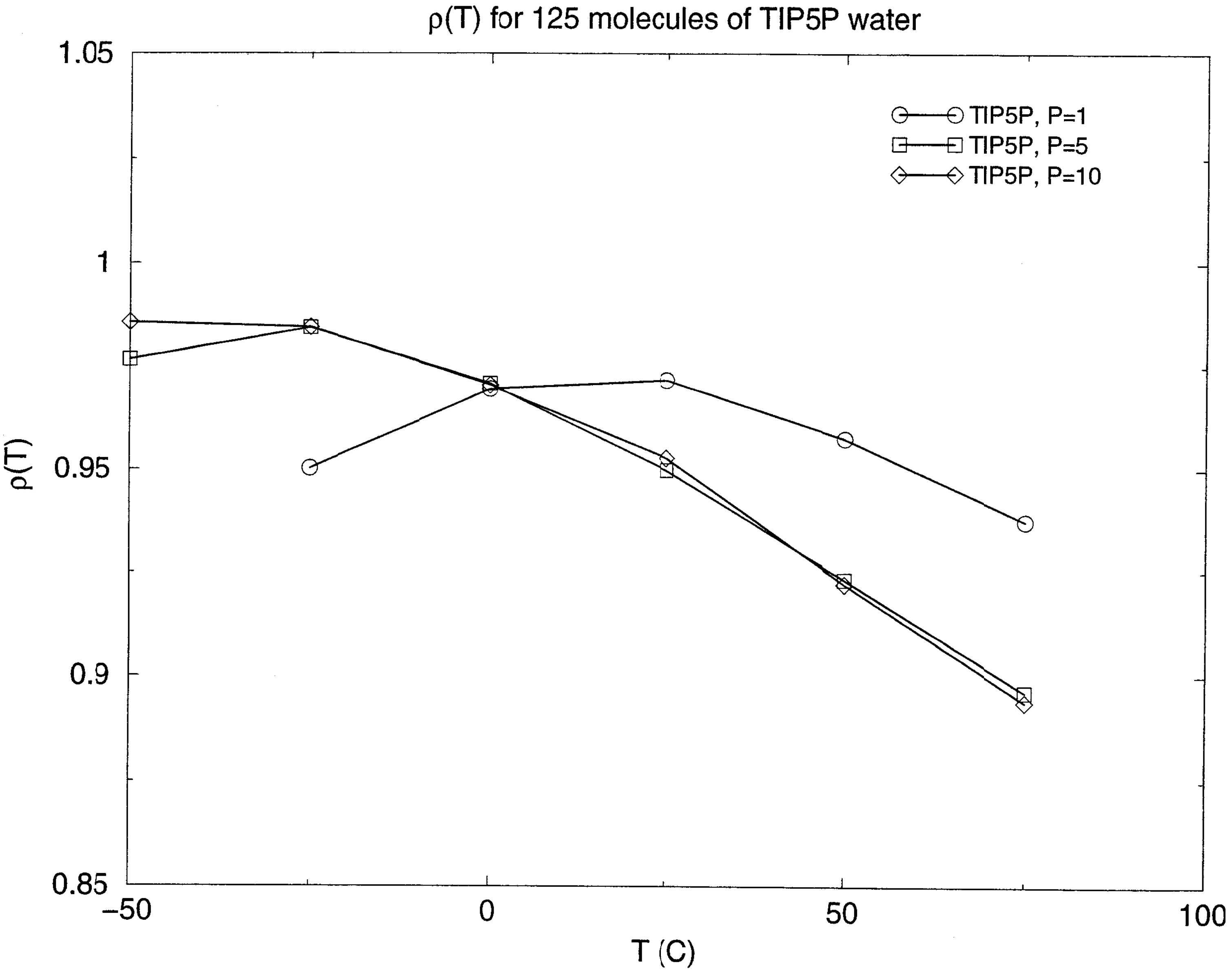
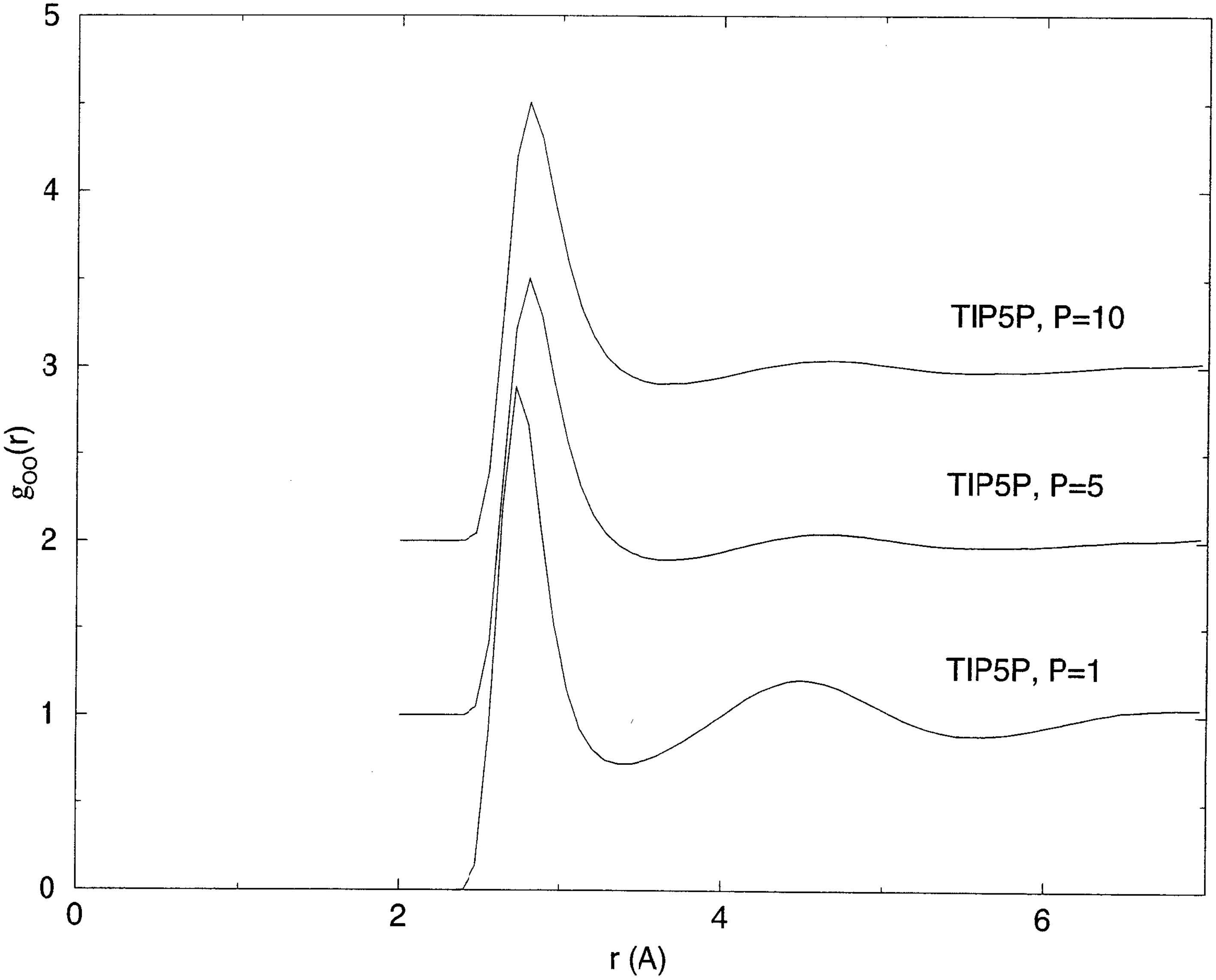


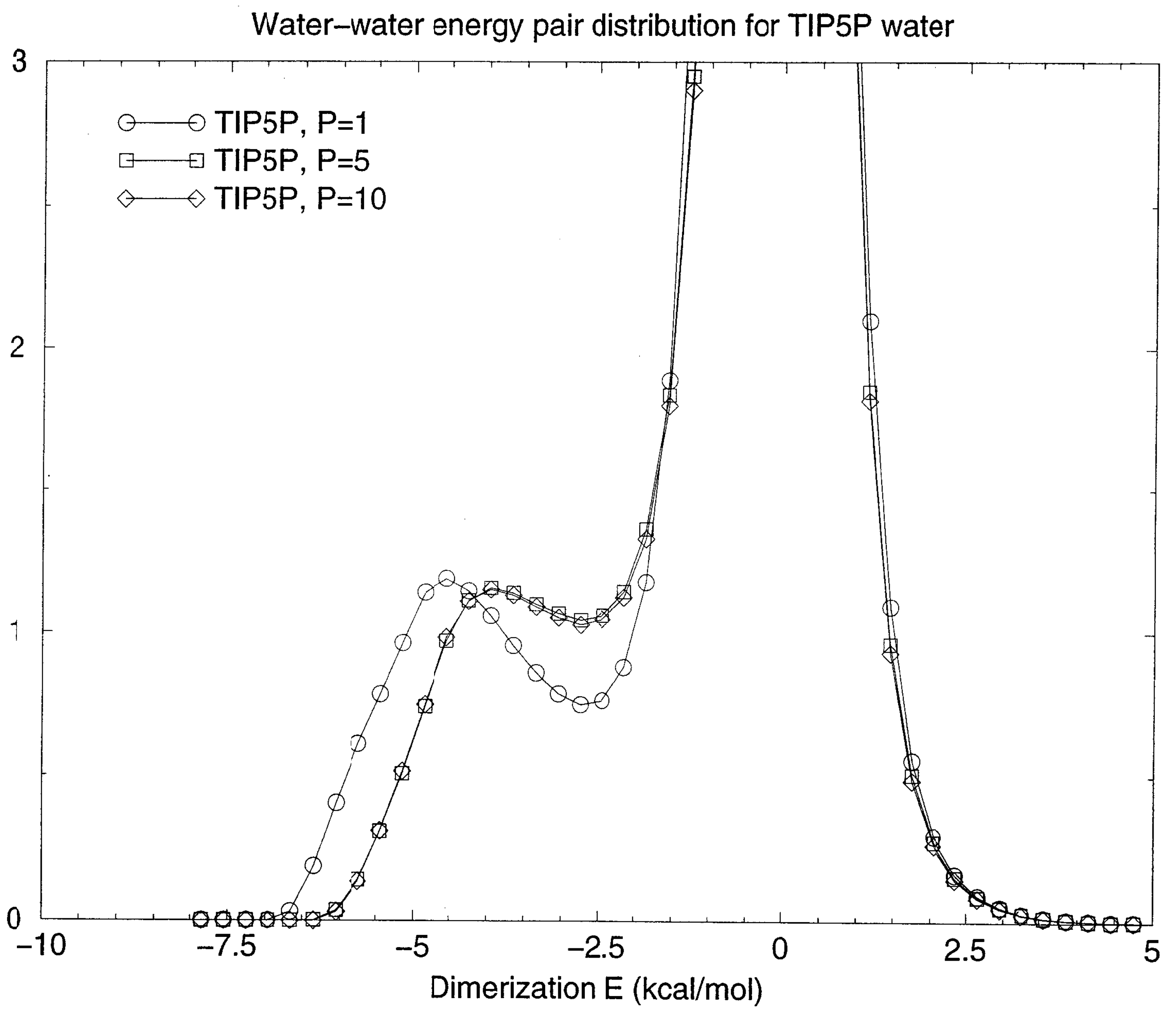
Figure 1: A traditional method for visualizing PIMC results.

Figure 2 illustrates an example where we an alpha shape (the green region) to delineate a shoreline for the point set shown to the left. Our approach supports a second option, where we center a disk on each point in the input and take the boundary of the union of disks as the shoreline. The blue region corresponds to the ball union. The ball union also covers the space covered by the alpha shape.

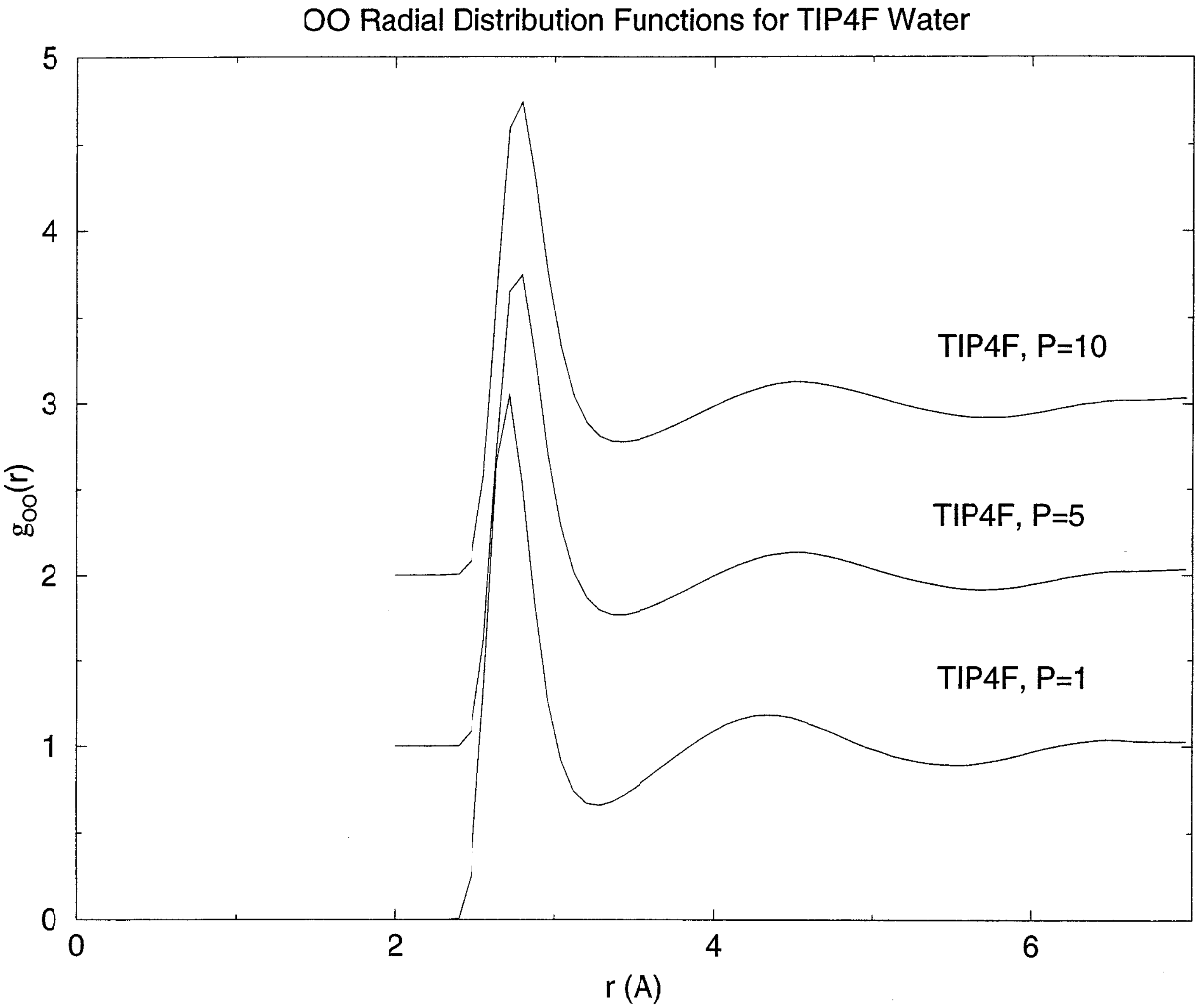

ρ(T) for 125 molecules of TIP5P water
TIP5P, P=1
TIP5P, P=5
TIP5P, P=10
ρ(T)
1.05
1
0.95
0.9
0.85
−50
0
50
100
T (C)

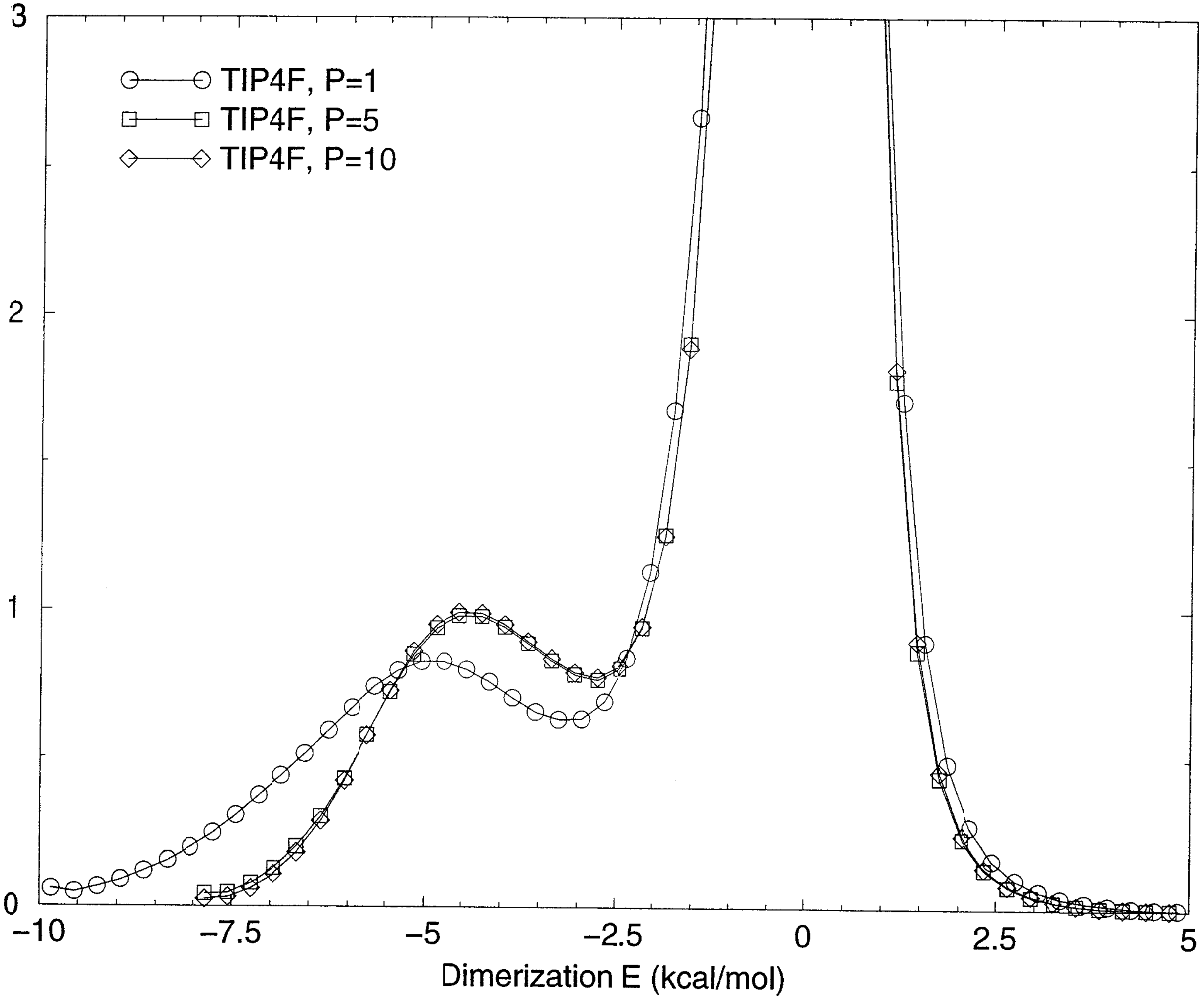


OO Radial Distribution Functions for TIP5P Water

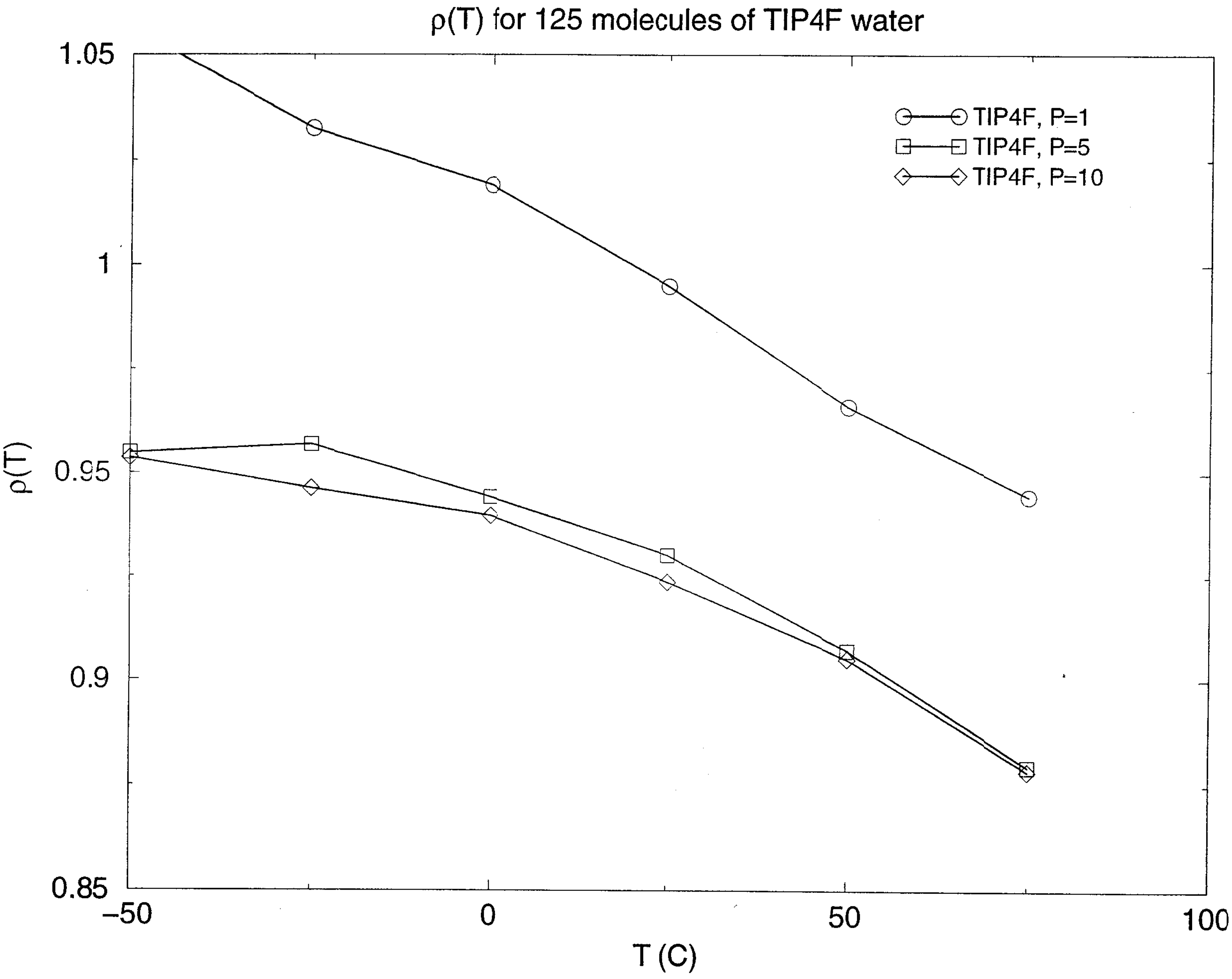


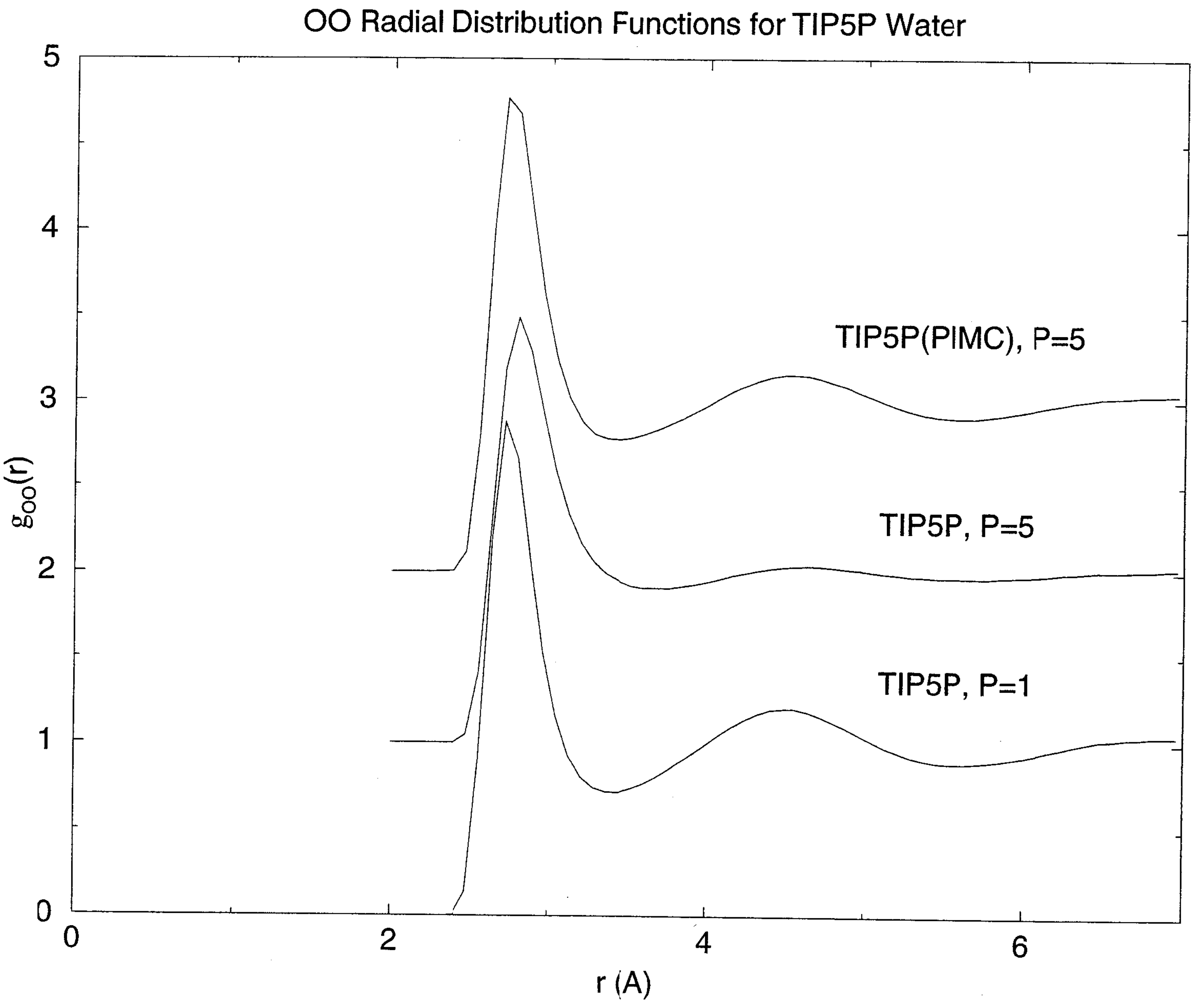
Water–water energy pair distribution for TIP5P water


OO Radial Distribution Functions for TIP4F Water
$g_{OO}(r)$
5
4
3
2
1
0
0
2
4
6
r (A)
TIP4F, P=10
TIP4F, P=5
TIP4F, P=1



Water–water energy pair distribution for TIP4F water


ρ(T) for 125 molecules of TIP4F water


OO Radial Distribution Functions for TIP5P Water
$g_{OO}(r)$
r (A)
0
1
2
3
4
5
0
2
4
6
TIP5P(PIMC), P=5
TIP5P, P=5
TIP5P, P=1

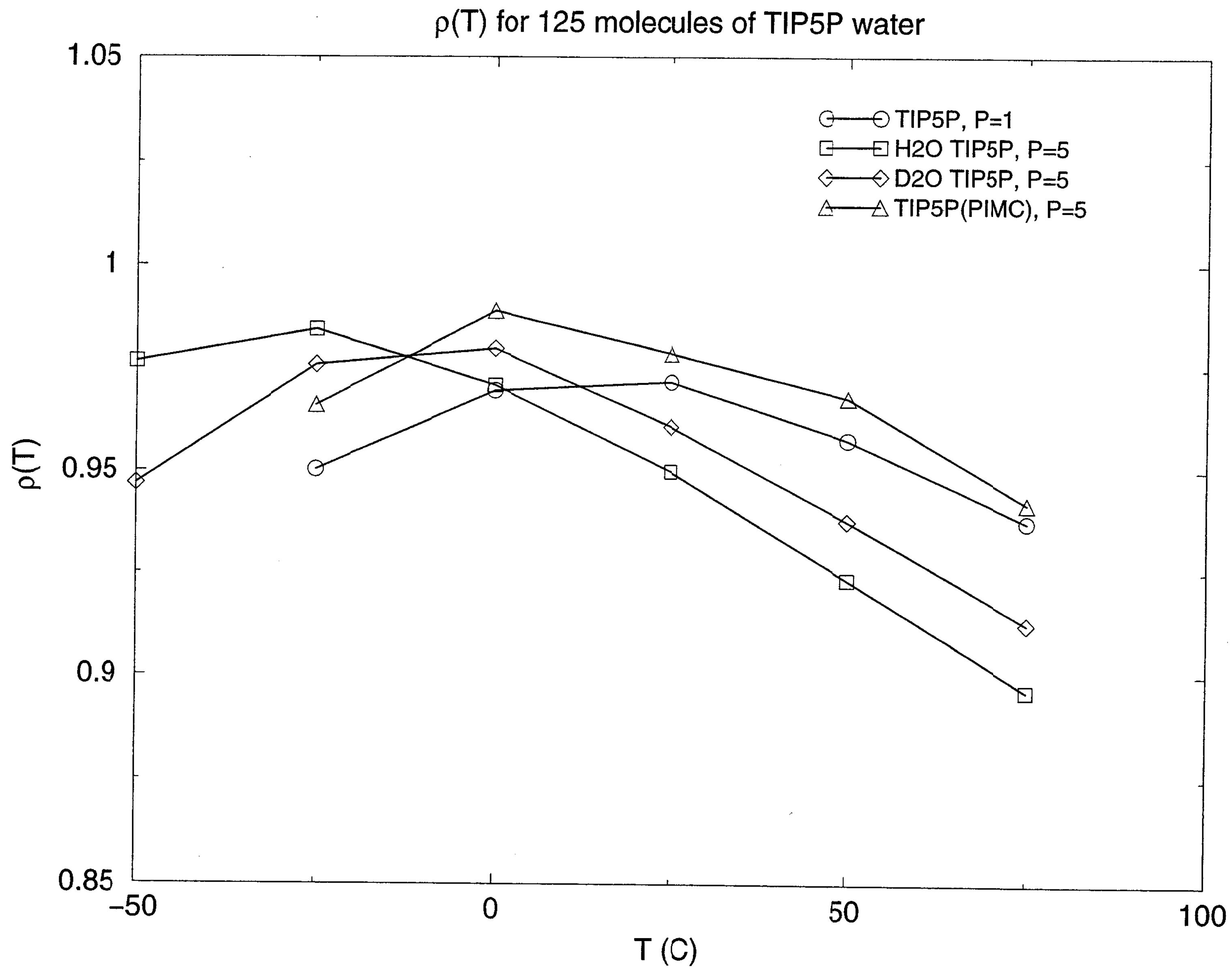

ρ(T) for 125 molecules of TIP5P water
1.05
1
0.95
0.9
0.85
ρ(T)
−50
0
50
100
T (C)
TIP5P, P=1
H2O TIP5P, P=5
D2O TIP5P, P=5
TIP5P(PIMC), P=5

TABLE I. Monomer geometry and parameters for the water models.

	TIP5P	TIP4F	Dang97	TIP5P(PIMC)
q_H (e)	0.241	0.511	0.519	0.251
q_O (e)	---	---	---	---
q_L (e)	-0.241	-1.022	-1.038	-0.251
σ_O (Å)	3.12	3.27	3.234	3.12
ε_O (kcal/mol)	0.16	0.10	0.1825	0.16
α_L (Å^3)	---	---	1.444	---
r_{OH} (Å)	0.9572	0.9572	0.9572	0.9572
θ_{HOH} (deg)	104.52	109.5	104.5	104.52
r_{OL} (Å)	0.70	0.175	0.215	0.70
θ_{LOL} (deg)	109.47	---	---	109.47
k_{OH} (***)	---	600.0	---	---
k_{HOH} (***)	---	75.0	---	---
k_{OL} (***)	---	900.0	---	---
k_{HOL} (***)	---	50.0	---	---

The Dang models I am using:

Dang93:

L.X. Dang and B.C. Garrett, J. Chem. Phys. **99**, 2972, 1993

3 point, 3 polarizable site, ~SPC geometry

$q_H = +0.365$, $\sigma_O = 3.205$, $\varepsilon_O = 0.16$, $\alpha_H = 0.170$, $\alpha_O = 0.528$

$NMOL = 216$, $RCUT = 9\text{A}$, $T = 25/28$

$U = -9.84 \pm 0.08$, $\rho = 1.003 \pm 0.015$

Dang97:

L.X. Dang and T.M. Chang, J. Chem. Phys. **106**, 8149, 1997

4 pt, 1 polarizable site, ~TIP4P geometry, M site = 0.215 A

$q_H = +0.519$, $\sigma_O = 3.234$, $\varepsilon_O = 0.1825$, $\alpha_M = 1.444$

$NMOL = 550$, $RCUT = 9\text{A}$, $T = 25$

$U = -9.84 \pm 0.07$, $\rho = 0.995 \pm 0.007$

Table 2. Representative Relative Timings for Approximation Methods

	Method Description	Dang93	Dang97
1	No Polarization	1	1
3	Full iteration to a tolerance = 10E-6	850	110
4	Two cutoffs (4A & 9A), two tolerances (10E-1 & 10E-6) and update correction every 100 steps	79	17
5	Two cutoffs (4A & 9A), two tolerances (10E-4 & 10E-6) and update correction every 100 steps	130	23
6	Two cutoffs (5A & 9A), two tolerances (10E-1 & 10E-6) and update correction every 100 steps	110	20
7	Two cutoffs (5A & 9A), two tolerances (10E-4 & 10E-6) and update correction every 100 steps	190	35
8	Two cutoffs (5A & 9A) and update correction every 100 steps	190	35
9	Two cutoffs (5A & 9A) and update correction every 100 steps	280	49
10	Two tolerances (10E-1 & 10E-6) and update correction every 100 steps	280	35
11	Two tolerances (10E-2 & 10E-6) and update correction every 100 steps	290	35
12	Two tolerances (10E-3 & 10E-6) and update correction every 100 steps	420	49
13	Two tolerances (10E-4 & 10E-6) and update correction every 100 steps	550	70
14	Iteration over moved molecules and its neighbors[a] and then neighbors of neighbors to a tolerance of 10E-2	100	14
15	Iteration over moved molecules and its neighbors[a] and then neighbors of neighbors to a tolerance of 10E-4	190	28
16	Iteration over moved molecules and its neighbors[a] to a toler. = 10E-2	29	7.4
17	Iteration over moved molecules and its neighbors[a] to a toler. = 10E-4	52	9.8
18	Perturbative modification of previous step	20	5.8
19	Perturbative modification of previous step, then #16	30	8
20	Perturbative modification of previous step, then #17	73	12

[a] neighbors within 4Å.

Techniques to speed up the estimation of the induced dipoles in Monte Carlo simulations of polarizable liquids

1. Use of a smaller cutoff criteria or weaker tolerance.

   Half of the matrix is zero due to spherical cutoff.

   Dipole term falls off faster than charge term.

   Allows iterator to take advantage of sparsity, which is relatively more important for less dense matrices.

   Additive cutoff correction may be recomputed every M~N steps.

   Make cutoff as low as 4A and tolerance as low as one iterative cycle.

2. Simulation within a simulation.

   Don't require $\vec{p} = \alpha \cdot \vec{E}_{tot}$ at each step.

   If $U = \frac{1}{2\alpha} p^2 - \vec{p} \cdot \vec{E}_{tot}$, then obtain $\vec{p} = \alpha \cdot \vec{E}_{tot}$ as ensemble average if $\delta U = 0$. Do minimization with mini-MC simulation each step.

   Dipoles fluctuate around B-O surface $\langle \vec{p} \rangle = \alpha \cdot \vec{E}_{tot}$ and $\langle p^2 \rangle \neq 0$

   Analogous to ab initio MD and uses simulated annealing, with T=5 or T=1.

Techniques to speed up the estimation of the induced dipoles in Monte Carlo simulations of polarizable liquids, cont.

3. Perturbation theoretic determination.

Given $A \cdot x = b$ at the i-th step, solve $A' \cdot x' = b'$ at the (i+1)-th step, with

$$A' = A + \delta A = A + \delta A_{rows} + \delta A_{cols},\ b' = b + \delta b,\ x' = x + \delta x,\ A \equiv D + N$$

$A' \cdot x' = b'$ can be rewritten as

$$D \cdot \delta x + N \cdot \delta x + \delta A_{rows} \cdot \delta x + \delta A_{cols} \cdot \delta x = \delta b - \delta A_{rows} \cdot \delta x - \delta A_{cols} \cdot \delta x$$

Ignore $\delta A_{\xi} \cdot \delta x$ terms as perturbative expansion and $N \cdot \delta x$ term to get the change in induced dipoles from one step to the next as

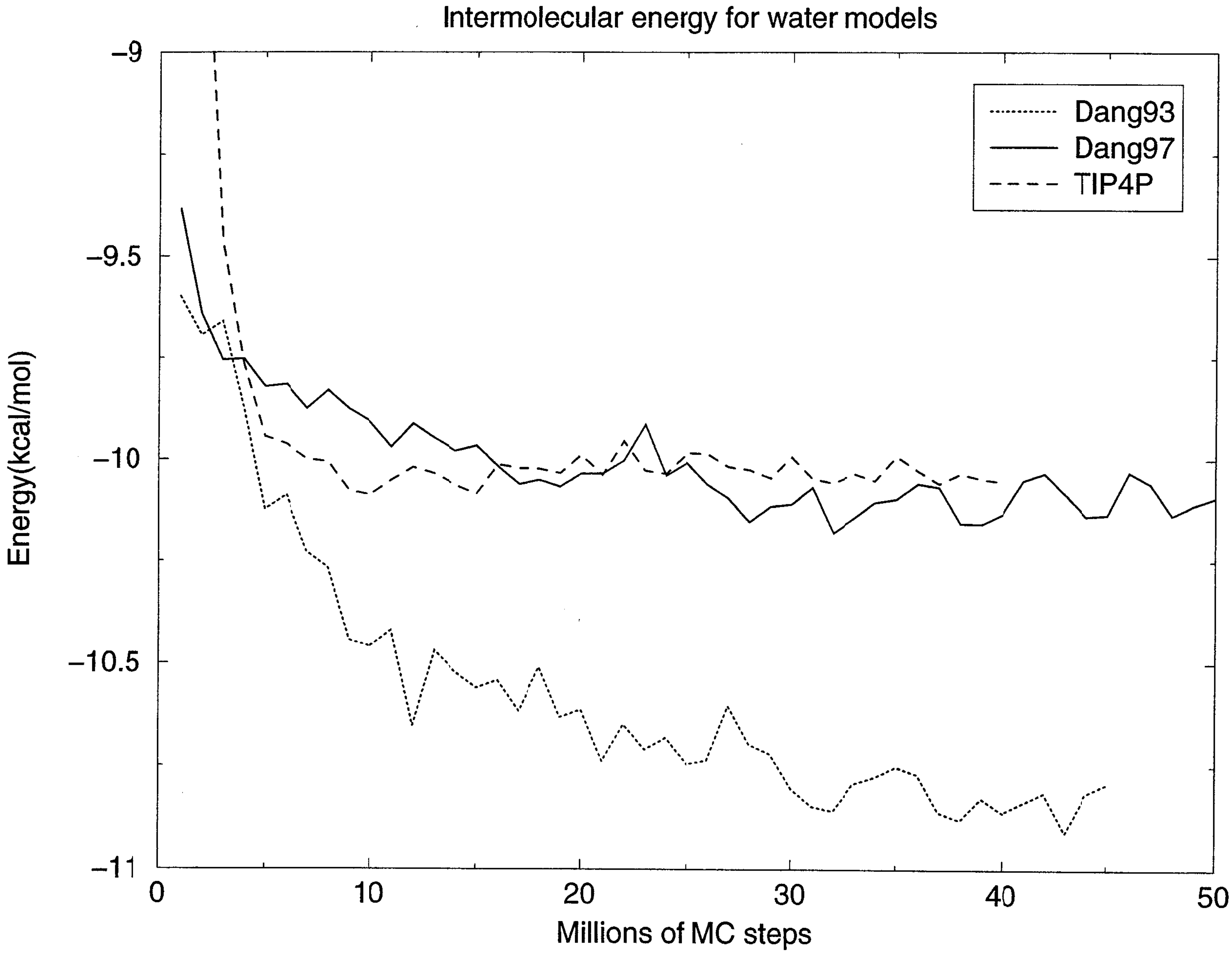
$$\delta x = D^{-1}(\delta b - \delta A_{rows} \cdot x - \delta A_{colx} \cdot x)$$

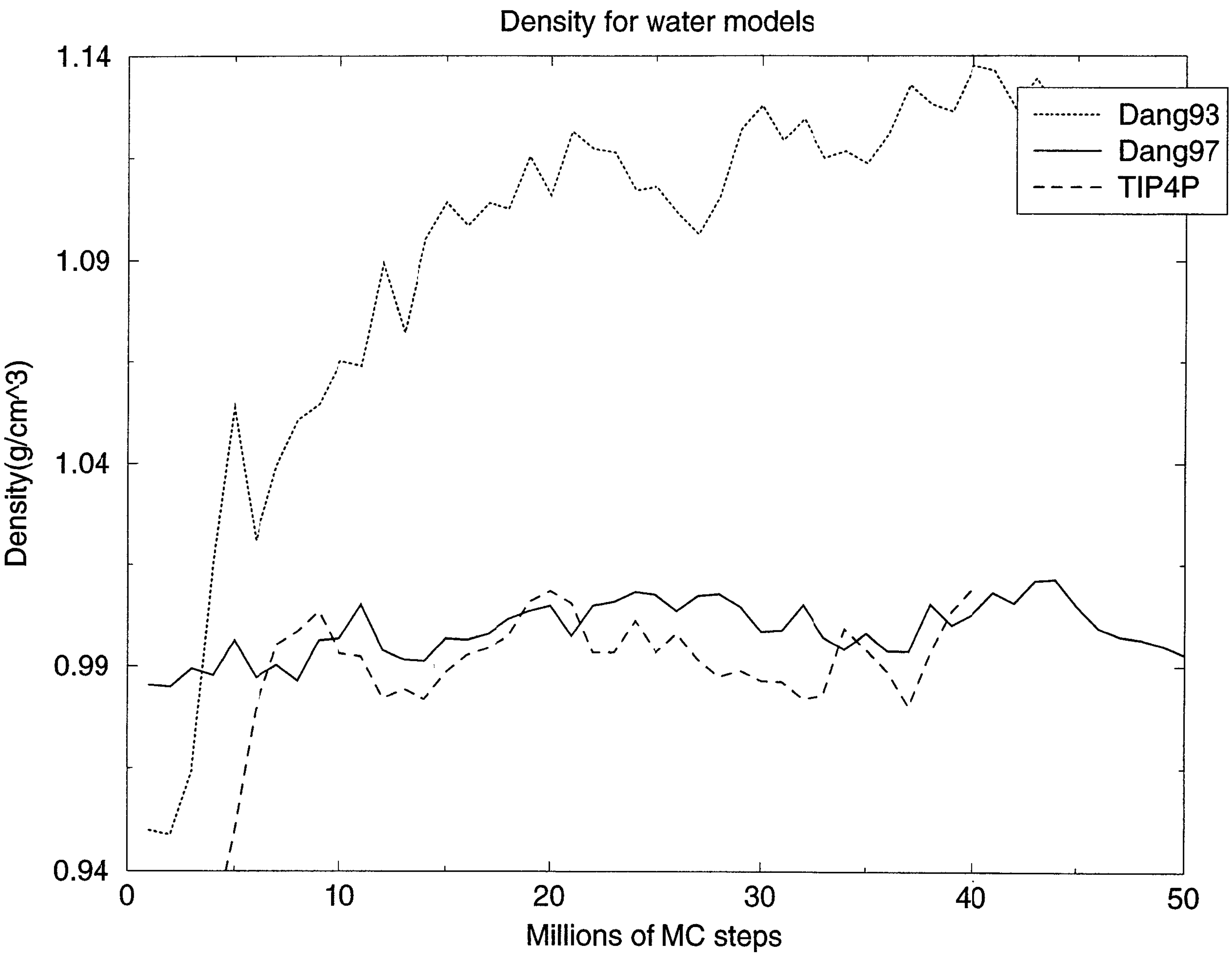
4. Iterate over many iterations.

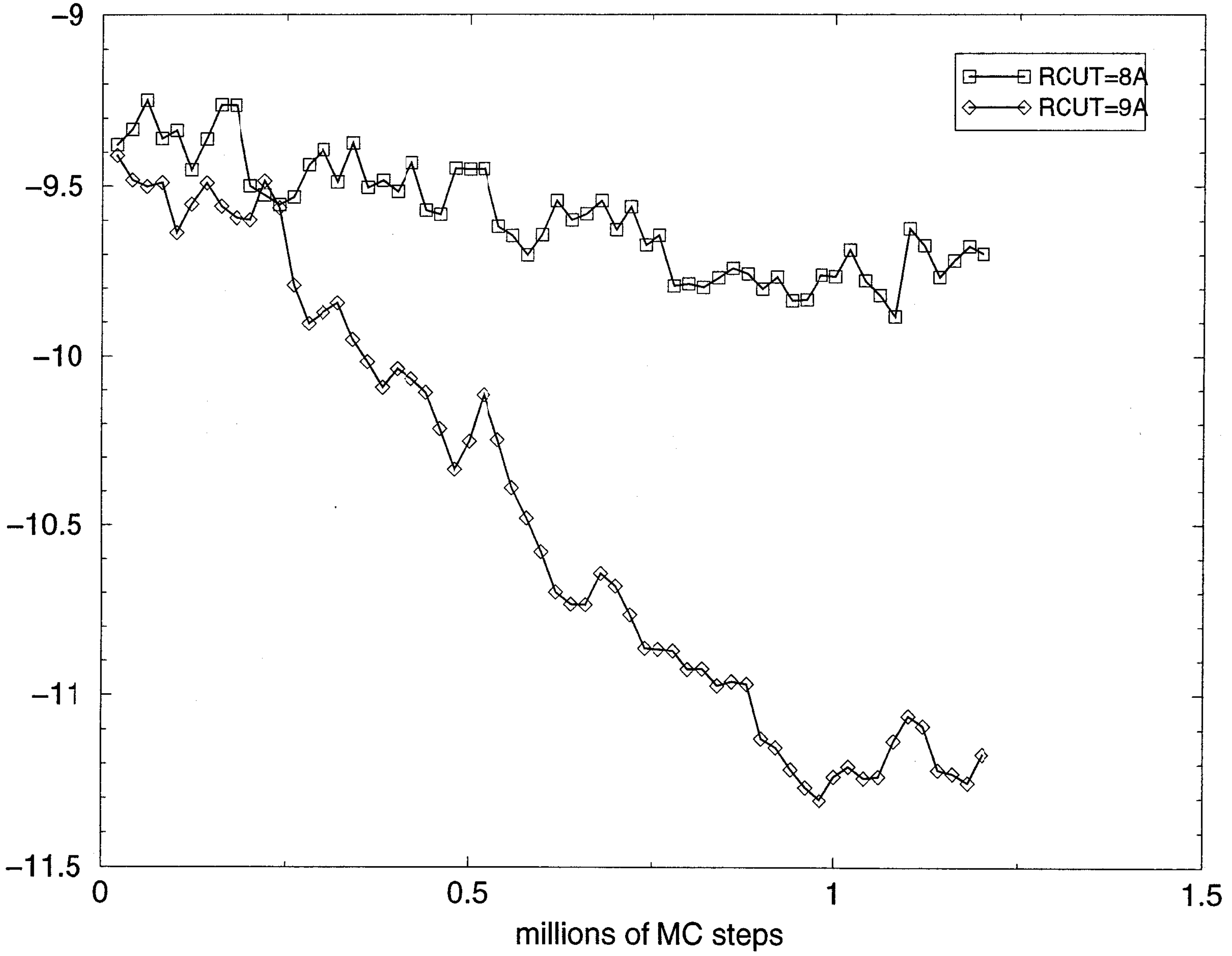
When a given molecule moves, the largest changes in induced dipoles are due to molecules near that molecule and molecules which cross the cutoff.

Iterate over just those molecules near (i.e. ~4A) the moved molecule.

Iterate over those molecules near the moved molecule and then those near them.

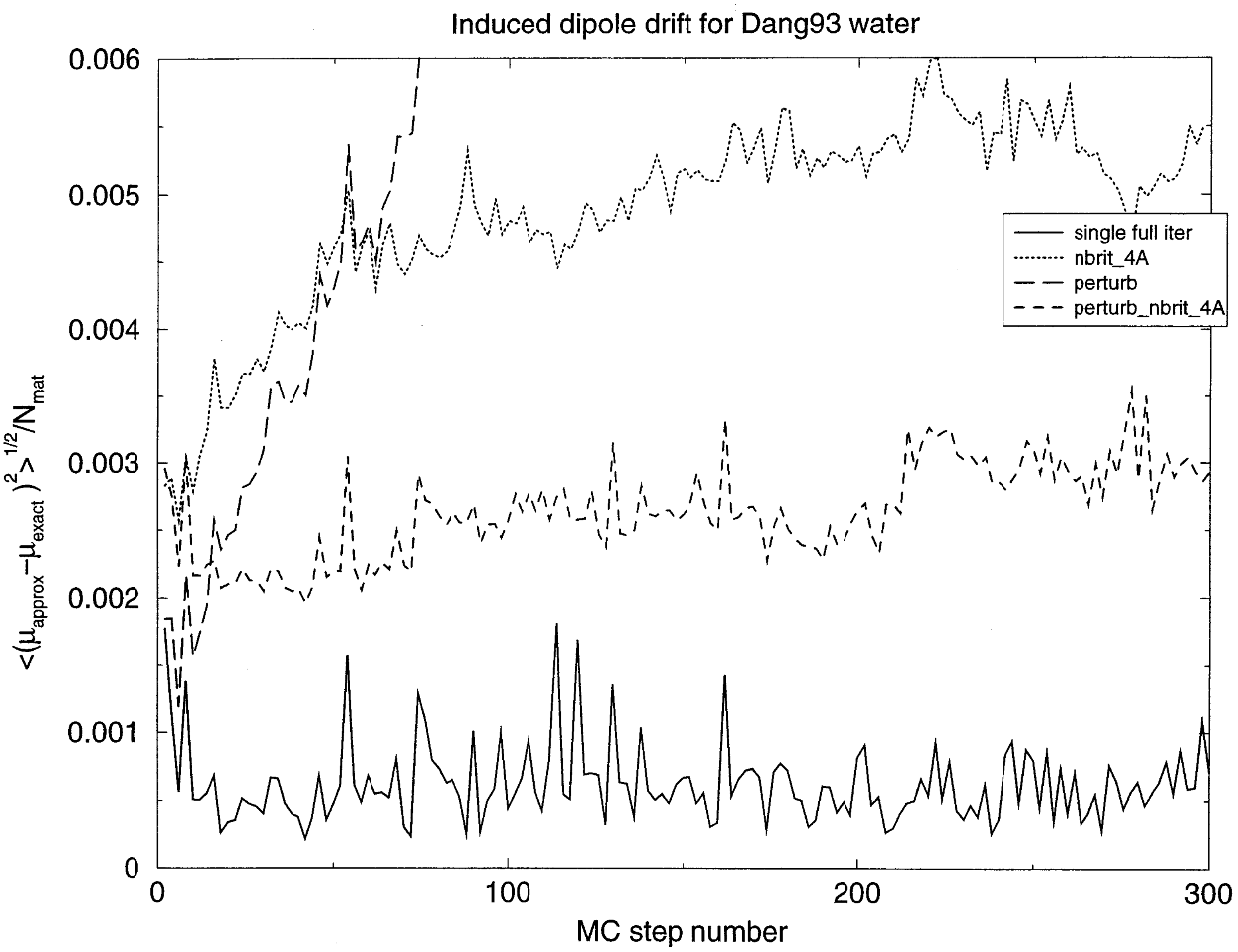

Intermolecular energy for water models
Dang93
Dang97
TIP4P
Energy(kcal/mol)
−9
−9.5
−10
−10.5
−11
0
10
20
30
40
50
Millions of MC steps

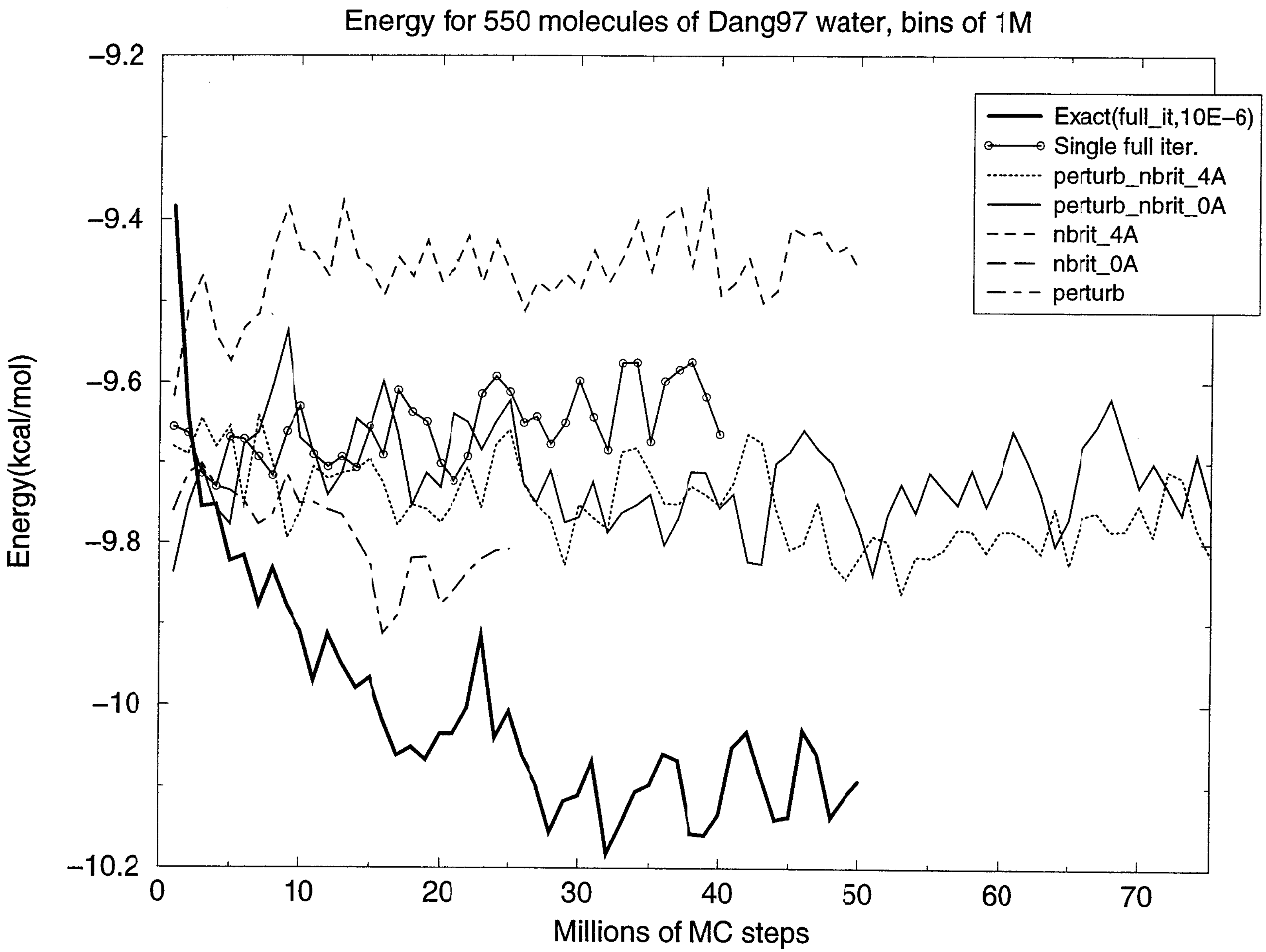

Density for water models
Density(g/cm^3)
1.14
1.09
1.04
0.99
0.94
0
10
20
30
40
50
Millions of MC steps
Dang93
Dang97
TIP4P

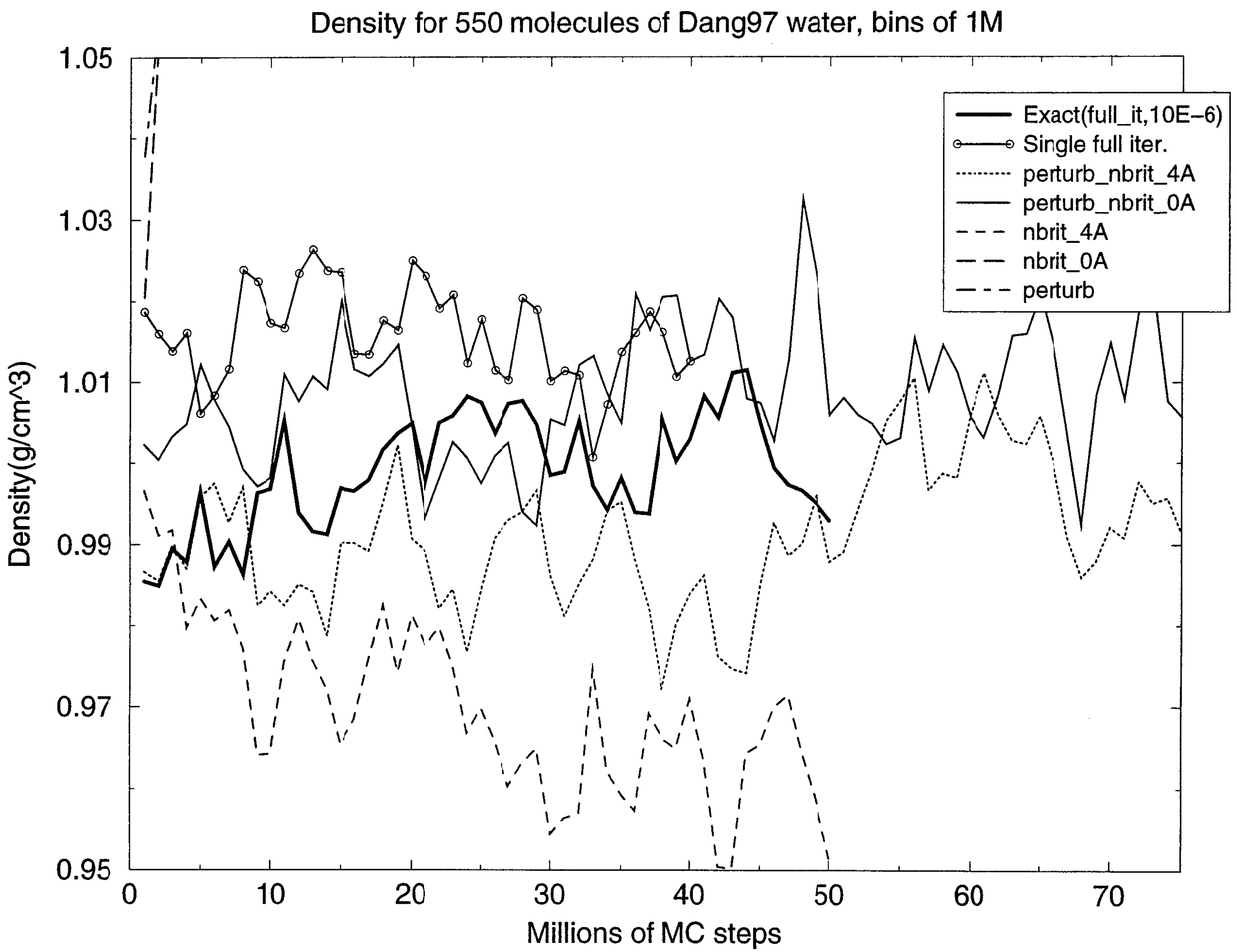


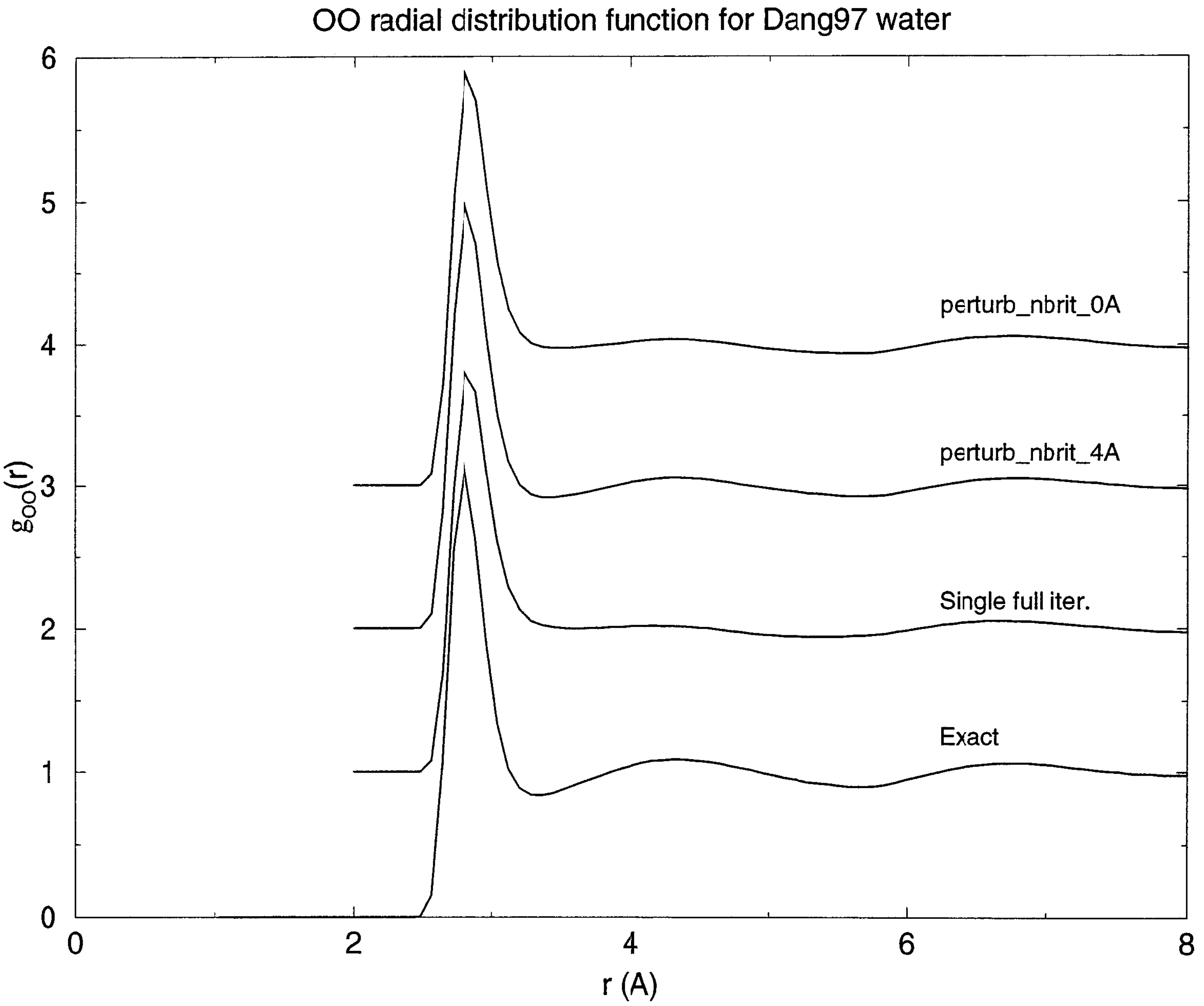
Dang97 Energy

NMOL=216, bins of 10K

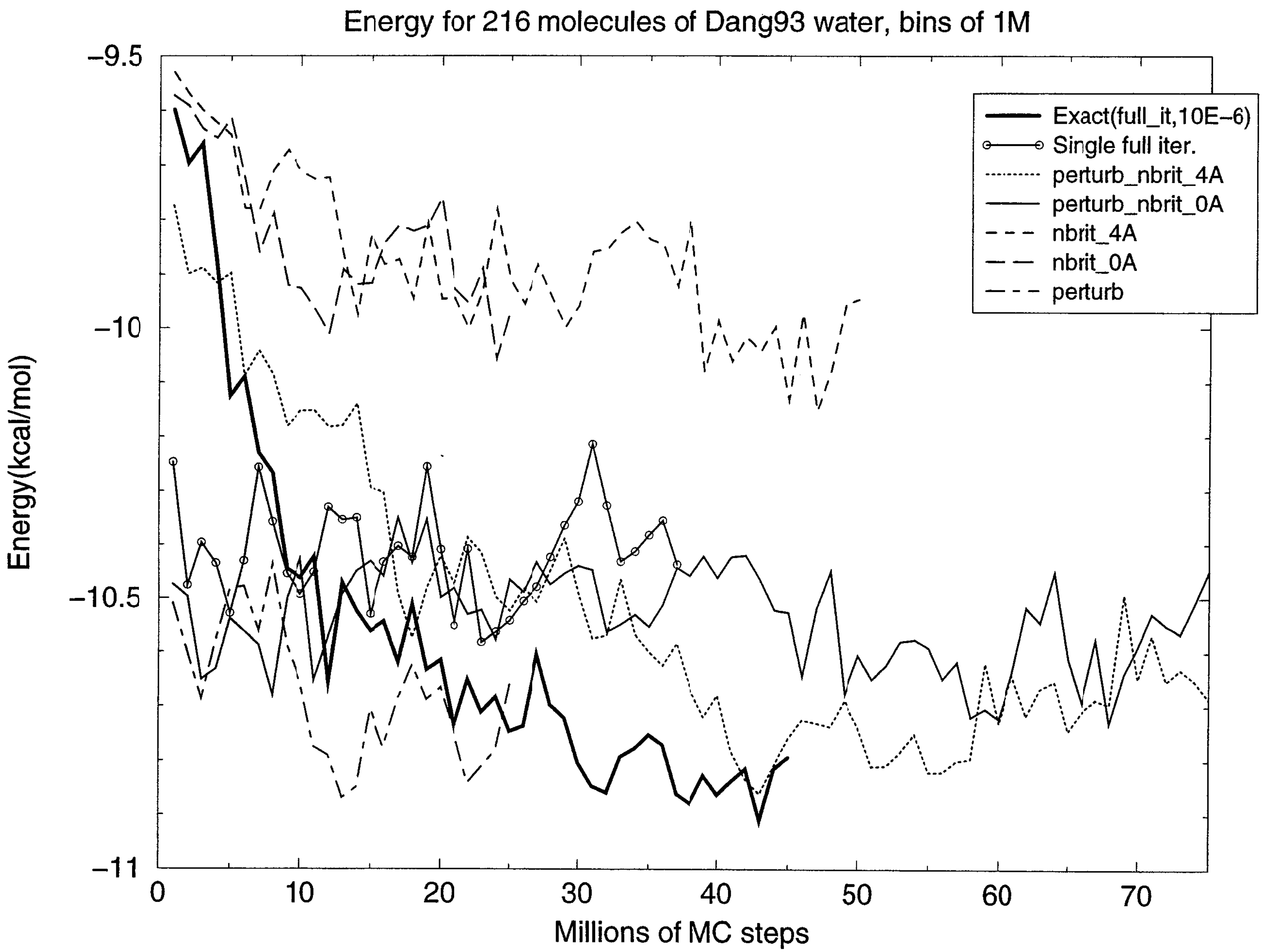

Induced dipole drift for Dang93 water
$<(\mu_{approx}-\mu_{exact})^2>^{1/2}/N_{mat}$
0.006
0.005
0.004
0.003
0.002
0.001
0
0
100
200
300
MC step number
single full iter
nbrit_4A
perturb
perturb_nbrit_4A


Energy for 550 molecules of Dang97 water, bins of 1M
Energy(kcal/mol)
-9.2
-9.4
-9.6
-9.8
-10
-10.2
0
10
20
30
40
50
60
70
Millions of MC steps
Exact(full_it,10E-6)
Single full iter.
perturb_nbrit_4A
perturb_nbrit_0A
nbrit_4A
nbrit_0A
perturb

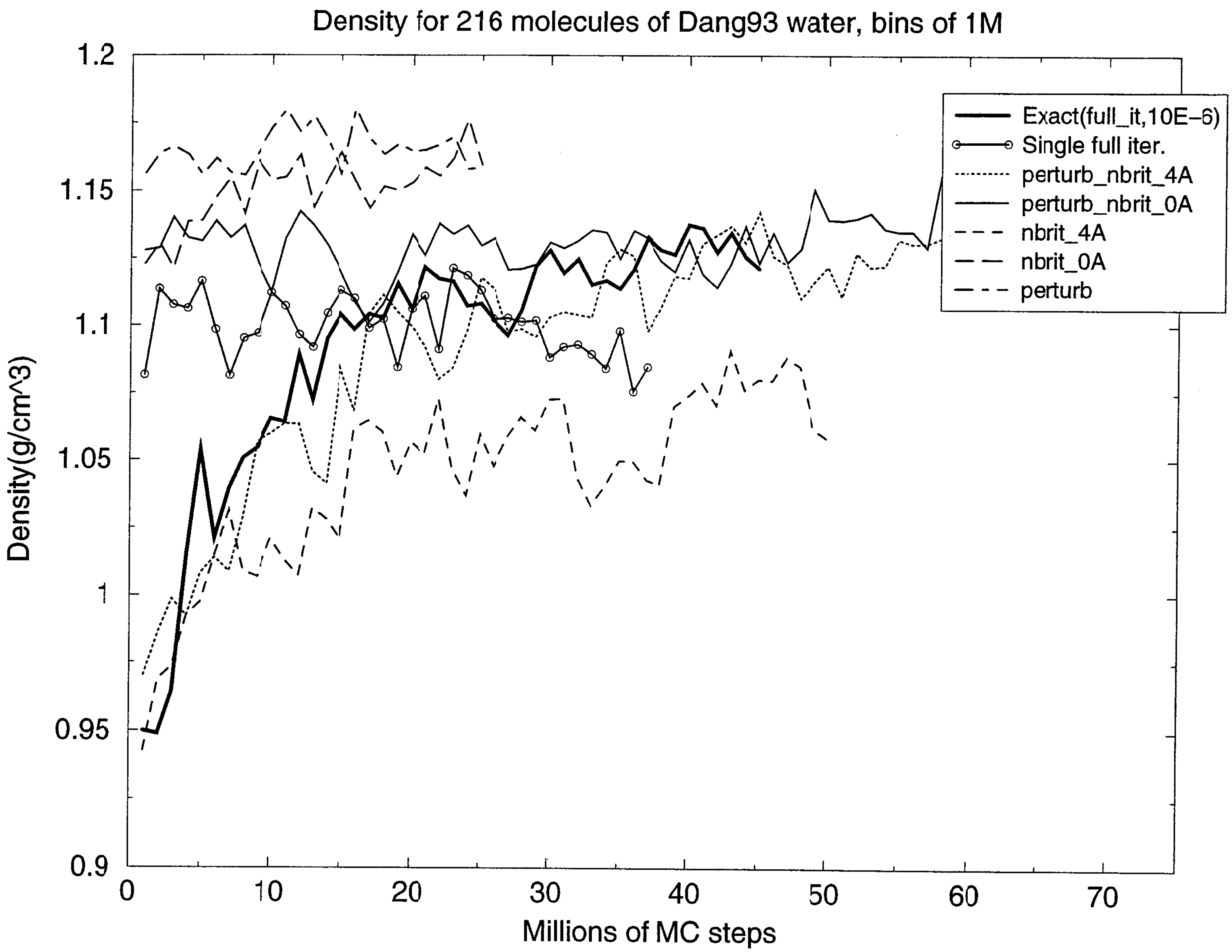

Density for 550 molecules of Dang97 water, bins of 1M
Density(g/cm^3)
1.05
1.03
1.01
0.99
0.97
0.95
0
10
20
30
40
50
60
70
Millions of MC steps
Exact(full_it,10E−6)
Single full iter.
perturb_nbrit_4A
perturb_nbrit_0A
nbrit_4A
nbrit_0A
perturb



OO radial distribution function for Dang97 water



Energy for 216 molecules of Dang93 water, bins of 1M


Density for 216 molecules of Dang93 water, bins of 1M
Density(g/cm^3)
Millions of MC steps
1.2
1.15
1.1
1.05
1
0.95
0.9
0
10
20
30
40
50
60
70
Exact(full_it,10E−6)
Single full iter.
perturb_nbrit_4A
perturb_nbrit_0A
nbrit_4A
nbrit_0A
perturb

Conclusions

TIP5P water has been developed and reproduces

- E, ρ at 25 °C and 1 atm,
- the TMD of liquid water,
- $g_{OO}(r)$,
- ε, the dielectric constant, and
- D, the diffusion constant.

Four-site models with classical intramolecular flexibility and electronic polarization have a worse density profile than TIP4P.

Quantum mechanical effects lead to worse results for non-reparameterized rigid models.

Quantum mechanical effects improve the results for classical flexible models.

Metropolis Monte Carlo on polarizable systems is difficult since

- N iterations per cycle and
- slower convergence as a function on Markov chain length.

Several novel rapid approximation methods have been developed and characterized for MC calculations on polarizable systems.