International Journal of Thermophysics, Vol. 7, No. 4, 1986

Monte Carlo Study of the Thermodynamics and Structure of Dense Supercritical Water[1]

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A system of 64 water molecules with a TIPS2 intermolecular pair potential was studied by the NPT-ensemble Monte Carlo method at 773 K and 100, 1000, and 3000 MPa. The values of enthalpy, specific volume, isobaric heat capacity, isothermal compressibility, and thermal expansion coefficients were obtained and found to be in good agreement with estimates from two equations of state of water. Computed atom–atom radial distribution functions agree well with recent high-temperature X-ray diffraction data. The effect of temperature and density increases on the O–O, O–H, and H–H correlations in water was analyzed. A quantitative comparison was made between thermodynamic properties and radial distribution functions of dense supercritical water and the simple Lennard–Jones fluid. The convergence rate was noted to increase under the conditions studied in comparison with Monte Carlo simulations of liquid water at normal temperature and pressure.

KEY WORDS: computer simulation; high pressures; high temperatures; Monte Carlo method; thermodynamic properties; water; water structure.

1. INTRODUCTION

In recent years, computer simulation methods have been much used in studies of complex associated molecular systems [1]. These methods enable one to compute thermodynamic properties and molecular distribution functions directly for a given intermolecular interaction potential.

With rare exceptions [2, 3], most studies of aqueous systems were done at normal temperature and pressure. Kataoka et al. [4] have studied about 300 points on the phase diagram of dense water and ice in a wide

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[1] Paper presented at the Ninth Symposium on Thermophysical Properties, June 24–27, 1985, Boulder, Colorado, U.S.A.

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temperature range. The intermolecular potential used in their study, however, gave only qualitative agreement between computed thermodynamic and structural properties and experimental data. O'Shea and Tremaine [5] have studied supercritical water by the Monte Carlo (MC) method with a quantum-mechanical potential, MCY [6]. They estimated the pressure under the conditions studied indirectly from an equation of state of water [7]. It is well known, however, that the MCY potential reproduces poorly the pressure at a given density (or volume at a given pressure) [1, 8]. The water structure was not studied under supercritical conditions either. The convergence rate of MC water simulations at high temperatures and pressures (densities) was also not estimated.

The aim of the present paper is to study in detail the dense supercritical water with a realistic intermolecular potential and to compare the results obtained with equations of state of water [7, 9] and recent high-temperature X-ray diffraction data [10].

Computer simulations are shown to provide a great deal of information concerning the properties of aqueous systems at high temperatures and pressures necessary for many applications, in part geochemical ones [11].

2. MONTE CARLO SIMULATION

The computations here used the conventional MC NPT-ensemble algorithm [12], with a cubic unit cell containing 64 water molecules with periodic boundary conditions. The water–water interaction pair potential TIPS2 [13] applied herein combines simplicity and good accuracy in describing the thermodynamics and structure of liquid water under normal conditions [1, 13].

Molecular configurations were generated using the procedure proposed by Barker and Watts [14]. A cyclically selected molecule was displaced randomly along each Cartesian axis. One axis (X, Y, or Z) then was choosen again at random, and the molecule rotated about this axis through a random angle. After every 320 moves the volume of the cell was changed randomly and all molecular coordinates were also changed.

The trial configuration was accepted with probability

$$\begin{aligned} p &= 1, && w \leqslant 0 \\ p &= \exp(-w/kT), && w > 0 \end{aligned} \tag{1}$$

where

$$w = \Delta U + P\Delta V - kT \cdot \ln(1 + \Delta V/V)^N \tag{2}$$

and ΔU and ΔV are the changes of the intermolecular potential energy and the volume of the system, respectively. Reiteration of such a procedure gives a chain of molecular configurations distributed in phase space with the probability density proportional to the pseudo-Boltzmann weight factor $V^N \exp[-(U+PV)/kT]$. To eliminate the input from the initial state and to equilibrate the system, about 150,000 attempted configurations at the beginning of every run were not included in the final averaging along the Markov chain.

The ranges of possible molecule displacement δl, rotation $\delta\varphi$, and volume increment δV were adjusted during the preequilibration run so that approximately one-half of the trial configurations was accepted and another one-half was rejected according to Eqs. (1) and (2) for both types of moves. The values obtained are given in Table I. (Here and elsewhere all linear dimensions are in angstroms: 1 Å $= 10^{-10}$ m $= 0.1$ nm.)

The energy of the molecule interaction with its neighbors was computed using the "minimum image convention" [12] without any corrections for truncation of long-range interactions. As has been shown by Andrea et al. [15], the errors involved using this procedure are very small.

In addition to the average enthalpy $\langle H \rangle = \langle U + PV \rangle$ and volume $\langle V \rangle$ at a given temperature and pressure, the values of the isobaric heat capacity C_P, isothermal compressibility κ, and thermal expansivity α were computed by the relations [16]

$$C_P = (\langle H^2 \rangle - \langle H \rangle^2)/NkT^2 \tag{3}$$

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = (\langle V^2 \rangle - \langle V \rangle^2)/NkT\langle V \rangle \tag{4}$$

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = (\langle HV \rangle - \langle H \rangle\langle V \rangle)/NkT^2\langle V \rangle \tag{5}$$

Table I. Characteristics of the Present MC Runs

T (K)	298	773	773	773
P (MPa)	0.1	100	1000	3000
L^a	480	160	120	120
δl (Å)	0.15	0.35	0.2	0.18
$\delta\varphi$ (deg)	15	45	30	22
δV (Å^3)	50	450	125	65
Acceptance ratio (%)	42	52	50	49

[a] Length of the Markov chain, 10^3 config.

To check this realization of the MC algorithm, all the properties of water under well-studied conditions (298 K and 0.1 MPa) were computed [17]. The thermodynamic and structural results of this simulation agree well with experimental data [10, 18] and Jorgensen' simulations [13, 19] for 125 and 256 molecules in the MC cell.

3. THERMODYNAMIC RESULTS

The thermodynamic properties of water on the 773 K supercritical isotherm at pressures of 100, 1000, and 3000 MPa are given in Table II. The values from equations of state of water derived by Jusa et al. (JSH) [9] and Haar et al. (HGK) [7] are taken for comparison as "experimental." The configurational enthalpy was estimated from these equations of state by [20]

$$H = H(T, P) - H(T, P = 0.1\ \text{MPa}) + NkT \tag{6}$$

Table II. Thermodynamic Properties of Water at 773 K

	P (MPa)		
	100	1000	3000
H ($\text{kJ} \cdot \text{mol}^{-1}$)			
MC	-14.49 ± 0.5	-8.51 ± 0.21	14.96 ± 0.25
JSH [9]	-14.66	-9.59	13.67
HGK [7]	-14.66	-9.51	15.17
V ($\text{cm}^3 \cdot \text{g}^{-1}$)			
MC	1.766 ± 0.049	1.038 ± 0.006	0.808 ± 0.002
JSH	1.893	0.988	0.787
HGK	1.893	0.972	0.751
C_P ($J \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$)			
MC	126.4 ± 16.8	59.0 ± 3.6	62.1 ± 4.6
JSH	100.2	64.0	61.3
HGK	100.1	63.6	61.4
$\kappa \cdot 10^5$ (MPa^{-1})			
MC	651 ± 119	24.19 ± 2.66	5.76 ± 0.78
JSH	548	21.0	6.95
HGK	543	23.1	8.0
$\alpha \cdot 10^5$ (K^{-1})			
MC	448 ± 82	40 ± 6	24.3 ± 4
JSH	330	46	25.9
HGK	328	41.1	12.2

The constant $3R$ ($\approx 24.94\ \mathrm{J \cdot mol^{-1} \cdot K^{-1}}$) was added to the computed C_P for the classical kinetic energy contributions from translation and rotation of molecules.

There are several methods to compute the quantum corrections to configurational properties of liquid water [1, 8, 21]. At high temperatures, the estimates by the method of Owicki and Scheraga [8] give corrections to the enthalpy of about $-3\ \mathrm{kJ \cdot mol^{-1}}$, which is considerably greater than the discrepancy between computed and experimental values at 1000 and 3000 MPa (see Table II). On the other hand, this discrepancy is not very large and, at high temperatures and pressures, can be connected with some inaccuracy of the potential TIPS2, whose parameters were choosen by fitting thermodynamic and structural properties of liquid water at 298 K and 0.1 MPa [13].

All the thermodynamic properties of water computed by the MC method agree well with those estimated from equations of state [7, 9] under a wide range of the conditions studied (Table II). One exception is the expansivity coefficient α at 3000 MPa. In this case, the MC and JSH values coincide, while HGK is less by half. This can be interpreted as the better extrapolability of equation JSH [9] at high pressures.

The present simulations show that the TIPS2 potential reproduces the water density in computer experiments with an accuracy of ~5% under a very wide range of conditions. This enabled us to get an adequate presentation of the dense supercritical water structure, which are discussed later in detail.

4. CONVERGENCE RATE

The convergence and statistical error bounds of MC simulations are usually estimated by the method of block averages (or batch means) [12]. Here the chain of configurations is divided into several nonoverlapping blocks of equal length, and the averages of every property are computed over each block. If $\langle A \rangle_i$ is the mean value of the property A computed over the block i, then statistical errors δA of the mean value $\langle A \rangle$ over the whole ensemble of configurations can be estimated as follows:

$$(\delta A)^2 = \frac{1}{M(M-1)} \sum_{i=1}^{M} [\langle A^2 \rangle_i - \langle A \rangle_i^2] \tag{7}$$

where M is the number of blocks.

Strictly, expression (7) is valid if all $\langle A \rangle_i$ are statistically independent and normally distributed. Thus in computer simulations of insufficient length, these error bounds are to be taken with caution [1]. However, the

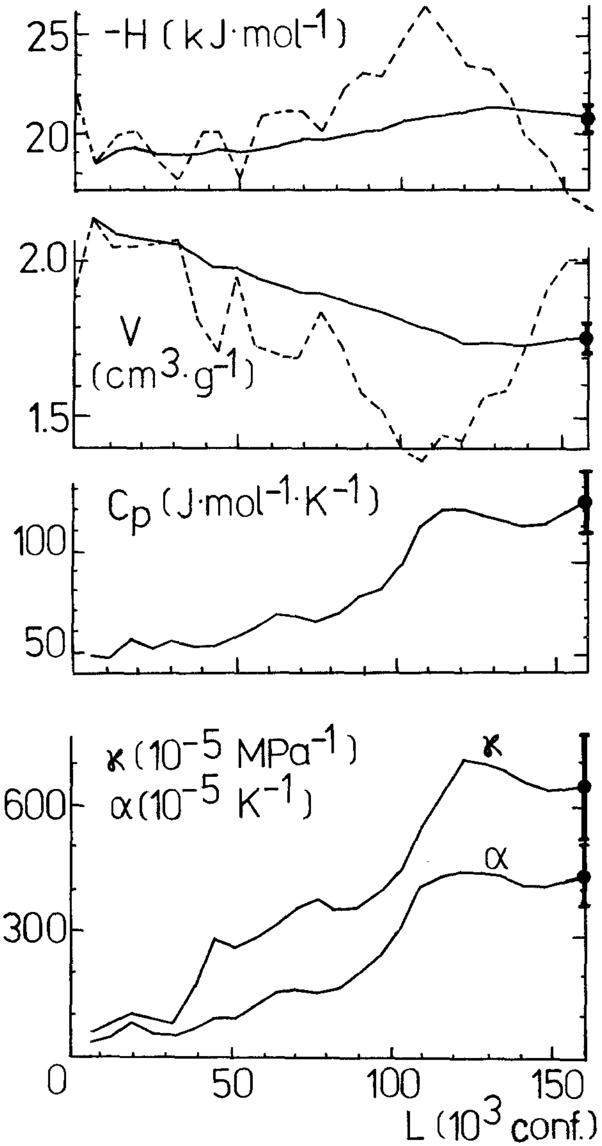

Fig. 1. Convergence profile for MC simulation of water at 773 K and 100 MPa. Dashed lines, block averages (see text).

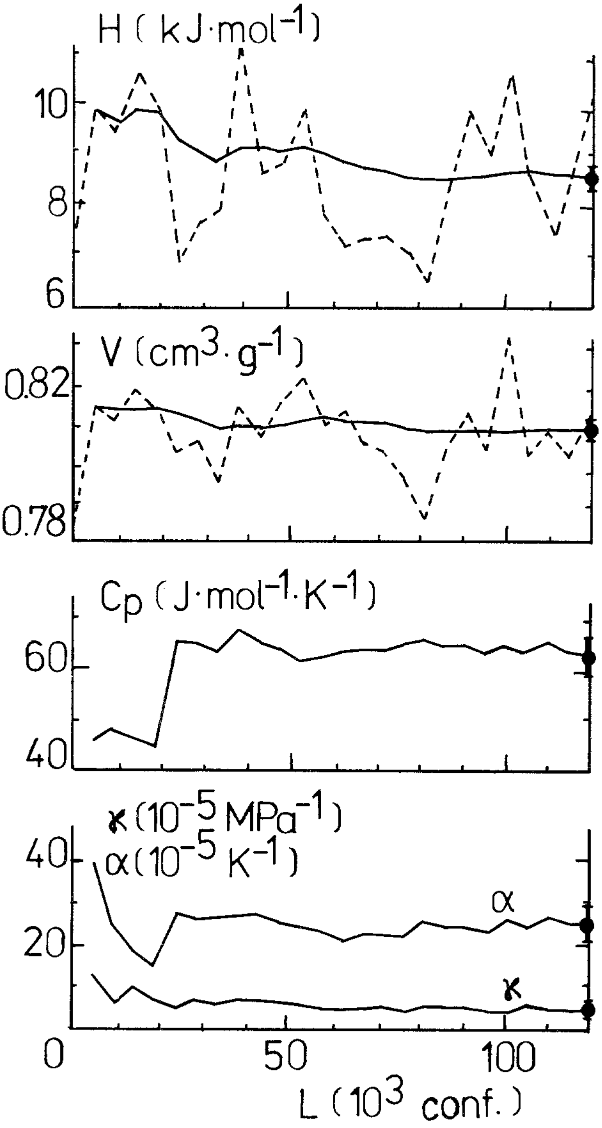

Fig. 2. Convergence profile for MC simulation of water at 773 K and 3000 MPa. Dashed lines, block averages.

calculations available show [22, 23] that such estimates are valid at least for $\langle H \rangle$ and $\langle V \rangle$.

One can also roughly estimate the error bounds as maximum variations in mean values during the final section of each run [5]. This results in error bounds of the same order as by Eq. (7) (see Figs. 1 and 2).

Since all the supercritical MC runs considered were about three to four times shorter in length than is usually recommended [1, 22] for simulations under normal conditions, a convergence analysis seems to be very useful. Figures 1 and 2 show convergence profiles of all the properties computed at two different pressures. It should be stressed that these diagrams demonstrate the convergence from equilibrium conditions.

Figures 1 and 2 show that a decrease in density decelerates considerably the convergence at supercritical temperature. This is not surprising (see, e.g., Ref. 24), in that fluctuations of thermodynamic properties (proportional to C_P, κ, and α) become significantly larger at 100 MPa compared to those at 3000 MPa.

Nonetheless, one can see from Figs. 1 and 2 and Table II that at 773 K a satisfactory convergence of all mean values (including such "badly converging" properties as C_P, κ, and α) is attainable after $2500 \cdot N$ and $1000 \cdot N$ configurations generated at 100 and 3000 MPa, respectively, in contrast to the $8000 \cdot N$ recommended for simulations of liquid water at 298 K and 0.1 MPa [22].

5. STRUCTURE OF SUPERCRITICAL WATER

Radial distribution functions reflecting the water structure under the supercritical conditions studied are shown in Figs. 3–5. Figure 3 demonstrates a very good agreement between computed and experimental [10] functions.

The water density at 773 K and 1000 MPa is virtually the same as at 298 K and 0.1 MPa (see Table II). Therefore Fig. 4 most explicitly shows the effect of high temperatures on the water structure. The tetrahedral nearest ordering of water molecules, which gives a second peak in $g_{OO}(r)$ at $\approx$4.5 Å, is seen to disappear under these conditions. The coordination number

$$n(r) = 4\pi\rho \int_0^r r^2 g_{OO}(r)\, dr \tag{8}$$

computed by integration to the first g_{OO} minimum, equals 11.6, in comparison to 4.5 under normal conditions [10]. However, the presence of a small first peak in g_{OH} at $\approx$2 Å indicates that hydrogen bonding still exists in water under the conditions studied.

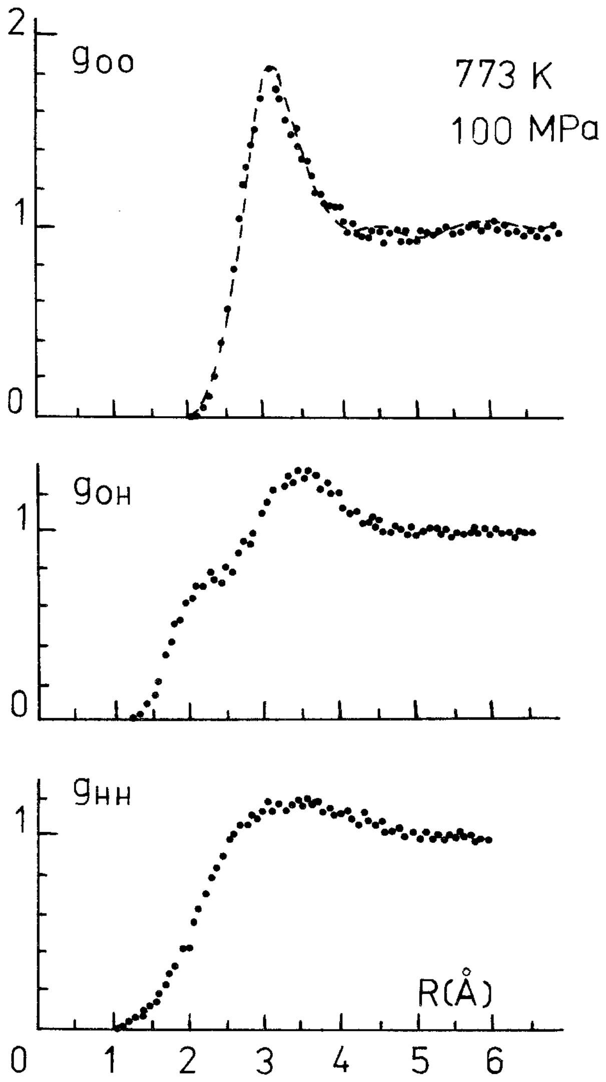

Fig. 3. Atom–atom radial distribution functions for water at 773 K and 100 MPa. Filled circles, present MC results; dashed line, X-ray experimental data [10].

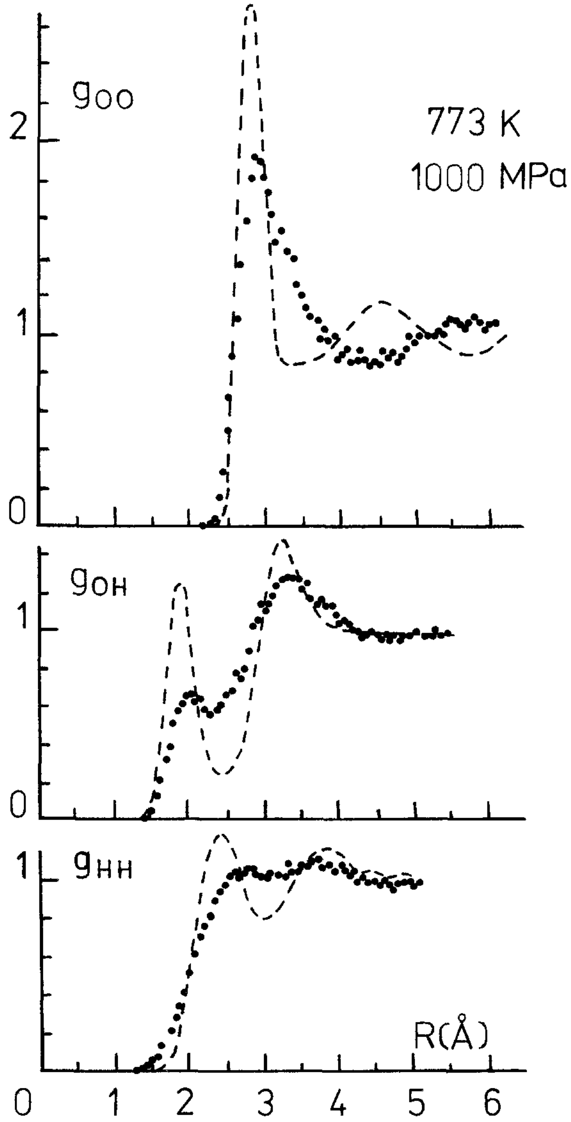

Fig. 4. Atom–atom radial distribution functions for water at 773 K and 1000 MPa. Filled circles, present MC results; dashed lines, MC results at 298 K and 0.1 MPa. The water density is virtually the same in both cases (see Table II).

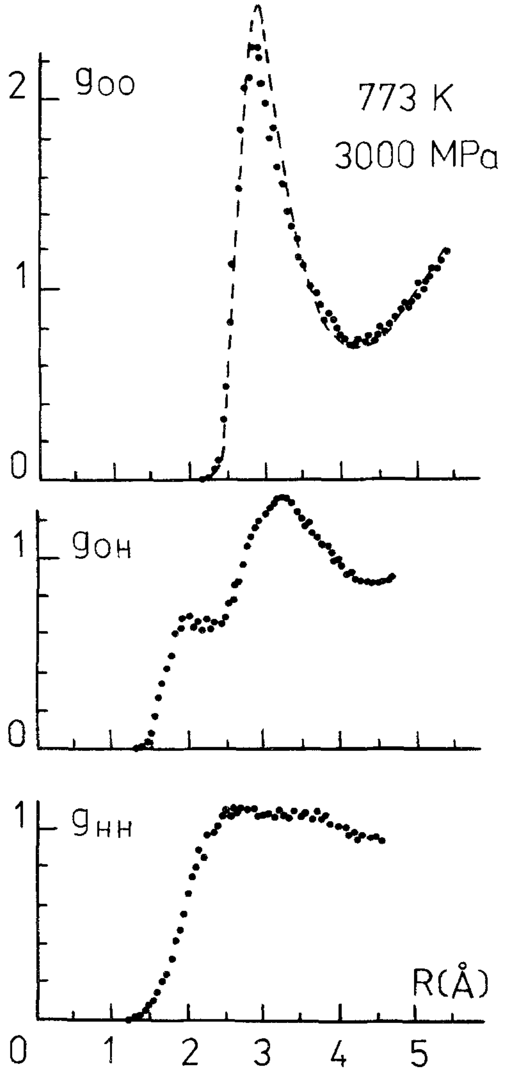

Fig. 5. Atom–atom radial distribution functions for water at 773 K and 3000 MPa. Filled cricles, present MC results; dashed line, Lennard–Jones radial distribution function at $T^* = 2.71$ and $\rho^* = 0.95$ [25] (see also Table III).

Table III. Comparison of the Thermodynamic Properties of Water at 773 K and 3000 MPa and Those of Lennard–Jones Fluid

	$\sigma^* = \frac{N\sigma^3}{V}$	$T^* = \frac{kT}{\varepsilon}$	$P^* = \frac{P\sigma^3}{\varepsilon}$	$H^* = \frac{H}{NkT}$
Water[a]	0.957	2.58	16.78	2.33
LJ fluid [25]	0.95	2.71	15.83	4.48

[a] For water the following is assumed: $\sigma = 2.85$ Å and $\varepsilon/k = 300$ K.

The comparison of g_{OH} and g_{HH} at 773 K and different pressures (Figs. 3–5) shows that an approximately twofold change in the density between 100 and 3000 MPa barely affects these functions. This confirms the inference that the number of hydrogen bonds in water depends chiefly on the temperature.

As has been noted earlier in computer simulations at elevated temperatures and densities [2, 3], the water structure becomes qualitatively similar to that of simple liquids. Figure 5 shows radial distribution functions for water at 773 K and 3000 MPa as well as for the Lennard–Jones fluid [25]. The agreement between these two curves is fair. The dimensionless thermodynamic properties of water and the Lennard–Jones fluid are given in Table III. Since the choice of the Lennard–Jones parameters σ and ε was largely arbitrary (only the value of σ was estimated more or less precisely from the first g_{OO} maximum), the agreement can be considered really good.

Obviously, this comparison of the thermodynamics and structure of water with those of a simple liquid needs more discussion. However, it is hoped that the water–water interaction might be treated as spherical-symmetric at lower temperatures and pressures than it was estimated by Ree [26] from the analysis of shock-wave data for water.

6. CONCLUSIONS

Our simulations have shown that the empirical intermolecular potential TIPS2 originally proposed for computer simulations of liquid water at 298 K and 0.1 MPa reproduces accurately the water thermodynamics and structure under a very wide range of conditions. The convergence of water MC simulations was analyzed. At high temperatures and pressures the Markov process was shown to converge considerably faster in contrast to the usual MC simulations under normal conditions. A quantitative similarity of the thermodynamics and structure of dense supercritical water and a simple Lennard–Jones fluid was also noted.

ACKNOWLEDGMENTS

The author is very grateful to Professor G. E. Norman and Dr. Yu. E. Gorbaty for helpful discussions and valuable remarks. The author also thanks Professor K. E. Gubbins, who kindly provided us with full tables of results of his Lennard–Jones simulations.

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