Monte Carlo Simulations of Water under Supercritical Conditions. II. Convergence Characteristics and the System Size Effects

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The size dependence and convergence rates of thermodynamic averages during Monte Carlo simulations of supercritical water in a wide range of densities have been analysed and compared with simulations under normal conditions. It is shown that the fluctuations of internal energy (enthalpy) in NPT-ensemble Monte Carlo simulations of high-temperature water are strongly correlated with fluctuations of volume and the convergence of the thermodynamic averaging under such conditions depends on the frequency of volume-changing moves and may be considerably improved by increasing this frequency by a factor of 3–10 relative to generally accepted values.

Key words: Monte Carlo computer simulations, Supercritical conditions, Thermodynamic properties, Convergence analysis.

1. Introduction

The knowledge of thermodynamic and structural properties of aqueous systems at high temperatures and pressures is of great importance for various scientific and technological applications, including geochemistry, chemical and power engineering, and environmental chemistry [1–4]. Monte Carlo (MC) and Molecular Dynamics (MD) computer simulations of these systems have long been considered highly desirable [5, 6] in order to understand of the correlations between the microscopic properties of the systems (e.g., positions, velocities and orientations of individual particles) and their macroscopic, experimentally measurable, thermodynamic and structural properties.

Although MD and MC simulations are now routinely applied to various rather complex aqueous systems under normal conditions (e.g., [7]), systematical simulations over a much wider range of thermodynamic conditions were started only in recent years. The results already obtained [8–17] unequivocally demonstrate that computer simulations can contribute significantly to a better understanding of the properties of high-temperature aqueous systems. However, many technical questions concerning, for instance, the applicability of available intermolecular potentials for high-pressure and high-temperature simulations, convergence of time averages (MD) and ensemble averages (MC) under these conditions, still require additional careful consideration.

In this paper the convergence characteristics and the system size dependence of recent MC results [16] on pure supercritical water are discussed. The technical details of the simulations are briefly described in Section 2. In Sect. 3 the convergence of the MC averages depending on thermodynamic and computational variables is analysed. The influence of the system size on the results is described in Sect. 4, followed by general conclusions in Section 5.

2. Methodology of the Simulations

A standard isothermal-isobaric MC algorithm (e.g., [18]) has been applied to a system of N water molecules in a cubic unit cell with periodic boundary conditions. The molecules were interacting via the TIP4P [19] rigid four-site effective pair potential. The minimum image principle [18] was applied to calculate the energy of the intermolecular interactions with a molecular cutoff criterion based on the coordinates of the oxygen atoms. No long-range corrections were made. As it was shown earlier [20] that such a method leads to only small errors in the resulting thermodynamic properties and atom-atom radial distribution func-

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tions even with $N=64$ which may be neglected in most cases.

New configurations were generated by cyclically selecting a water molecule, translating it randomly along all three Cartesian axes, and rotating it randomly about of the axes, again chosen at random. After a random number of trial configurations, amounting in the preset average to n_V, attempts were made to change the volume of the system by scaling all intermolecular distances. For both types of moves the new configuration was accepted with probability

$$p=\begin{cases}1 & \Delta H \le 0;\\ \exp(-\Delta H/k_B T) & \Delta H > 0,\end{cases} \tag{1}$$

where

$$\Delta H=\Delta U+P\,\Delta V-k_B T\,\ln(1+\Delta V/V)^N, \tag{2}$$

and ΔU and ΔV are the changes of the intermolecular potential energy and the volume of the simulation cell, respectively. Such a procedure results in a chain of molecular configurations distributed in the phase space of the system with the probability density proportional to the pseudo-Boltzmann weight factor $V^N \exp[-(U+PV)/k_B T]$ corresponding to the isothermal-isobaric statistical ensemble [18].

Eight thermodynamic states along two supercritical isotherms 773 and 673 K in a wide pressure range from 0.3 to 30 kbar (1 kbar = 0.1 GPa) have been studied. This pressure range corresponds to molar volumes from ≈14 to ≈100 cm^3/mol; thus a rather wide range of water densities has been sampled. Thermodynamic and structural results of these simulations as well as their comparison with experimental data have been discussed at length in [16].

Table 1. Parameters of the Monte Carlo runs.

Run	T/K	P/bar	N	n_V	Configs. $\times 10^{-6}$
1 B	773	30	64	128	1.10
1 C	773	30	64	128	0.60
1 D	773	30	64	320	0.62
1 E	773	30	64	25	0.42
1 F	773	30	216	432	1.10
2 A	673	0.5	64	128	1.60
2 B	673	0.5	64	320	1.60
2 C	673	0.5	64	32	1.60
3 A	673	0.3	64	32	1.73
3 B	673	0.3	64	128	1.73
3 C	673	0.3	216	216	1.60

Besides the trivial averages for the configurational enthalpy

$$H=\langle U\rangle+P\langle V\rangle, \tag{3}$$

and molar volume

$$V_m=\langle V\rangle\, N_A/N, \tag{4}$$

also the isobaric heat capacity C_P, isothermal compressibility $\varkappa$, and thermal expansivity α have been calculated from the corresponding fluctuation relations

$$C_P=(\langle H^2\rangle-\langle H\rangle^2)/N\,k_B T^2, \tag{5}$$

$$\varkappa \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T=(\langle V^2\rangle-\langle V\rangle^2)/N\,k_B T\,\langle V\rangle, \tag{6}$$

$$\alpha \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P=(\langle HV\rangle-\langle H\rangle\,\langle V\rangle)/N\,k_B T^2\,\langle V\rangle, \tag{7}$$

where angular brackets stand for the averaging over the ensemble of MC configurations.

The statistical uncertainties ($\pm 1\,\sigma$) of the thermodynamic properties were calculated from separate averages over batches [18] of 64 000 configurations. These batches are supposed to be large enough to get reasonable estimates of uncertainties for all the properties except, probably, thermal expansion coefficients.

Three thermodynamic states corresponding to the highest and the lowest pressures (densities) studied have been chosen for a more careful analysis of the dependence of the final results and their statistical uncertainties on the length of the simulation, the frequency of volume-changing MC moves (n_V), and the size of the batches. Technical parameters of these MC runs are given in Table 1. In every case from 0.5×10^6 to 1.5×10^6 preequilibration configurations were generated before the averaging actually started.

3. Convergence of Monte Carlo Simulations

During every run the convergence of the MC simulations has been monitored by plotting both running averages for all the thermodynamic properties calculated and local averages over batches of 64 000 configurations. The corresponding convergence diagrams are shown in Figures 1–3.

It has been noted before [21] that, contrary to normal conditions, where the enthalpy and volume fluc-

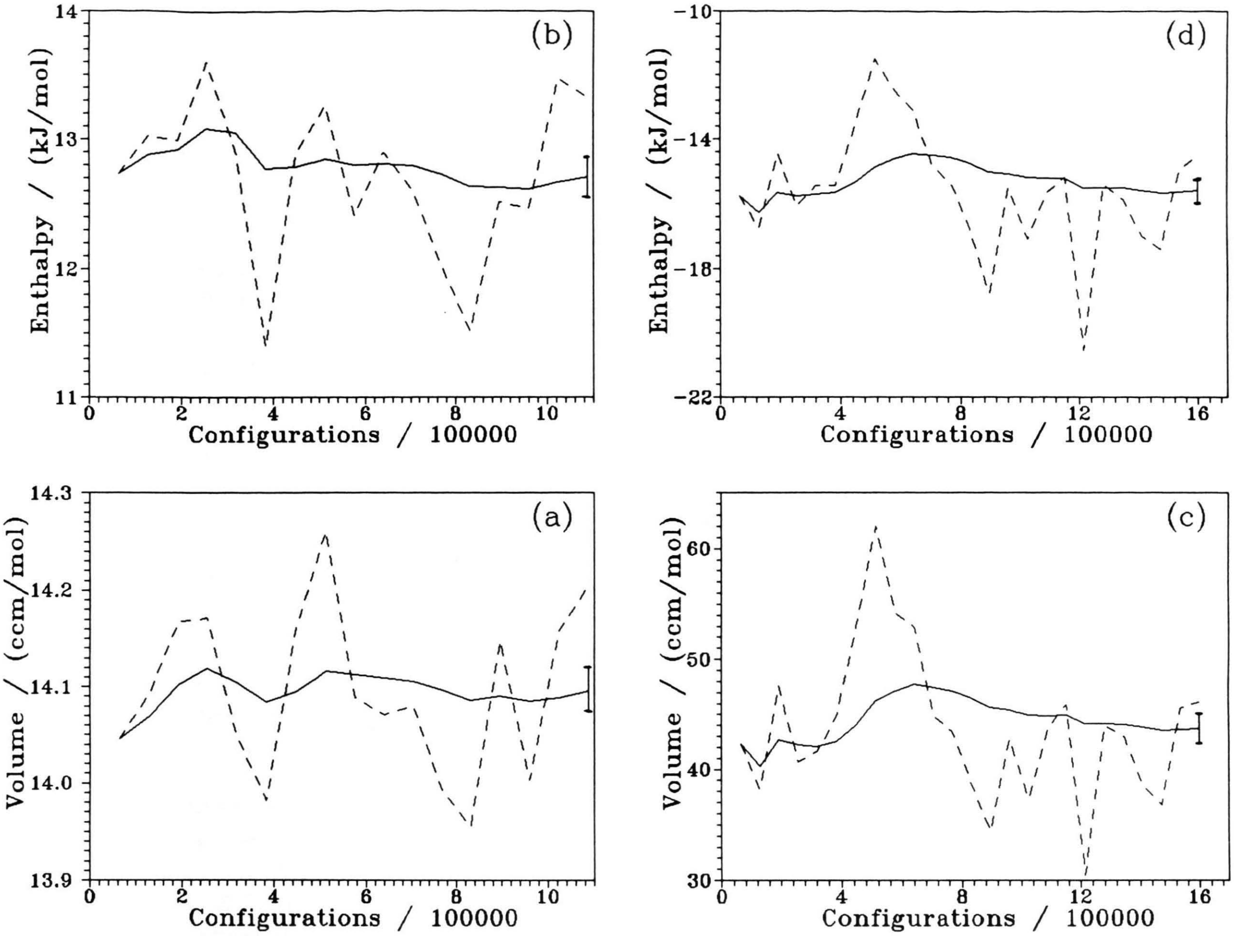

Fig. 1. Convergence of the molar volume (a), (c) and the configurational enthalpy (b), (d) for MC runs under high-density (773 K, 30 kbar; run 1 B) (a), (b) and low density (673 K, 0.5 kbar; run 2 A) (c), (d) conditions. Full lines represent running averages while dashed lines are for local averages over batches of 64 K configurations. Error bars show estimated statistical errors of the simulations. The attempts to change the volume of the system were made in both cases on the average after very $n_V = 128$ configurations (see Sect. 2 for the description of the algorithm).

tuate during an NPT-ensemble MC water simulation fairly independently [22], the fluctuations of both properties are significantly correlated under high-temperature conditions. Although this correlation is not very much pronounced at high densities (Fig. 1 a and b), it becomes very strong at low densities (Fig. 1 c and d). The reason for such a behaviour could be seen in the criterion for acceptance of new MC configurations, (2), where the last two terms become more important with decreasing density and increasing fluctuations of volume. A detailed analysis of the relative influence of all three terms in (2) on the acceptance criterion in NPT-ensemble MC simulations under high-temperature, high-pressure conditions deserves special attention and will be presented elsewhere [23]. However, preliminary estimates show that at least in the case of low-density simulations the main reason for the correlation between the fluctuations of H and V is not the increasing contribution of the PV term to the configurational enthalpy, (3), but a strong dependence of the configurational energy U on V.

Because of this correlation between H and V in our simulations, convergence characteristics of heat capacity, compressibility, and even thermal expansion coefficient (see (5)–(7)) are also strongly correlated. This leads us to the assumption that more frequent than it is usually recommended ($\approx 5N$) [18, 22] attempts to change the volume of the system may help to speed up significantly the convergence of NPT-simulations. The results of high-density simulations (runs 1 C–E)

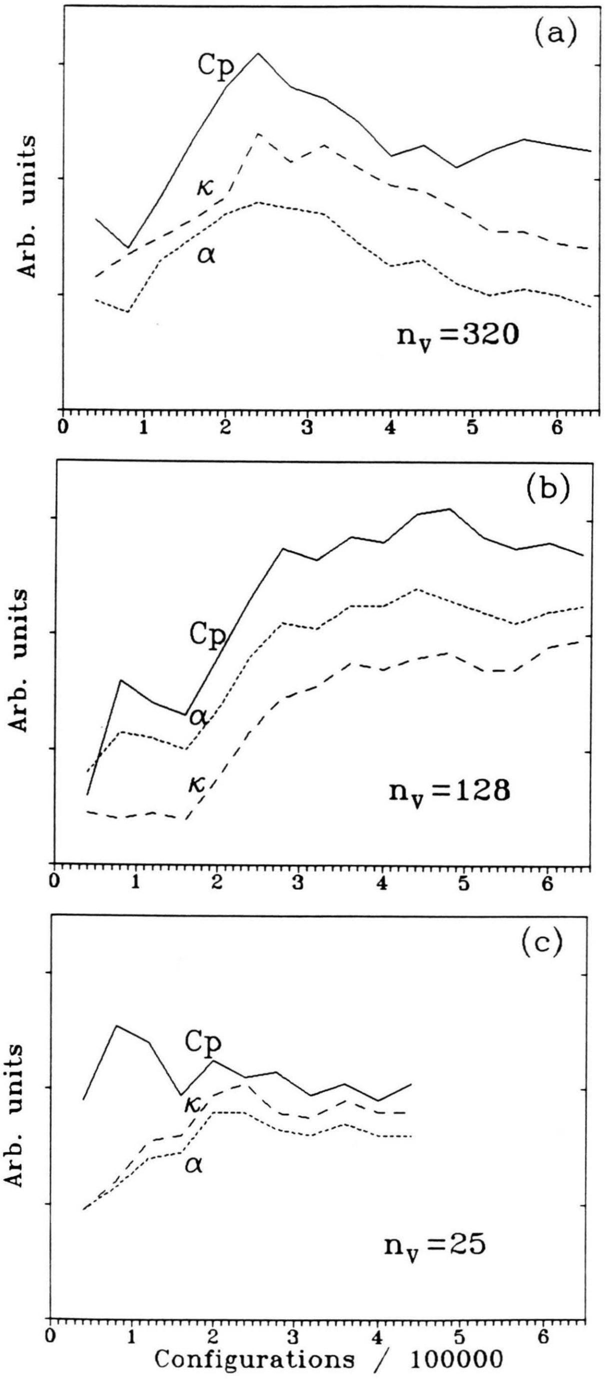

Fig. 2. Dependence of the convergence rate on the frequency of volume-changing MC-moves (n_V) at 773 K and 30 kbar (runs 1 C–E in Tables 1 and 2). All three simulations started from the same initial configuration. Full, dashed, and dotted lines represent running averages for C_P, $\varkappa$, and α, respectively, in arbitrary units. Final values of every property and corresponding error estimates are given in Table 2.

started from the same preequilibrated initial configuration but with different values of n_V are shown in Fig. 2 and Table 2. As can clearly be seen from the convergence diagrams, with $n_V = 25$ all properties including α converge very well after $\approx$200 k configurations, at $n_V = 128$ it already takes $\approx$400 k configurations, while in the case of $n_V = 320$ all three fluctuational properties have seemingly still not converged even after $\approx$600 k configurations.

The comparison of the results of the two high-density runs 1 B and 1 C in Table 2 shows that only a run almost twice as long (with the same n_V parameter) improves the statistical errors, while the average thermodynamic properties remain virtually unchanged.

In low-density simulations (runs 2 B–C and 3 A–B) the discussed effect is not so profound because it is screened by large fluctuations of all properties. As can be seen in Fig. 3, however, more frequent volume-changing moves help to improve significantly the statistics of batch averages even for C_P, which does not depend directly on volume (see (5)). In the case of $n_V = 128$ (Fig. 3 c–d) the size of the batch used (64 k configurations) is clearly too small to get reasonable batch averages, and error bars for the run 3 B must be considered as underestimated.

It should be noted that volume-changing moves in the NPT-ensemble MC simulations of molecular liquids are much more computer-time-consuming than the usual MC moves because of the necessity to rescale the coordinates of all interaction sites in the system and to recalculate correspondingly all pair interaction energies. However, if a vectorization is possible (as in our case), a tenfold increase of the frequency of volume-changing moves slows down the average speed of the calculations by only $\approx 25\%$, which may be generally considered an acceptable price for the improvement of the convergence.

It is well known (see e.g., [22]) that structural properties converge very rapidly, even in the case of liquid water simulations under normal conditions. We observed that the situation only improves with increasing temperature. Therefore, the convergence of atom-atom radial distribution functions obtained in the present supercritical simulations deserves no special discussion.

4. Influence of the System Size

For two extreme cases of the highest and the lowest densities studied the effect of the system size on the

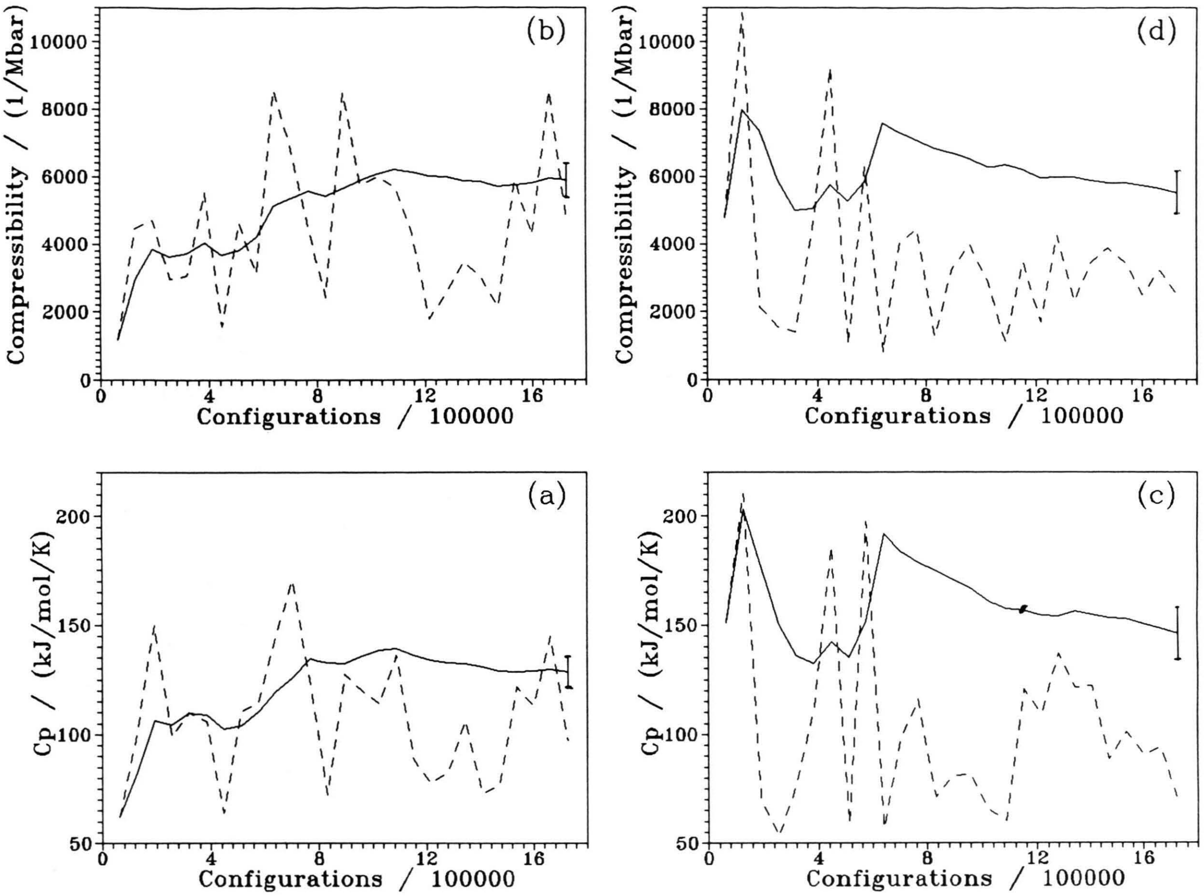

Fig. 3. Convergence diagrams for C_P and $\varkappa$ at 673 K and 0.3 kbar. (a), (b): $n_V = 32$; (c), (d): $n_V = 128$ (runs 3 A–B in Tables 1 and 2). Full lines represent running averages and dashed lines local averages over batches of 64 K configurations. Error bars show estimated statistical errors of the simulation.

Table 2. Convergence of thermodynamic results.

Run	T K	P kbar	n_V	V_m cm^3/mol	H kJ/mol	C_P J/(mol · K)	$\varkappa$ 1/Mbar	$\alpha \cdot 10^5$ 1/K
1 B	773	30	128	14.10 ± 0.02	12.72 ± 0.17	59.8 ± 2.1	6.9 ± 03	27.5 ± 1.6
1 C	773	30	128	14.13 ± 0.05	12.84 ± 0.38	64.4 ± 5.0	7.1 ± 0.6	30.4 ± 3.0
1 D	773	30	320	14.13 ± 0.05	13.05 ± 0.42	72.8 ± 8.8	8.4 ± 1.3	39.7 ± 5.0
1 E	773	30	25	14.12 ± 0.05	12.76 ± 0.38	57.3 ± 2.1	6.9 ± 0.5	26.3 ± 2.2
2 B	673	0.5	320	46.23 ± 1.22	−14.85 ± 0.33	117.6 ± 10.5	1540 ± 210	580 ± 80
2 C	673	0.5	32	47.21 ± 0.99	−14.60 ± 0.25	122.6 ± 7.5	1680 ± 160	620 ± 60
3 A	673	0.3	32	96.91 ± 2.20	− 8.24 ± 0.21	128.9 ± 6.7	5900 ± 490	850 ± 70
3 B	673	0.3	128	97.34 ± 2.50	− 8.28 ± 0.29	146.0 ± 11.7	5530 ± 600	890 ± 100

thermodynamic and structural results of the simulations has also been examined. The computed thermodynamic properties for these runs are given in Table 3. As in the case of normal liquid water simulations [24], under high-temperature, high-density conditions (runs 1 B and 1 F) the configurational enthalpy and the volume are only slightly lower for the larger system while differences in all other properties can hardly be considered statistically significant.

In low-density simulations the difference in molar volumes becomes as large as 7.8%. The difference between the calculated enthalpies for the runs 3 A and

Table 3. Size dependence of thermodynamic results.

Run	T K	P kbar	N	V_m cm^3/mol	H kJ/mol	C_P J/(mol · K)	$\varkappa$ 1/Mbar	$\alpha \cdot 10^5$ 1/K
1 B	773	30	64	14.10 ± 0.02	12.72 ± 0.17	59.8 ± 2.1	6.9 ± 0.3	27.5 ± 1.6
1 F	773	30	216	14.03 ± 0.02	12.35 ± 0.10	61.1 ± 2.2	6.7 ± 0.5	24.6 ± 2.6
3 A	673	0.3	64	96.91 ± 2.20	-8.24 ± 0.21	128.9 ± 6.7	5900 ± 490	850 ± 70
3 C	673	0.3	216	89.70 ± 1.50	-9.04 ± 0.18	120.2 ± 10.8	4500 ± 600	725 ± 100

3 C in Table 3 is not too important, because it can be completely attributed to the difference of densities (see discussion of the thermodynamic results in [16]).

It should be noted here that during the simulations at low-density close to the critical point (673 K and 0.3 kbar in our case) the volume of the system experiences extremely large fluctuations which leads, in turn, to large fluctuations of enthalpy and all other properties. For instance, during the run 3 A, the volume fluctuated from 49 to 168 cm^3/mol with the average value of 96.7 cm^3/mol, while the experimental value at the given pressure is only 50.31 cm^3/mol. The amplitude of these fluctuations decreases for the system with $N = 216$ (run 3 C), resulting, however, in only slightly better agreement with experiment (see Table 3). It seems therefore hardly probable that further increase of the system size could significantly improve the results.

5. Conclusions

Convergence rates of the thermodynamic averages of Monte Carlo simulations of supercritical water over a wide range of densities have been analysed and compared with simulations under normal conditions. It is shown that fluctuations of the internal energy (enthalpy) in isothermal-isobaric MC simulations of high-temperature water are strongly correlated with fluctuations of the volume and the convergence of MC averages under such conditions can be considerably improved by increasing the frequency of volume-changing moves by a factor of 3–10 relative to generally accepted values.

An examination of the size dependence of the present results has shown that simulations with only 64 molecules in the basic cell are reasonably accurate, as it was previously stated for simulations of liquid water under normal conditions [20, 22, 24]. At lower densities the size dependence of thermodynamic properties becomes seemingly stronger, and a larger number of molecules must be used in simulations. This findings is in accordance with recent results on simple model fluids [25], where the governing role of long-range attractive interactions has been established for the correct description of the structural and dynamical behavior of low-density fluids.

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