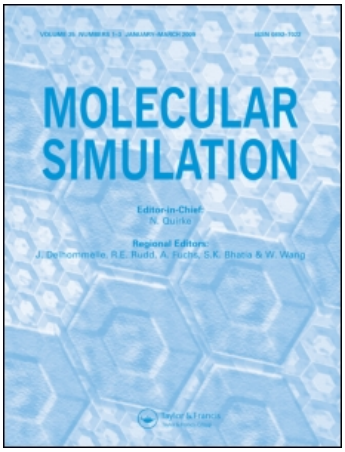

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Isochoric Temperature Differentials from the Computed Density of the Extended Simple Point Charge Model of Water

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ISOCHORIC TEMPERATURE DIFFERENTIALS FROM THE COMPUTED DENSITY OF THE EXTENDED SIMPLE POINT CHARGE MODEL OF WATER

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The temperature dependent density profile of liquid water is investigated for the SPC/E model in the vicinity of its density maximum. Isochoric temperature differentials and the differences in the number of neighbours with temperature, are computed and compared with X-ray scattering results. The successes and failings of the model help to the understanding of the implications of the aforementioned functions, and highlight the needed changes of the force field. The work also explores convergence of the computed density in current molecular dynamics simulations.

Keywords: Water density; isochoric temperature differentials; molecular dynamics

INTRODUCTION

The study of pure liquid water with computer simulation has been the subject of innumerable works for more than a quarter of a century [1]. Moreover, water as a solvent intervenes in several important fields and as such, simple water models are routinely used in studies for nonhomogeneous systems [2]. However, an important property such as the temperature dependence of the bulk density is still under scrutiny. While the initial works pointed to the existence of the density maximum at approximately the right temperature [3, 4], more recent work [5, 6] has underlined that a correct computation requires much longer simulation times, making the initial estimations unreliable. Because of this, the density profile has not been accurately computed until much improved computer capabilities have been

available. Recently [7], the density maximum of water was found to exist for the popular SPC/E model [8] (albeit at 40 K below its experimental value).

The unambiguous location of the density maximum for SPC/E water offers the opportunity to investigate what can be learned from this model in connection with the structural properties around the density maximum. Although SPC/E water has some definite limitations [7, 9], it is the most studied one probably because, among simple models, it shows the widest range of coincidence with experiment [10]. Its utility in the present context is justified given the amount of computation required, so that properties around the density maximum can only be investigated with this type of model at the present moment. This work provides the first direct comparison with X-ray isochoric temperature differentials (ITD) in the region of the maximum [11]. ITD have been proposed as a mean to help understand the structural changes that explain the density maximum existence [12], and are much less uncertain than radial distribution functions [11], which up to now have been the only sources of structural information. Actually, one of the aims of the experimental work was to help test the accuracy of molecular dynamics calculations [11], a probe that had not been possible so far. The present comparison shows some remarkable successes. In particular, averaged properties, such as the differences in the number of neighbours with distance, between two isochoric points, are in very good accord with experiment. The discrepancies suggest that the main inadequacies of the potentials are limited to the region of nearest neighbours, where structure is too marked. Recent neutron scattering results [13] have also indicated that the standard experimental results [14] overestimate water structure in this same region.

In addition, it is also shown that the computed density is still dependent on the parameters used for the simulation, most specially on the cut-off distance, to the point that values as high as 14 Å (requiring samples of the order of 1000 molecules) due not achieve convergence. The lack of full convergence is an issue that should be taken into account in future parameterization work, but does not necessarily imply that computations performed up to now are meaningless. Most of the important characteristics, such as the location of the maximum and its shape, are found to be largely insensitive to parameter variation.

METHODS

The simulations have been performed with standard Molecular Dynamics methods [15], with an in-house simulation code. The system consists of a

cubic box with periodic boundary conditions. The number of molecules has been varied between 108 and 900 water molecules, depending on the properties being studied. The model employed has been the SPC/E [8], maintaining the internal constraints with the SHAKE procedure [16] with a tolerance of 10^{-6}. The algorithm for the integration of the equations of motion has been the leap-frog with coupling to temperature and pressure baths of Berendsen *et al.* [17]. The time constant for the temperature bath has been set at 0.1 ps and the reference temperature varied from 298 K to 220 K (see below). For the pressure bath the time constant has been set at 0.5 ps, the isothermal compressibility at $4.8 \times 10^{-5}\,\text{bar}^{-1}$, and the reference pressure at 1 bar. The pressure has been computed from the virial expression. A time step of 1 fs has been used in all cases. The length of the simulations has basically depended on the temperature being studied, and ranges from a maximum of some 25 ns for $T = 220$ K, to a minimum of some 1.5 ns for $T = 280$ K. The length required for each temperature has been inferred from the indeterminacy computed with the statistical inefficiency method [15]. All the computed densities have an associated statistical indeterminacy of about $0.5 \times 10^{-4}\,\text{g/cm}^3$. Finally, a charge-group truncation scheme has been used, with a cut-off that has been varied between 7 Å and 14 Å (see below).

RESULTS AND DISCUSSION

Density Profile

The main purpose of this work consists in an accurate computation of radial distribution functions, along the temperature dependent density profile of liquid SPC/E water at constant pressure, in order to obtain ITD as free of noise as possible. The low temperatures at which the maximum appears for this model demand an intensive computation and thus, the number of molecules has been limited to 108, with a cut-off of 7 Å. These parameters allow comparison with the results of Ref. [7], where 360 molecules were used, with a cut-off of 9 Å (tests with the same parameters as in Ref. [7] have resulted in fully coincident results). The computational procedure has been performed as follows. An initial configuration has been generated at 298 K and equilibrated for 300 ps. The resulting final configuration has initiated a long production run at this same temperature. The same equilibrated configuration has been used as starting point for an equilibration run at a lower temperature (the downward temperature jumps have been of some 10 K). A similar procedure has been followed for the rest of the temperatures for the

equilibration and production times. The times involved in the calculation together with the values of the densities obtained for each temperature, are listed in Table I.

The computed densities, with associated confidence intervals, are displayed in Figure 1, together with the results of Ref. [7], and the experimental results. Several aspects are worth considering from this plot. First, the density maximum is still present for this sample size, with some of its characteristics unaltered. In particular, its position (about 235 K) and shape (it can be seen that the superposition of both profiles is coincident within statistical indeterminacy). Therefore, two of the main characteristics appear to be robust under substantial changes in both the number of molecules and force range. However, there is a nonnegligible difference between the two computed density profiles, and of these two curves with the experimental values. The exact experimental density is only achieved for 298 K and 108 water molecules, a coincidence explained by the fact that the original fitting was aimed to reproduce the density at room temperature for small samples [8]. Moreover, although the experimental and computed density profiles have very similar shapes, the mismatch in the location of the maximum is also very substantial as it has already been mentioned, and will be further discussed in the next section. What is remarkable from the methodological point of view is the nonnegligible difference between the two calculated density profiles, which is of the order of the difference with the experimental values. Indeed, if the difference between the maximum of the experimental density and the one for 108 molecules is of $0.016\,gr/cm^3$, the difference between the two computed curves is a comparable $0.011\,gr/cm^3$. That is, a reasonable change in the conditions of the simulation (computations of the density profile have been reported for these two sets of parameters), results in density differences which are of the order of the mismatch with experiment. The investigation of the effect of the cut-off and system size on the absolute value of the computed density will be the subject of the last section. In the next section though, a detailed comparison with structural

TABLE I Computed densities at several temperatures for a system size of 108 molecules. τ_e indicates the equilibration time, and τ_r the total production time of the runs

$T(K)$	$\tau_e(ns)$	$\tau_r(ns)$	*Density* (g/cm^3)	$T(K)$	$\tau_e(ns)$	$\tau_r(ps)$	*Density* (g/cm^3)
219.6	0.9	24.3	1.0149 ± 0.0009	260.6	0.3	6.2	1.0137 ± 0.0005
229.8	0.9	17.1	1.0159 ± 0.0008	269.9	0.3	2.7	1.0094 ± 0.0007
239.0	0.9	14.8	1.0160 ± 0.0005	280.2	0.3	1.2	1.0046 ± 0.0007
250.4	0.9	9.0	1.0148 ± 0.0005	298.7	0.3	3.8	0.9969 ± 0.0004

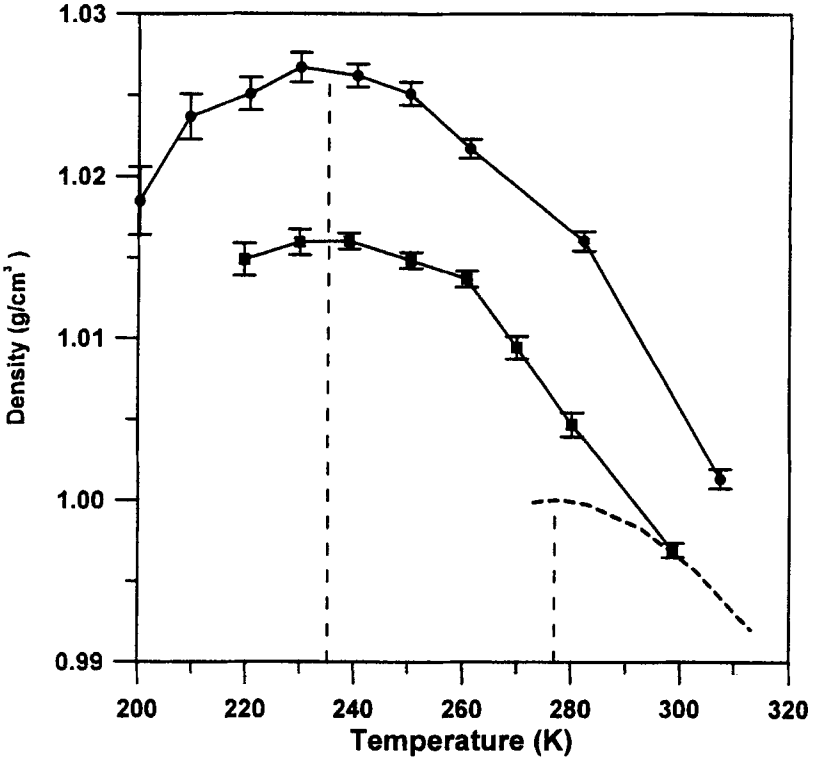

FIGURE 1 Density profile for SPC/E water. Full squares: density computed in this work; full circles: density computed in Ref. [7]; dashed curve: experimental density; vertical dashed lines: temperatures of the density maximum for the computed and experimental densities.

experimental results will be presented. The rationale for this comparison is that the main effect of the parameters of the simulation appears to be an overall shift of the densities, which does not alter the qualitative features of the profile. Given that the quantities of study are constructed as *differences* for pairs of different temperatures (see below) the possible effects of the shift most likely cancel out.

Isochoric Temperature Differentials

Temperature differentials were introduced for the study of the subtle temperature variations of water structure present in scattering data [18]. They can be defined for both the structure factor and for its Fourier transform, the radial distribution function ($g(r)$). The latter will be the one

used here, as it is more directly accessible with computer simulation. It is defined for a pair of different temperatures as

$$\Delta g(r) \equiv g(r, T_1) - g(r, T_2), \tag{1}$$

where one of the temperatures (say T_1) is usually taken as a fixed reference, and $g(r)$ refers to the oxygen–oxygen centres (as these are the main contributors in X-ray scattering). Isochoric temperature differentials (ITD) constitute a particular case [19]. In this technique pairs of points located on opposite sides of the density maximum, corresponding to identical densities, are used in Eq. (1). The benefit obtained from this procedure is that density corrections to the experimental data cancel out to first order, and the results are of much higher precision than those for the radial distribution function [11]. Detailed X-ray scattering data were published [11] a rather long time ago with the aim to allow comparison with computation results. This work also introduced a new quantitative measure to help understand the structural features of the density maximum,

$$\Delta N(R, \Delta T) = \rho \int_0^R \Delta g(r, \Delta T) 4\pi r^2 dr, \tag{2}$$

with $\Delta g(r, \Delta T)$ being an ITD. By construction $\Delta N(R, \Delta T)$ provides the difference in coordination number, for a pair of isochoric points, up to a distance R. Inspection of this quantity, and of ITD, showed that the most important differences between isochoric points were located in the region between first and second neighbours, rather than on structural rearrangements of the first shell [11, 12, 20]. Figure 2 displays an scaled plot of the region of the maximum, together with the two isochoric pairs that will be used in the analysis. As stated in the previous section, the density maximum for SPC/E is located at approximately 235 K, and consequently the pairs (230 K, 240 K) and (220 K, 250 K) are good isochoric points (Tab. I shows that the corresponding densities are almost identical within statistical indeterminacy).

In Figure 3 the differences in coordination number are compared with the experimental values. Actually, both the experimental and computed curves have been scaled by ΔT, so that the plotted functions are $N(R, \Delta T)/\Delta T$. When normalised in this way the computed curves for different isochoric pairs collapse on a single curve, as it also occurs with the experimental ones. Therefore, there exists an exact linear scaling of the computed and experimental curves with temperature, which reflects the scaling that ITD also show. This linear behaviour of the computed data, coincident with the

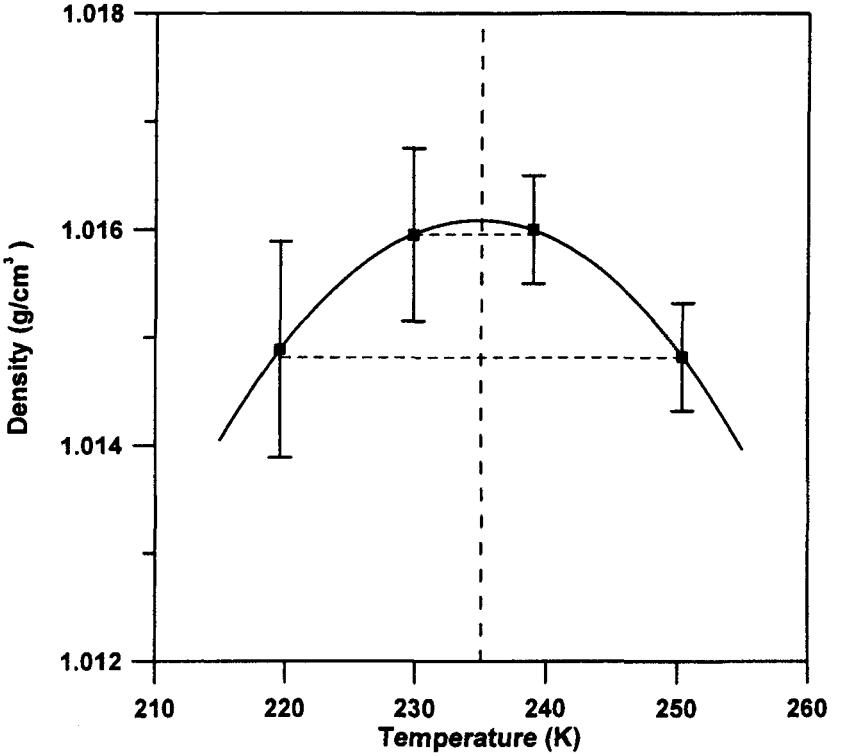

FIGURE 2 Squares: computed densities in the density maximum vicinity; solid line: parabolic fit; horizontal dashed lines: isochoric pairs. (Units g/cm^3).

experimental trend, is remarkable if we consider that the linear behaviour occurs for a rather large temperature difference (30 K), comparable with the maximum experimental temperature difference (51 K) [11]. Moreover, there is an excellent quantitative accord for almost all distances, specially considering the very subtle nature of the variations involved. Only at about 3 Å the simulated curve is more peaked than the experimental one. However, this minor mismatch is mainly quantitative. The function attains zero value for both curves in about the same location after this first peak (that is $R \approx 3.2$ Å). This distance corresponds to the limit of the first hydration shell, and thus the net effect is coincident for this shell. It is interesting to note that the accord is specially good in the region between first and second neighbours (the first positive peak at about 3.8 Å). This particular feature has been suggested to be central to the very existence of the density maximum [11, 20] and is well reproduced here. However the averaged nature of this function (see Eq. (2))

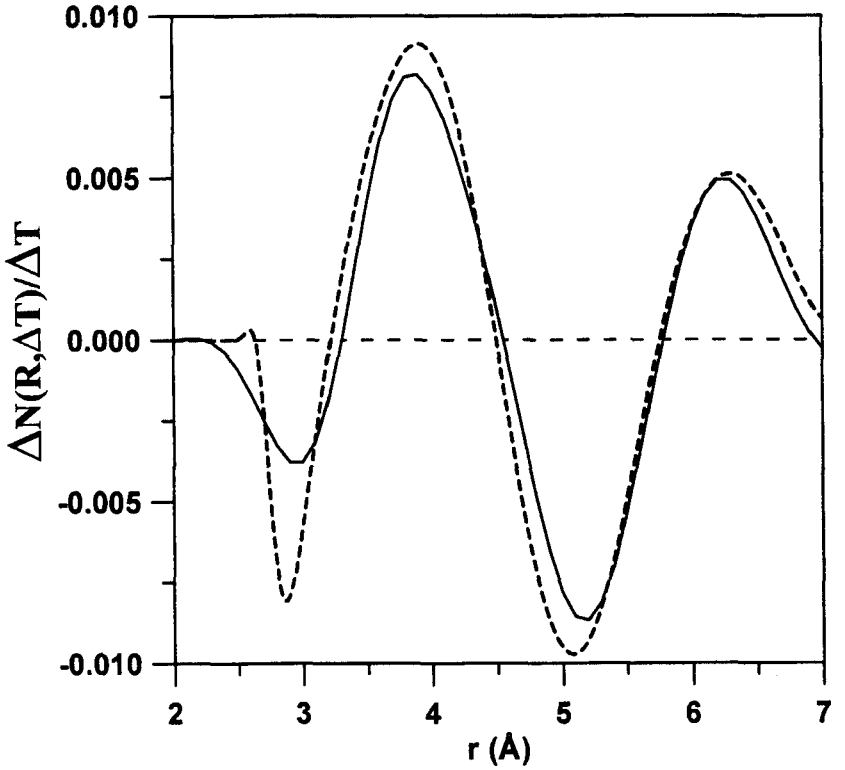

FIGURE 3 Variation of the number of neighbours with distance normalised by the temperature difference ($\Delta N(r, \Delta T)/\Delta T$). Dashed line: result from simulation; solid line: experimental result of Ref. [11].

may probably be relevant for this good coincidence, and is somewhat misleading about the strengths of the SPC/E model. As will be seen below some of these good properties are lost when analysing less averaged properties, like bare ITD.

Figure 4 displays the computed and experimental [11] ITD together with simple (non-isochoric) temperature differentials computed at several temperatures (see below for their definition). As it was the case for $N(R, \Delta T)$, the results have also been scaled by the temperature difference (ΔT). Regarding the accord with experiment, it is certainly good for medium to long range but the peak between 2 and 3 Å is substantially sharper and narrower. For this function the accord is thus poorer than for $N(R, \Delta T)$. This feature might be directly related to the known overestimation of the first peak of the oxygen–oxygen radial distribution function which is

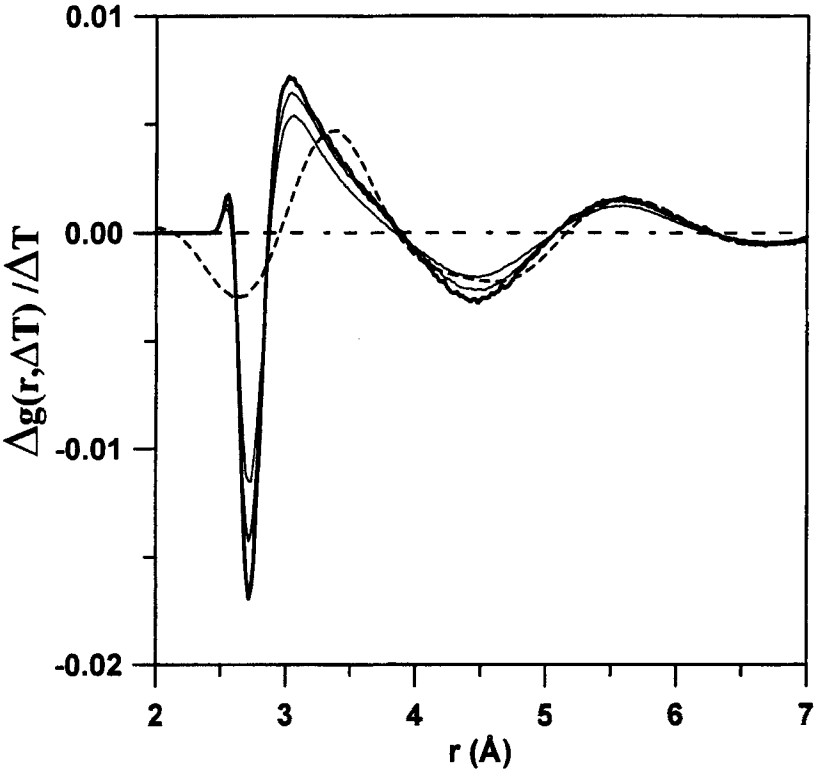

FIGURE 4 Temperature differentials (scaled by temperature differences). Thick solid line: isochoric temperature differentials (ITD); thin solid lines: temperature differentials centred at (in order of decreasing proximity to ITD) 255 K and 275 K; dashed line: experimental X-ray ITD.

common in classical models of water [13]. Structure is not so marked, and in better accord with experiment, for *ab initio* calculations [21] (the isotopic shift of the maximum is a clear sign of the importance of quantum effects). This confirms that the major shortcoming of the SPC/E model (and of other similar models [22] as well) is an overestimation of the structure of the first neighbour shell of a water molecule. The minor disagreements for $\Delta N(r, \Delta T)$, most prominent at short distances, underline this same fact.

It might be asked if the structural differences that exist between isochoric points, reflected in the oscillatory nature of ITD, are a distinct feature of the density maximum. To this end non-isochoric differentials have also been computed and compared with ITD. Non-isochoric differentials have not been defined, as it is usually done, for a fixed reference temperature. Instead,

the method mimics that for ITD: for a given temperature, pairs symmetrically centred on it have been used. In this way, when scaled by the temperature difference, all the curves collapse on a single curve (characteristic of that central temperature). If differentials for a fixed reference temperature are computed, this scaling effect is hidden. Computed in this way, non-isochoric differentials are very close to ITD, and show the same temperature scaling. There is no distance range for which there is a qualitatively different behaviour. The only noticeable differences with ITD are limited to the height of the peaks, which increases as the temperature (at which the intervals are centred) is lowered. Temperature scaled ITD appear to be the just one more step in the sequence. Therefore, from the present model it might be inferred that ITD do not seem to indicate any structural rearrangement different from that characteristic of a simple temperature difference.

Cut-off and System Size Effects

Once the main physical aspects have been discussed, in this section a further investigation of the effects of the parameters of the simulation on the computed density will be presented. This is motivated by the discrepancies noted in the first section, and further explores the effect of different parameters. The resources available limit this study to the span [7, 14] Å for the cut-off and 108–900 molecules for the system size. In the most recent computations of the density as a function of temperature [5–7, 12] the number of molecules is more limited, with the values 108 [12], 216 [5, 6] and 360 [7]. The respective cut-off distances are also smaller, usually being 9 Å [6, 7, 12], with the exception of Ref. [5] (11.7 Å). The confidence that these parameters are sufficient to provide converged results probably stems of older works which suggest that structural quantities (including the density) do not show any noticeable drift [23–25]. While this notion is approximately true, it is not applicable in the present case, given the degree of accuracy required (about one part per thousand). It might be argued that since the differences are so small, this effect is not worth considering. What makes this lack of convergence remarkable, as noted previously, is that the disagreement between computed curves is of the same order as the difference with the experimental value.

Given the amount of computation required, this part of the study has been limited to a single temperature (298 K), the one for which minimum length runs are required. The equilibration time has been of roughly 150 ps in all cases, and the production time of about 200 ps. Figure 5 displays the

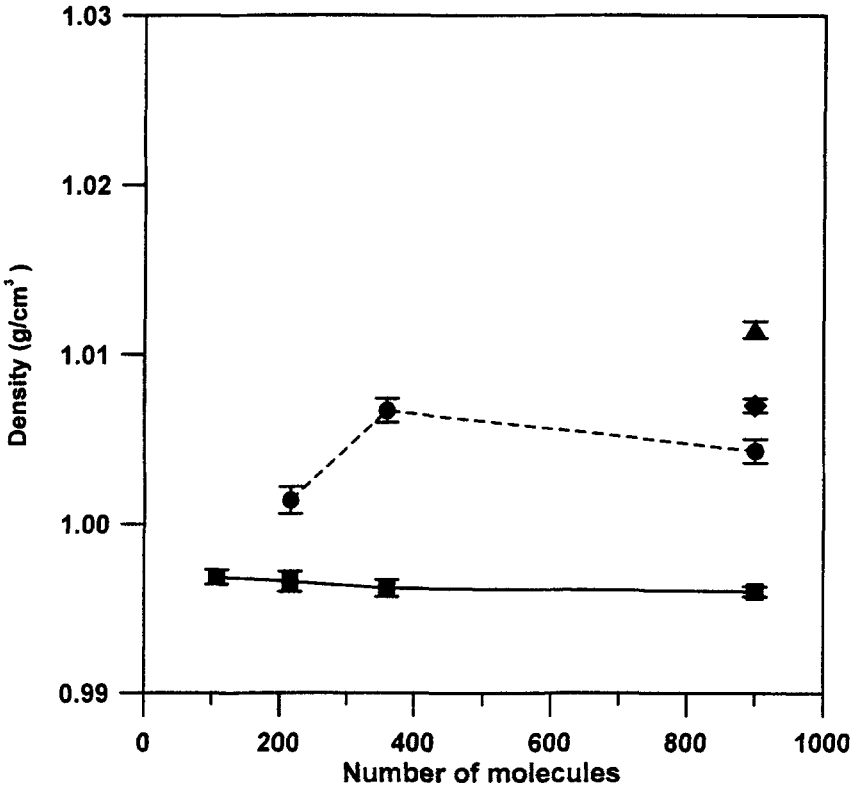

FIGURE 5 Computed density at $T = 298\,K$ for varying system size and cut-off. Squares: cut-off at 7 Å; circles: 9 Å; diamond: 11 Å; triangle: 14 Å. The x axis indicates the system size as measured by the number of molecules (the scale of the density axis has been maintained as in Fig. 1).

values obtained for the density as a function of the number of molecules. The chosen values of the cutoff have been: 7 Å (for 108, 216, 360 and 900 molecules), 9 Å (for 216, 360 and 900 molecules), 11 Å (only for 900 molecules) and 14 Å (only for 900 molecules). The bottom curve in Figure 5 (which corresponds to 7 Å) shows that the density is largely independent of the system size (notice that with even very small error bars the confidence intervals still overlap each other). The situation is similar for 9 Å (see Fig. 5). Although in this case the density dependence on system size appears to be initially less smooth, it levels off for larger number of molecules. Overall, a rather constant value of the density is also obtained regarding size variations. Figure 5 also includes the values obtained for a cutoff of 11 Å and 14 Å (both obtained for 900 molecules). These values indicate a

continuous increase in density with cutoff distance. Figure 6 makes this trend more clear, as here only the cutoff is varied for the largest system size (900 molecules). The main conclusion that can be drawn from this plot is that the density increases continuously with cutoff, and has clearly not attained full convergence for the rather high value of 14 Å. The values obtained indicate that doubling the cutoff results in an 1.5% increase in the value of the density. Although these considerations imply that fully converged results have not been obtained, the same plot (Fig. 6) also indicates a trend to convergence. The straight dashed line drawn between the density values for 7 Å and 14 Å shows the expected curvature for the density: the middle points fall above this curve and thus are a sign of saturation. Finally, it should be said that this cut-off effect was to be expected. Studies for the much simpler Lennard-Jones liquid had already

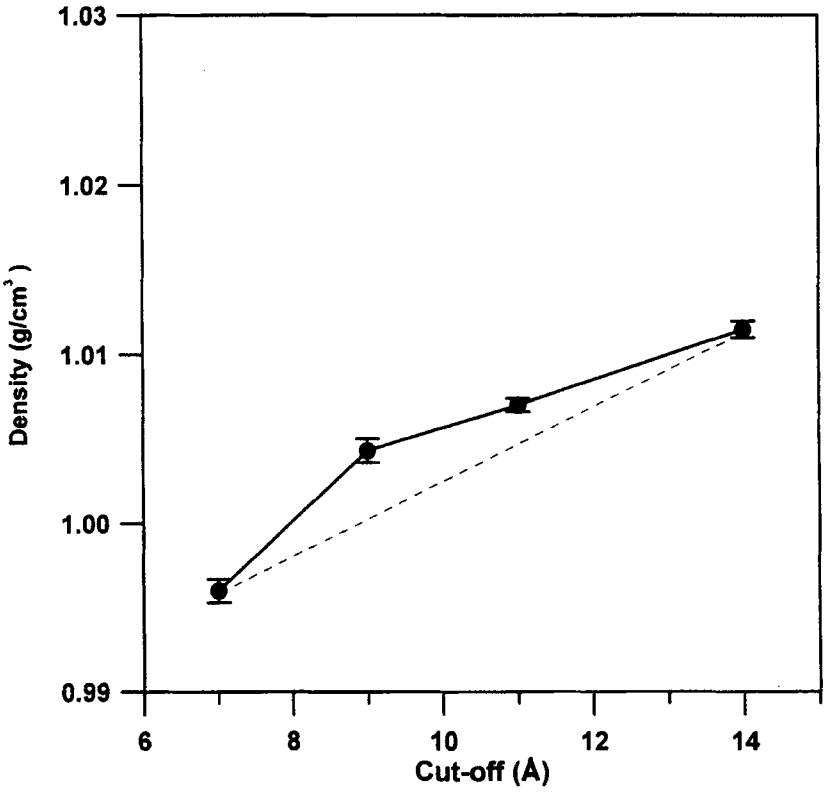

FIGURE 6 Computed density for 900 molecules and variable cut-off. Dashed line shows curvature of the density increase (the scale of the density axis has been maintained as in Fig. 1).

pointed to the importance of the cut-off in the determination of the density [26]. The situation should be worse for water, as here the long ranged Coulomb forces are present. A way to improve convergence probably consists in implementing long range corrections for all the forces, requiring a time consuming method like the Ewald sum for the Coulomb contribution. Unfortunately, this will imply an additional computational effort for a problem which is already quite demanding.

CONCLUDING REMARKS

Although simple models of water have notorious limitations, their widespread use in other fields, where computational economy is important, justifies the need for improvement. As it has been argued here on the basis of the calculation of isochoric temperature differentials, there is probably still some room for it, specially regarding the structure at short distances. Basically, the structure in this range is too localised resulting in higher peaks than found in experiment for radial distribution functions. These defects propagate directly into ITD, but is blurred when the variation of number of neighbours is computed. Thus, this last property, which is in excellent accord with experiment, is not so sensitive to fluctuations of local structure.

It has also been shown that convergence of the computed density is still a non-negligible problem in the present context even with the present computer resources. It depends mainly on the cutoff and shows small dependence on system size (as long as the cutoff is smaller than half the box length). A first consequence of this artefact is that in the parameterization of water models with small system sizes, densities a few per cent under the experimental value should be acceptable. Moreover, it also implies that long range corrections are a necessary requirement in accurate computations of the density.

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