# Molecular Physics
## An International Journal in the Field of Chemical Physics

## A Monte Carlo study of structural and thermodynamic properties of water: dependence on the system size and on the boundary conditions

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# A Monte Carlo study of structural and thermodynamic properties of water : dependence on the system size and on the boundary conditions†

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The structural and thermodynamic properties of water are studied using the force bias Monte Carlo simulation. In particular for ST2 water, the effect of system size is examined with 27, 125 and 216 water molecules. The role played by the truncation of the intermolecular potential is analysed using two different truncations, the spherical cut-off and the cubic cut-off. Also a recent simulation with the Watts potential using Ewald summation by McDonald and Klein is compared with one employing the spherical cut-off. In all cases the angular correlation functions show a strong dependence on the type of boundary condition used, whereas the usual radial functions $g_{OO}(r)$, $g_{OH}(r)$ and $g_{HH}(r)$ do not depend much on the boundary conditions. Because of this dependence of angular correlations on the boundary conditions, care must be exercised in comparing simulation results from small systems to real experiments.

## 1. INTRODUCTION

Computer simulation is now widely used to understand the structure and dynamics of not only simple classical fluids but also of more complex liquids like water [1–19]. Such studies involve the application of molecular dynamics (MD) or Monte Carlo (MC) techniques to the study of systems containing a small number of molecules interacting with a model potential. The properties of the bulk fluid are mimicked by employing periodic boundary conditions to avoid surface effects. Further, the pairwise potential generally assumed in these studies is truncated beyond a certain specified distance $r_c$ to reduce the computational expense. Recently it has been suggested that for liquid water [11, 16, 20] and also for dipolar hard sphere fluids [21, 22] the truncation scheme employed and the size of the periodic primary cell have an important effect on the properties of the system and that a detailed study is needed to obtain the thermodynamic limit. It was also shown that for systems with large dipole moments the structure was considerably perturbed by the type of truncation scheme employed. It has been suggested that when there are both dipolar and large quadrupole moments the results might be less sensitive to boundary conditions [23]. In the case of water where the dipole moment is quite large but there is also a quadrupole

moment, such a study is essential before a meaningful comparison of the simulation results with experiments can be made. In this paper we present such a study of the effect of using different truncation schemes on the structure of water.

Using the ST2 model potential for water, we first compare two different truncation schemes—namely, the spherical cut-off (SC) and the cubic cut-off (CC) methods. We restrict the comparison of the different truncation schemes in this paper largely to the differences in structures obtained for the simulated water. It is well known that truncation of the potential leads to errors in the energy and other thermodynamic quantities, though tail corrections can be applied to compensate for these errors. Our studies show that while the differences in the radial structure between CC and SC are small, the angular correlations display a more dramatic dependence on the truncation scheme employed in the simulation. Furthermore, the *range*, $r_c$, of the cut-off in the SC scheme also plays an important role in determining the angular correlations. These observations raise an important question regarding the size of the system used for the simulation : how large must the system be so that the structure and other measurable properties are weak functions of the truncation scheme ?

Given a generous allowance of computer time, it is possible to simulate a system with long range forces without invoking any truncation. This method relies on the Ewald technique for computing lattice sums. Although it is clear that Ewald summation when applied to the simulation of small systems may impose extra correlations on the system, due to the periodicity of the primary cell, the technique has been used with considerable success in the study of plasmas. A simulation based on this technique was recently reported [7] for the Watts [23] model for water. In this paper we present a detailed comparison of liquid properties obtained from the Watts model of water and ST2 water, both using spherical truncation. We also present a comparison of the Watts model with spherical cut-off with results using Ewald summation as reported in [7].

In § 2 we define the various truncation schemes and stress the important features in applying them to molecular fluids. The results are presented and discussed in § 3. Finally in § 4 we draw attention to the important conclusions arising from this study.

## 2. TRUNCATION SCHEMES

We briefly discuss the various truncation schemes employed in our work. A detailed discussion is available in [24]. However, a few points related to non-central force models need a comment.

(*a*) *Spherical cut-off*: This is the most commonly used scheme in the simulation of fluids. In a Monte Carlo simulation the pair interaction potential is set equal to zero if the oxygen pair distance is larger than a cut-off distance $r_c$. In a MD simulation the force between a pair of molecules is set equal to zero if the distance between them is larger than $r_c$. Thus the potential used in MC is not the same as in MD unless the potential is shifted by an amount depending on the cut-off. In the case of spherically symmetric molecules this shift is just a constant and can be corrected easily to make both Monte Carlo and molecular dynamics give the same structure, thermodynamics and fluctuations. In this case ' tail corrections ' to the simulation results on small systems give the

pressure and energy [5, 27] in the thermodynamic limit. In the case of non-spherical molecules, the shift depends on their relative orientations, and for water can be quite large. A molecule which moves out of the sphere of influence of another molecule reorients, and then moves back into the sphere of influence of the same molecule will experience a discontinuous jump in energy. Thus the energy will not be conserved in a molecular dynamics simulation of non-spherical molecules, unlike the case with spherical molecules. Since many particles will be moving in and out of this sphere of influence with different orientations there will be fluctuations introduced in the system which depend strongly on the orientational correlations near the cut-off distance. The effect usually diminishes with increasing $r_c$. In the case of ST2 water, for any particular $r_c$ the potential energy of interaction of a pair of molecules separated by $r_c$ can can be either attractive or repulsive depending on their relative orientation. The larger $r_c$, the smaller the difference. Most of the thermodynamic properties depend on the two particle distribution function, $\rho(1, 2)$ and the pair interaction potential, $v(1, 2)$. If the short range part of $\rho(1, 2)$ does not depend very much on the neglected tail of the interaction beyond $r_c$, then simple tail corrections can be made. However, in the case of water the short range part of $\rho(1, 2)$ depends on the value of $r_c$ used and also on the type of boundary condition employed, as we shall show in this paper.

(*b*) *Cubic cut-off* : The interaction potential is set equal to zero (or the force in the case of MD simulation) whenever one molecule crosses the surface of a cube with the other molecule at the centre. The orientation and dimension of this truncation cube are usually chosen to be the same as that of the primary cell. In the case of spherically symmetric molecules the potential has the periodicity of the primary cell, with the consequence that the particle crossing the surface does not experience any change in energy. This was originally called the minimum image convention [24]. However, in ST2 water, where the interaction depends on the relative orientation, the potential does not have the periodicity of the primary cell. Since there is no periodicity in angle space, whenever a molecule leaves the cube of influence, an image will enter the cube with a different relative orientation with respect to the central molecule (see figure 1). This again has the consequence that energy will not be conserved in a MD simulation. The potential can be made continuous by using a site–site
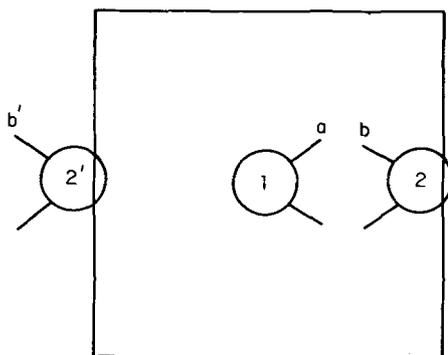


Figure 1. The relative orientation of a particle labelled 1 with respect to another particle 2 and its image 2'.

cubic cut-off rather than a cut-off based on the centres of mass of the molecules. This has the advantage that in an MD simulation, energy will be strictly conserved. However, it has the unfortunate unphysical effect that the integrity of the long range electrostatic potential is destroyed. Our results show that this convention while conserving energy in a MD simulation leads to very different thermodynamic properties, structure and fluctuations compared to the spherical or the cubic cut-off. Because of the unphysical nature mentioned above we shall not discuss this cut-off.

(*c*) *Ewald summation* : The fully replicated periodic cube is considered in the computation of the interaction potential. Thus all the particles and their images are included in the interaction potential. Though time consuming, this method is exact for the periodic model system considered. However, the real infinite system may not bear any resemblance to the small model system due to the extra correlations introduced by the periodicity. In principle, Ewald summation has the advantage that the size dependence can be extrapolated to study the thermodynamic limit. Also this method conserves energy in a MD simulation.

For systems in which the dimensions of the primary cell are larger than the longest correlation length, and in which the potential cut-off is also larger than the correlation length the structure and the sampled distribution functions should be independent of the boundary conditions and the results should give thermodynamic limiting values. However, in the next section we show that for simulations of water involving of the order of a few hundred molecules the structure is quite sensitive to the type of boundary condition used. It is therefore important to ask which boundary condition, if any, can be used to deduce the properties of macroscopic aqueous systems from small system computer simulations.

## 3. RESULTS AND DISCUSSION

### 3.1. *The effect of cut-off radius on the liquid properties*

As noted in § 2 the most common truncation scheme is the spherical cut-off. This has been used in the development of the ST2 potential [4] and also in judging the suitability of the Clementi potential [13, 14, 15] in simulating the properties of liquid water. In this section we first describe the effect of changing the cut-off radius, $r_c$. Although one could, in principle, vary $r_c$ but keep the size of the system constant it is more economical to scale the size of the system with $r_c$. This procedure will yield the correct $r_c$-dependence of the liquid properties as long as the $N$-dependence is small or better still negligible. No $N$-dependence was observed for the BNS potential when $r_c$ was left unchanged [11]. Three different systems are considered corresponding to $r_c = 1\cdot5\ \sigma$, $2\cdot5\ \sigma$ and $2\cdot7\ \sigma$ (where $\sigma = 3\cdot1$ Å). In order to ensure that the interaction between any pair of molecules is counted only once, it is necessary that :

$$r_c \leqslant \tfrac{1}{2} \left( \frac{N}{\rho} \right)^{1/3},$$

where $N$ is the number of molecules in the system and $\rho$ is the density. If $\rho = 1$ g cm$^{-3}$, then three system sizes appropriate for the $r_c$s above are $N = 27$,

125 and 216. In the case of 27 and 125 molecule systems the cut-off lengths correspond to half the length of the primary cell. For the 216 molecule system, the cut-off length is the same as was used elsewhere [4, 25]; that is, $r_c = 2.73\ \sigma$. A force bias Monte Carlo [25] simulation is used in which the random walk of the individual molecule is biased in the direction of the force and torque acting on the molecule. In all cases the translation and rotational step sizes are chosen to be $\Delta r = 0.2\ \sigma$ and $\Delta \theta = 0.898$ rad. The temperature is set at 283 K.

We now describe the main results.

### (i) *The internal energy*

Some thermodynamic properties for the systems considered are presented in table 1. The potential energy per particle $\langle e \rangle$ is surprisingly independent of the system size considered. (The unit of energy is $\epsilon = 0.3169$ kJ mol$^{-1}$.) A similar conclusion was reached by Beveridge *et al.* [26] using a Metropolis Monte Carlo simulation of 64, 155, and 216 ST2 water molecules, while an $N$-dependence was observed by Ladd [16] and Watts [11].

Table 1. Thermodynamic properties of ST2 water with spherical cut-off comparing the simulations using different system sizes.

| Number of particles in the system | Potential | Boundary condition | Number of passes | $\langle e \rangle$ units of $\epsilon$† | $\langle \delta e^2 \rangle$ units of $\epsilon^2$ | $C_v$ J mol$^{-1}$ K$^{-1}$ | $n$‡ |
|---|---|---|---|---|---|---|---|
| 216 | ST2 | SC | 10000 | $-140.28$ | 2.60 | 110.2 | 5.67 |
| 125 | ST2 | SC | 6000 | $-139.92$ | 3.25 | 86.9 | 5.58 |
| 125 | ST2 | CC | 4000 | $-146.25$ | 3.38 | 89.2 | 5.86 |
| 27 | ST2 | SC | 10000 | $-140.22$ | 23.61 | 121.8 | — |

† $\epsilon = 0.3169$ kJ mol$^{-1}$. ‡ $n$ is the number of nearest neighbours up to $r = 1.13\sigma$

The fluctuations in the potential energy are better understood by studying the probability function $p(e)$ which gives the frequency with which configurations occur with energy between $e - (\Delta e/2)$ and $e + (\Delta e/2)$. These functions for the three system sizes are shown in figure 2. The width $\langle \delta e^2 \rangle^{1/2}$ of $p(e)$ is related to the heat capacity $C_v$ of the system (see [25] for a detailed discussion of these functions)

$$C_v = \frac{N_A N^2}{RT^2} \langle \delta e^2 \rangle + 3R, \tag{3.1}$$

where

$$\langle \delta e^2 \rangle = \langle e^2 \rangle - \langle e \rangle^2. \tag{3.2}$$

$N_A$ is the Avagadro number and $R$ is the gas constant. Clearly the smaller the system, the larger are the fluctuations. In our simulations it is observed that in order to sample all the fluctuations allowed by the partition function, the Monte
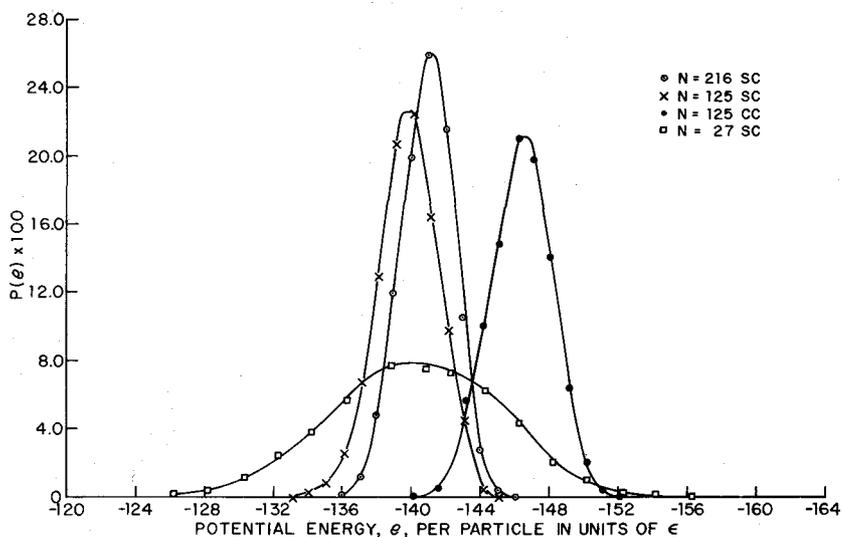
Figure 2. The normalized probability, $p(e)$, of the configurational potential energy per particle for different system sizes. The open circles denote ST2 water with 216 particles and a spherical cut-off. The crosses denotes the 125 particle system with spherical cut-off. The squares denote the 27 particle system with spherical cut-off.

Carlo walk must be carried out to at least a certain number of passes† $\tau = \tau_c$. For $\tau > \tau_c$ the width of $p(e)$ is independent of $\tau$. But for $\tau < \tau_c$, the width increases with $\tau$. Therefore in order to obtain reliable information on the thermodynamics and fluctuations at least $\tau_c$ passes must be used. Unfortunately $\tau_c$ cannot be estimated *a priori* but can be approximately assessed by studying the variation of $\langle \delta e^2 \rangle$ as a function of $\tau$ (the number of passes). This point has been extensively studied in reference [25]. We also observe slow cycles in energy fluctuations whose amplitude increases with decreasing system size. This arises from the fact that only a small portion of the full fluctuations, $p(e)$, is sampled in any small interval $\tau$. The specific heats are shown in table 1. The difference in specific heats between the 125 and 216 molecule systems is 21 per cent. Since the specific heat of the 125 molecule system changes only by 8 per cent from 4000 passes to 6000 passes, the large difference between two system sizes may be real. The 27 molecule system has been equilibrated for 20 000 passes and another 10 000 passes are used to calculate the heat capacity. This may not be a long enough run for a reliable estimate of specific heat. One cannot over-emphasize the importance of lengthy runs for measuring the specific heat. Several authors in the past have obtained misleading results regarding fluctuations from very small runs [26].

To explore the (lack of) dependence of the average potential energy per particle, $\langle e \rangle$, on $r_c$ let us define the function

$$e(r) = \int_{D(r)} \rho_2(1, 2) v(1, 2) \, d1 \, d2. \tag{3.3}$$

† A pass is defined as $N$ attempted moves and each move involves both translation and rotation.

Here $\rho_2(1, 2)$ is the pair distribution function involving the six positions and six angles of the pair molecules, $v(1, 2)$ is the ST2 pair potential and the domain $D(r)$ is a sphere of radius $r$ centred on molecule 1. The quantity $e(r)$ is the interaction energy of molecule 1 with all water molecules lying within a sphere of radius $r$ centred on molecule 1. Comparison of the curves in figure 3 show that $e(r)$ is a very sensitive function of the cut-off $r_c$, particularly in the region of the first neighbour shell, $r \leqslant 1.5 \, \sigma$. As we shall see later in this section, this is precisely the region where the angular correlations for the three systems are also very different.
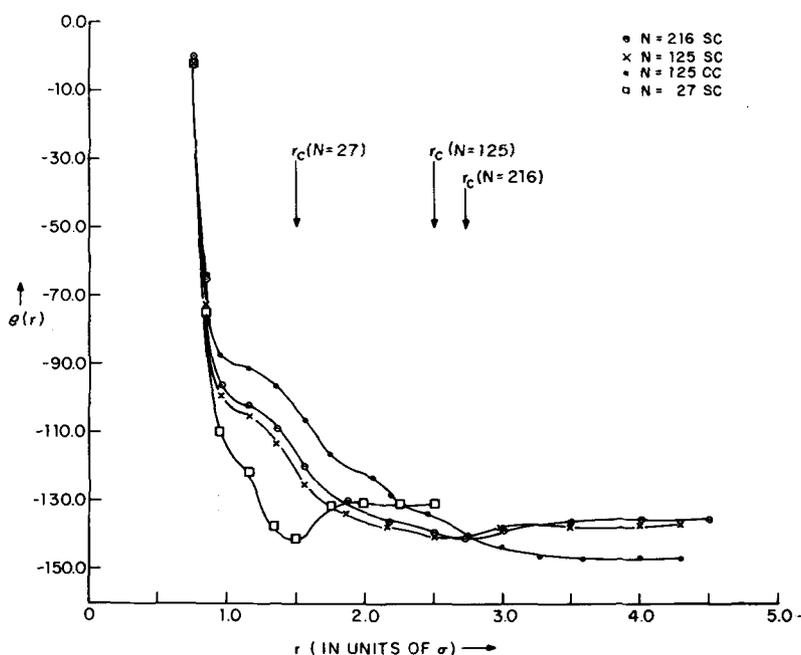


Figure 3. The angular correlation function $e(r)$ as a function of $r$. The symbols are the same as in figure 2.

Interestingly, $e(r)$ for all the curves converges to the same value $e(r_c)$ as $r \rightarrow r_c$. Note that $e(r_c) = \langle e \rangle$. Since $2e(r_c)$ is the total binding energy per particle, it is found that this quantity appears to be independent of the cut-off. Thus ST2 water, like dipolar hard sphere systems [21], has the property that when the cut-off is changed, the structure changes in such a way as to leave the binding energy unchanged. This result is in contrast to the conclusions of Ladd [16] and of Watts [11]. Both of them found a strong dependence of $e(r_c)$ upon $r_c$, a result that we now believe is attributable to the small lengths of the runs employed for their larger systems. One aspect of figure (3) that may be confusing to the reader concerns the dependence of $e(r)$ on $r > r_c$. In these studies the liquid configurations were generated using a cut-off potential. Two options were open to us in computing the function $e(r)$. In the first option, the truncated pair potential—the same potential used in generating the walk—could be used in equation (3.3). Then $e(r)$ would vary strongly for $r < r_c$, but would reach a plateau value around $e(r_c)$ and stay at this value for $r > r_c$ since $v(1, 2) = 0$ for

$r > r_c$. This is entirely expected since molecules at a distance $r > r_c$ from another molecule do not interact with it. Strictly speaking, this is the only option consistent with the model. The other option is to compute $e(r)$ using the full (untruncated) ST2 potential albeit with configurations generated with a truncated potential. This option is inconsistent with the hamiltonian used in the simulation. The function $e(r)$ so calculated will agree with the previous $e(r)$ for $r \leqslant r_c$, but will vary with $r$ for $r > r_c$. This variation will be largely due to multipolar forces, and should reflect the angular correlations at long range. Thus differences in $e(r)$ for $r > r_c$ for different cut-offs simply show differences in the angular correlations. For this reason we chose to compute $e(r)$ using the second option.

## (ii) *Hydrogen bonding*

In the previous paragraph we remarked that as the cut-off radius is decreased, the nearest neighbours appear to become more tightly bound to the central molecule. We therefore expect stronger hydrogen bonds for the system with the smaller $r_c$, other factors being equal.
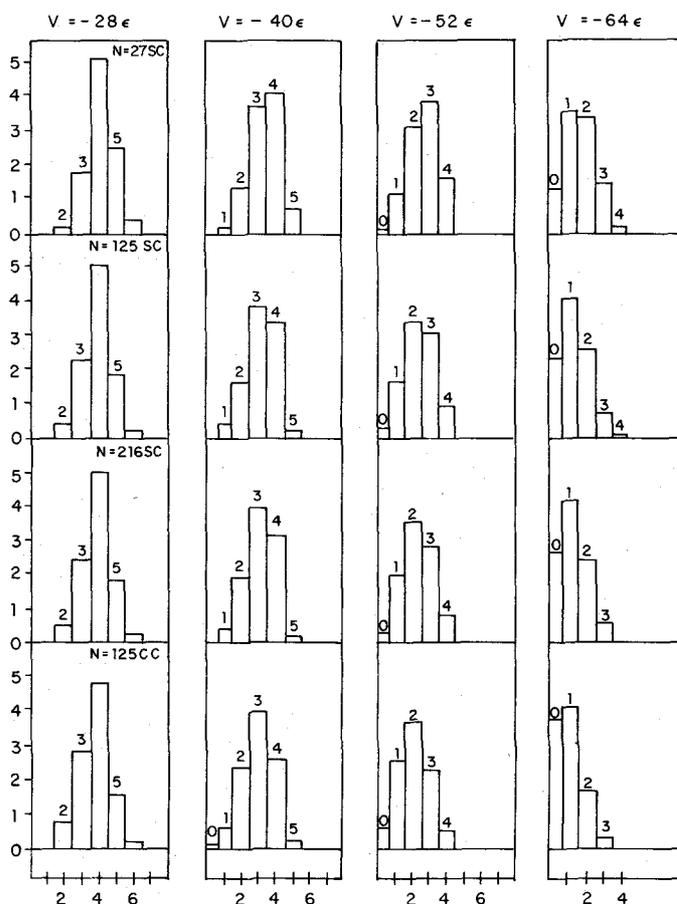


Figure 4. Histograms showing the fraction of molecules with given number of hydrogen bonds for four choices of $V$.

In order to get a quantitative feel for the increase in hydrogen bonding with decrease in the cut-off distance $r_c$, a bond energy analysis along the lines proposed by Rahman and Stillinger [5] is performed. A pair of molecules $i$ and $j$ is designated to be hydrogen bonded if the interaction energy $V_{ij}$ for the pair lies below a preassigned cut-off energy, $V$. In this way it is possible to determine $N_{HB}$, the number of hydrogen-bonded interactions per molecule. Of course the distribution of $N_{HB}$, $p(N_{HB})$, depends on $V$, a very large choice of $V$ results in very few bonds being classed as hydrogen bonds. With four choices for $V$ we find that the fraction of molecules with a large number of hydrogen bonds decreases with increasing $r_c$ (see figure 4). This trend is much more noticeable with larger values of $V$, i.e. $V = -52\,\epsilon$ or $V = -64\,\epsilon$ in figure 4. For example, with $V = -64\,\epsilon$ the fraction of molecules with exactly three hydrogen bonds decreases by $\sim 50$ per cent in going from $r_c = 1\cdot5\,\sigma$ to $r_c = 2\cdot73\,\sigma$. Thus as $r_c$ is increased, the number and strength of the hydrogen-bonded interactions per molecule diminish. This is an important point because in the analysis of aqueous solutions one is often interested in the change in HB in the vicinity of the solute [29]. Our work demonstrates that such measurements could be qualitatively different with different cut-offs.

(iii) *Structure in the liquid*

The radial distribution functions $g_{OO}(r)$, $g_{OH}(r)$ and $g_{HH}(r)$ for the two systems $N = 125$ (shown in crosses) and $N = 216$ (shown in open circles) are compared in figures 5–7. These two sets of curves for the two different size systems are identical within statistical errors. This might lead one to conclude
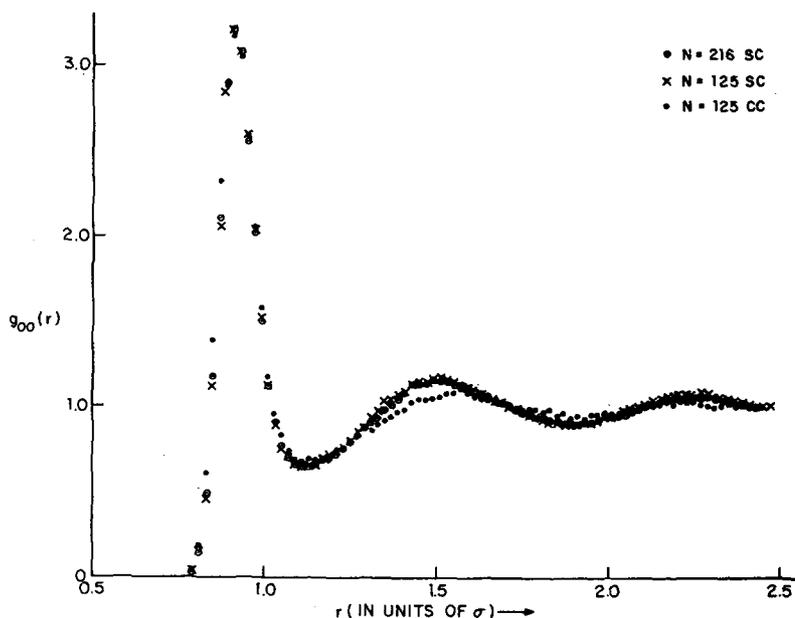


Figure 5. Oxygen–oxygen pair correlation functions of ST2 water as a function of $r$ in units of $\sigma$. The symbols are the same as in figure 2.
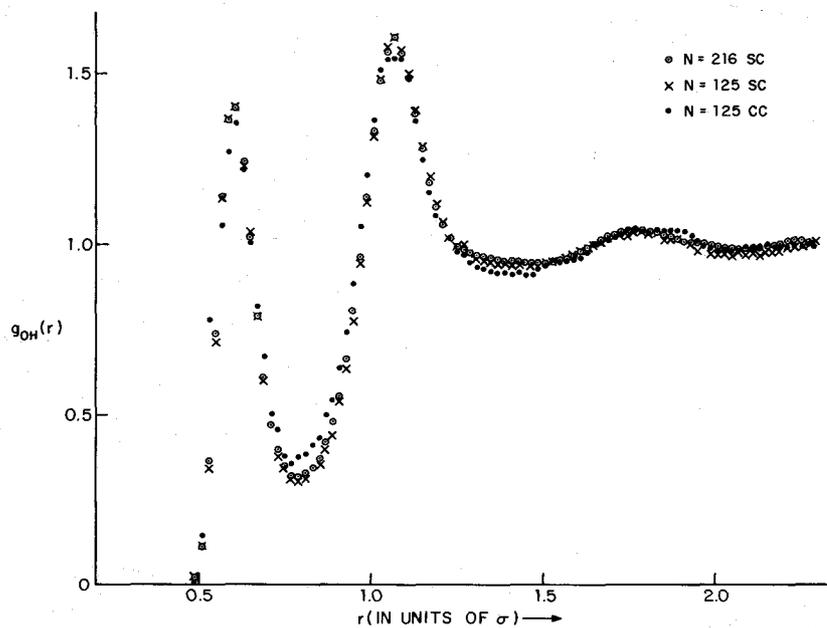
Figure 6. Oxygen–hydrogen pair correlation function of ST2 water. The symbols are the same as in figure 2.
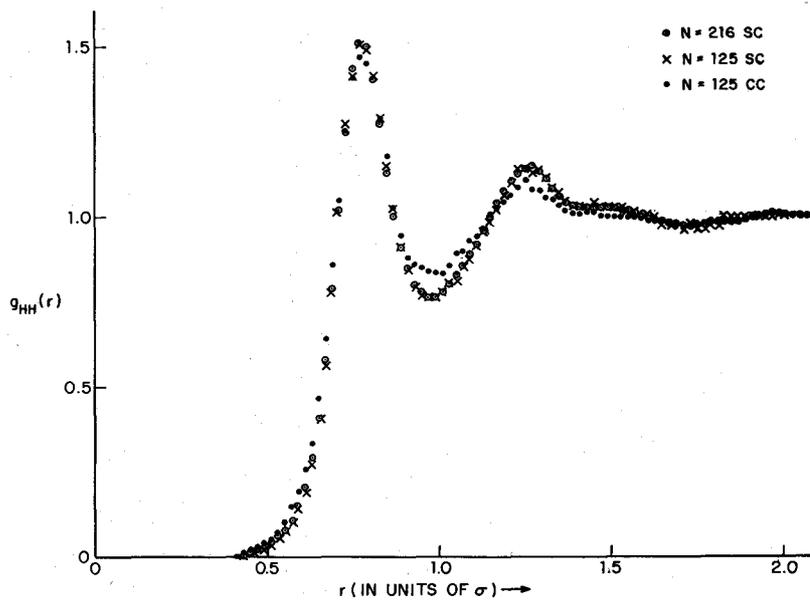


Figure 7. Hydrogen–hydrogen pair correlation function of ST2 water. The symbols are the same as in figure 2.

that the thermodynamic limit has been attained and one can use small systems to study the properties of water [17]. Unfortunately this conclusion does not hold when the orientational correlations are studied in detail. Even though the radial distributions are the same, there exist large differences in the orientational structure of the water molecules relative to one another. To study these correlations we define two functions $h_1(r)$ and $h_2(r)$ as follows :

$$h_1(r) = \frac{\int\limits_{D_1} \rho_2(1, 2)\mu_1\mu_2 \, d1 \, d2}{\int\limits_{D_1} \rho_2(1, 2) \, d1 \, d2}, \tag{3.4}$$

$$h_2(r) = \frac{\int\limits_{D_1} \rho_2(1, 2)(\tfrac{3}{2}(\mu_1 \cdot \mu_2)^2 - \tfrac{1}{2}) \, d1 \, d2}{\int\limits_{D_1} \rho_2(1, 2) \, d1 \, d2}. \tag{3.5}$$

Here $\rho_2(1, 2)$, the pair distribution function, completely specifies the positions and relative orientation of the pair molecules, 1 and 2, $v(1, 2)$ is the ST2 pair potential, $\mu_i$ is the dipole moment vector of molecule $i$ and $di$ denotes a volume element of the coordinates of $i$. The domain $D_1$ is a shell of thickness $\Delta r$ at a distance $r$ from molecule 1. $h_1(r)$ is the dipolar correlation function. It gives a measure of how two water dipoles separated by a distance $r$ are correlated. If at this distance the two dipoles are likely to be parallel, $h_1(r)$ will be positive whereas if they are likely to be antiparallel $h_1(r)$ will be negative. $h_2(r)$ on the other hand will be positive for both these cases. It gives a separate measure of the angular correlations. Both these functions should have limiting values of zero as $r \to \infty$ in an infinite system. In a finite system, both of these functions will be very sensitive to the cut-off and the boundary conditions.

There is an interesting interplay of dipolar and higher multipolar (principally the quadrupolar) forces in the ST2 model. For pair separations larger than $1 \cdot 6 \, \sigma$ the dipolar interaction predominates, resulting in collinearity of the molecular symmetry axes for the minimum energy configuration. On the other hand the quadrupolar forces favour the hydrogen bonded configuration for a pair separated by less than $1 \cdot 6 \, \sigma$, and in the most stable configuration the symmetry axes of the pair are aligned at an angle of $105 \cdot 4°$ with an oxygen–oxygen separation of $2 \cdot 852$ Å[4]. However, the network structures [28] normally found in either the myriad of ice forms or in liquid water have the comparatively less stable hydrogen bond configurations where the symmetry axes of the hydrogen bonded pairs are almost parallel [28].

In figure 8 (*a*) we show $h_1(r)$ for the two principal forms of ice, namely cubic ice and hexagonal ice. These functions have been computed from the data of Rahman and Stillinger [28]. The lack of long range correlations is striking. The nearest neighbours have their dipole vectors parallel as indicated by the first peak.

In figure 8 (*b*) we see that while all the curves for $h_1(r)$ show a positive peak at a position closer than the first neighbour, $r = 0 \cdot 75$, the magnitude of the peak diminishes with decreasing cut-off. For comparison we note that the first peak in $g_{OO}(r)$ occurs at $r = 0 \cdot 91 \, \sigma$. The positive peak in $h_1(r)$ indicates that molecules separated by roughly the hydrogen bond distance are more likely to have their
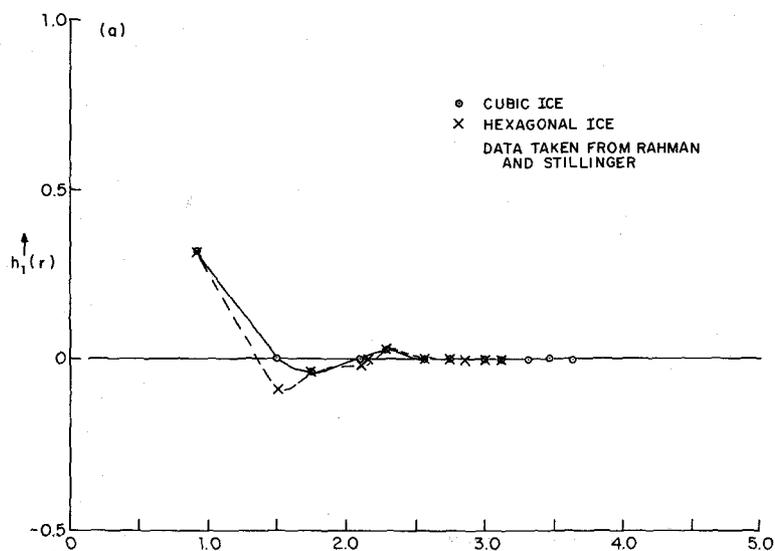
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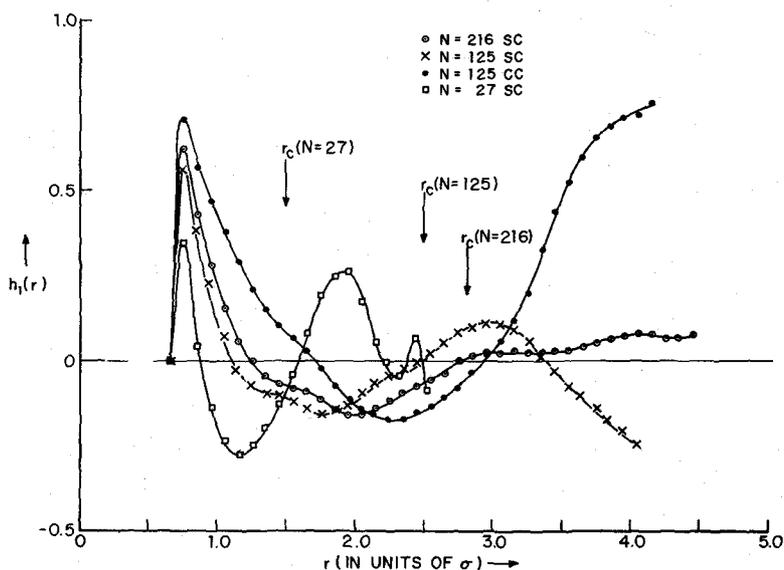


(b)

Figure 8 (a).  The angular correlation function $h_1(r)$ for cubic ice and for hexagonal ice.
    The figures are based on the data of Rahman and Stillinger (reference [28]).  (b) The
    angular correlation functions $h_1(r)$ for ST2 water obtained from the present study.
    Symbols as in figure 2.

symmetry axes parallel to one another.    The smaller peak height with smaller
$r_c$ is consistent with the conclusion drawn previously that systems with smaller
$r_c$ have stronger hydrogen bonds.    At larger separations the tendency to align-
ment diminishes ;  with the smallest cut-off used here pairs of molecules at

separations corresponding to the second neighbour have their symmetry axes preferentially antiparallel. Similar behaviour is found for cubic and hexagonal ice forms (figure 8 (*a*)), though the minima are not as deep as for the systems studied here.

It is interesting to note that for all three cases $h_1(r)$ decays to zero at $r = r_c$. This contradicts some earlier work [11] which indicated significant correlations at the cut-off for small $r_c$. The functions $h_1(r)$ are seen to continue smoothly beyond the cut-off ; the second maximum in $h_1(r)$ for $N = 27$ arises from the strong correlations of the molecules in the corners of a cube centred on the central molecule.

### 3.2. *Comparison of cubic cut-off and spherical cut-off*

Next we present results for ST2 water with 125 molecules using the cubic cut-off. The extra interaction involved in the corners of the cube affect the radial distribution functions $g_{OO}(r)$, $g_{OH}(r)$ and $g_{HH}(r)$ for all $r$. The deviations from the spherical cut-off functions are, however, small as shown (dots) in figures 5–7. The differences in the radial correlations betwen the SC and CC truncations are most marked around $r = 1\cdot0\ \sigma$ to $r = 1\cdot5\ \sigma$. Thus it appears that the structure in the second shell is slightly different for the two boundary conditions. As before, the radial correlations are fairly insensitive to changes in cut-off and boundary conditions. Again, the other properties are much more sensitive to these different truncation schemes. In figure 3 we see from the function $e(r)$ that the first shell of neighbours is much less strongly bound with CC than with SC. This diminution in hydrogen bonding can also be inferred from figure 4 where focusing on, say, the fraction of molecules with exactly four hydrogen bonds for various cut-offs we find the fraction to be significantly smaller with CC than SC. However, the net interaction or binding energy is larger with CC than SC (figure 3) because of the much larger number of interactions per particle permitted with the CC. In table 2 we compare the average energy and specific heat.

Table 2. Thermodynamic properties of ST2 water with different boundary conditions.

| Property | Spherical cut-off | Cubic cut-off |
|---|---|---|
| Passes | 6000 | 4000 |
| $\langle e \rangle$ (reduced units) | $-139\cdot92$ ($-136\cdot78$)† | $-146\cdot25$ ($-133\cdot60$)‡ |
| $C_v$ (J mol$^{-1}$ K$^{-1}$) | $86\cdot9$ | $89\cdot2$ |

† Energy measured with cubic cut-off convention.
‡ Energy measured with spherical cut-off convention.

The dipolar correlations for CC are qualitatively similar to those for $N = 125$ SC or $N = 216$ SC (figure 8 (*b*) and figure 9) for $r \leqslant 2\cdot5$. However, in the corners of a cell centred around a molecule, the overwhelming majority of the molecules are aligned parallel to the central molecule. This is very similar to the behaviour found by Levesque *et al.* [21] for the dipolar fluids.
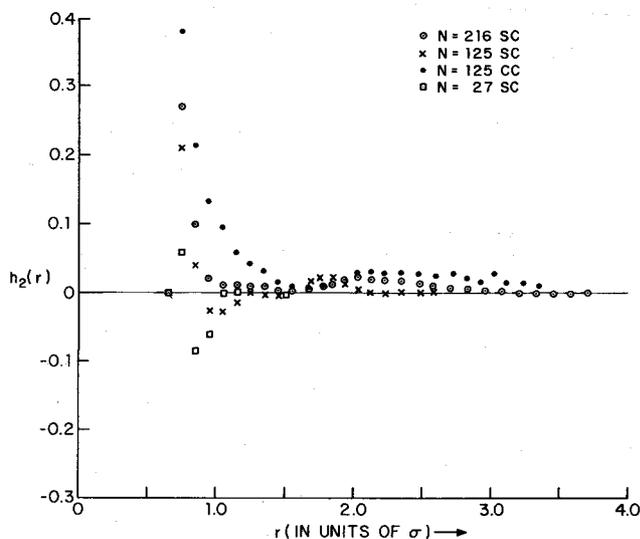
Figure 9.   The angular correlation function $h_2(r)$ as a function of $r$.   The symbols are the same as in figure 2.

The cubic cut-off convention does not appear to offer any advantages over the spherical cut-off convention.   In fact the former consumes twice as much computer time as the latter.   Furthermore it introduces correlations along the diagonals which are a consequence of the fact that CC reinforces the artificial cubic symmetry generated by the periodic boundary conditions.   Our purpose in studying the cubic cut-off was to examine the influence of various boundary conditions upon the interior of a system.   It is apparent that with system sizes considered here the type of boundary condition used affects the structure for all $r$. The differences between CC and SC are most pronounced beyond the first neighbour structure.   However, the distribution of binding energy (as shown by $e(r)$ in figure 3) exhibits the largest variation between the two truncation schemes in the region of the first shell of neighbours.

### 3.3. *Comparison of Ewald and spherical cut-off*

It has been suggested that Ewald summation is a better alternative to the spherical cut-off for long range potentials.   Such a simulation for water using a recently developed potential due to Watts has been reported [7].   In this paper we present a simulation of this potential [23] using the spherical cut-off to study the differences between the two boundary conditions.   Using 216 molecules interacting with a Watts potential, a force bias Monte Carlo simulation was performed.   The density of the system was 1 g cm$^{-3}$ and the temperature $T =$ 273 K.   These are identical conditions to those used in the simulation [7] with Ewald sums.   The latter used the molecular dynamics method for the simulation. Apart from this the only difference between the two simulations was that a SC truncation with $r_c = 8 \cdot 1$ Å was applied in the Monte Carlo simulation.   3000 passes were used to equilibrate the system.   A further 6000 passes were then

generated and used to obtain the structure and thermodynamics. The convergence was checked using the $p(e)$ function (see figure 10). In figure 11 we present the radial distribution functions $g_{OO}(r)$, $g_{OH}(r)$ and $g_{HH}(r)$ obtained from this simulation and compare these with those determined by Ewald summation from [7].
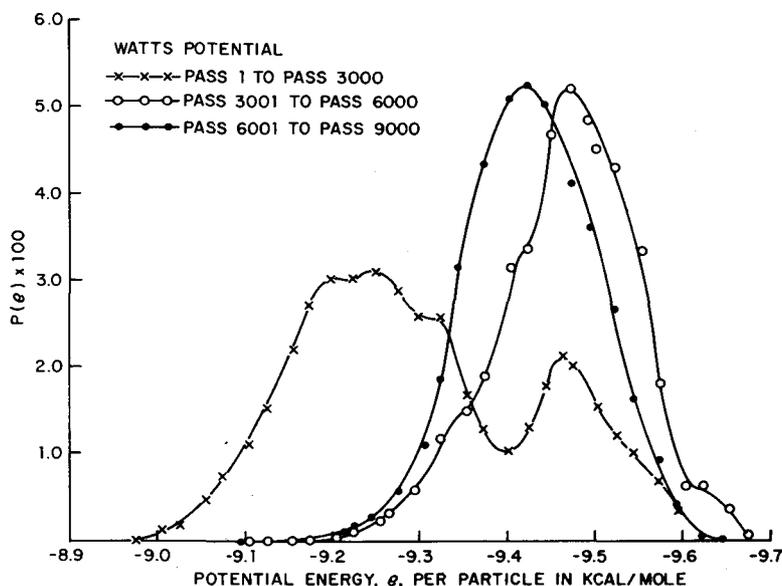


Figure 10. The probability distribution function $p(e)$ as a function of $e$ in the case of Watts potential with spherical cut-off boundary condition showing the slow convergence (1 kcal = 4·184 kJ.)
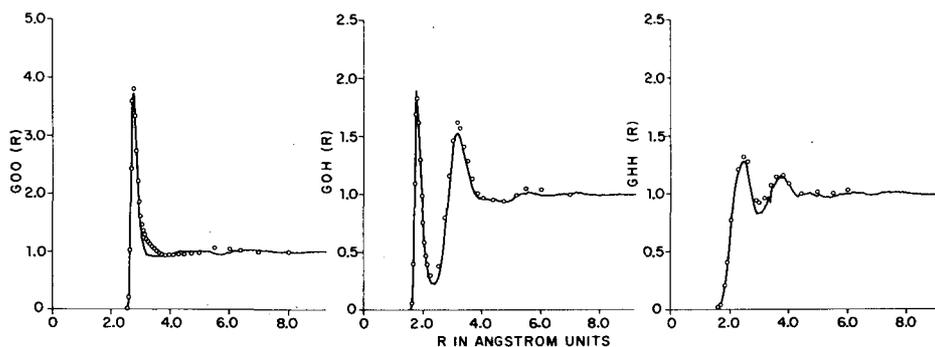


Figure 11. The radial distribution functions for Watts water comparing the Ewald sum results (circles) with the spherical cut-off results (full line.)

It is interesting to note that the angle averaged radial distribution functions in both simulations are identical within error bars. This observation suggests that when one is interested only in the angle averaged properties, the spherical which is less expensive is sufficient.

Unfortunately, the angular correlation functions have not been reported in [7] ; thus we are unable to extend the comparison of SC and Ewald summation to these functions. However, we shall comment on the angular correlations for the Watts water in the next paragraph.

### 3.4. *Watts water compared with ST2 water*

Although it is not directly relevant to the theme of this paper, we shall present a brief comparison of the structure of Watts water with the well-established ST2 water. The reason for so doing is that this is the first opportunity for comparing the two models under similar conditions of simulation. The ST2 simulation was based on 216 molecules at a density of 1 g cm$^{-3}$ at 283 K, while the Watts water is generated with 216 molecules at 273 K and $= 1$ g cm$^{-3}$. The radius of truncation was slightly different in the two simulations : $r_c = 8 \cdot 1$ Å for Watts water and $r_c = 8 \cdot 46$ Å for ST2 water. As we observed in the first part of this section, such a small difference in $r_c$ should not lead to dramatic differences in structure. If significant differences in structure are observed, between ST2 and Watts water in the present comparison, they must therefore be attributed directly to the model potentials and not to any artifacts of simulation.

It is clear from figure 12 that appreciable differences exist between the Watts water and ST2 water. For instance $g_{OO}(r)$ is much less structured for Watts water. And in $g_{OH}(r)$ the first peak is larger than the second with the Watts potential, although the areas under the first peak seem to be the same for the two potentials. Finally, $g_{HH}(r)$ for the Watts potential also displays less correlation than the corresponding function with the ST2 potential. It appears that the Watts potential has a structure corresponding to a higher effective temperature than the ST2 potential.

In figures 13 and 14, $h_1(r)$ and $e(r)$ corresponding the Watts and ST2 potentials with cut-offs of $8 \cdot 1$ Å and $8 \cdot 26$ Å respectively are presented. Although the two simulations were performed at slightly different temperatures (as shown in figure 13) certain qualitative differences are worth noting. A small second maximum is observed in $h_1(r)$ for the Watts potential at the position of the second neighbour. The $e(r)$ curves (figure 13) for the two potentials are qualitatively very similar for $r \lesssim 3 \cdot 3$ Å ; however, the interactions beyond the first shell are much more binding for the ST2 potential. The Watts potential gives rise to much less structural order beyond the first shell as evidenced by a very smooth $e(r)$ and the small magnitude of the second peak in $g_{OO}(r)$. It would be of interest to compare the angular correlation functions discussed here with those obtained with the Ewald summation method.

### 4. Conclusions

In this paper an attempt is made to study the effect of system size and boundary conditions on the structure and thermodynamics of liquid water using a force bias Monte Carlo simulation. The results are similar to those observed in a dipolar hard sphere fluid [21, 22]. The structure, thermodynamics, and
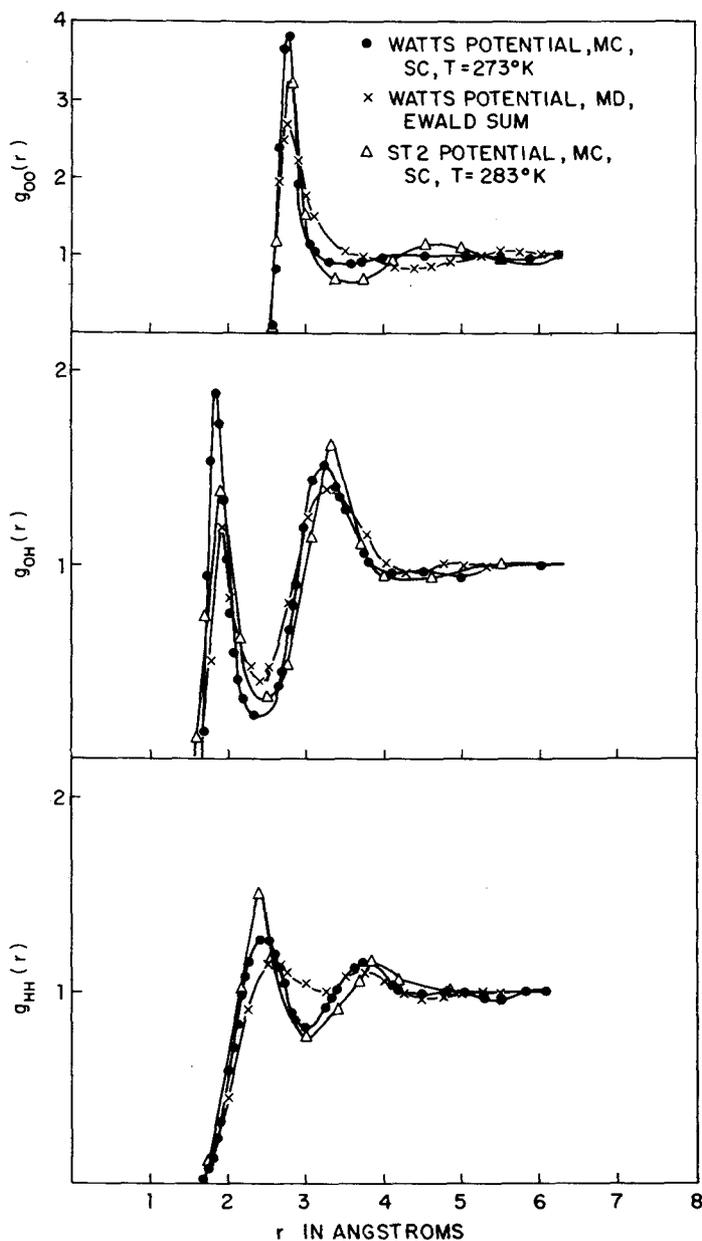
Figure 12. The oxygen–oxygen radial distribution function for the Watts potential. The dots indicate Monte Carlo simulation using spherical cut-off. The crosses indicate molecular dynamics simulation (at 410 K) using Ewald summation, obtained from reference [7]. The triangles denote the ST2 results ($N = 216$, SC).
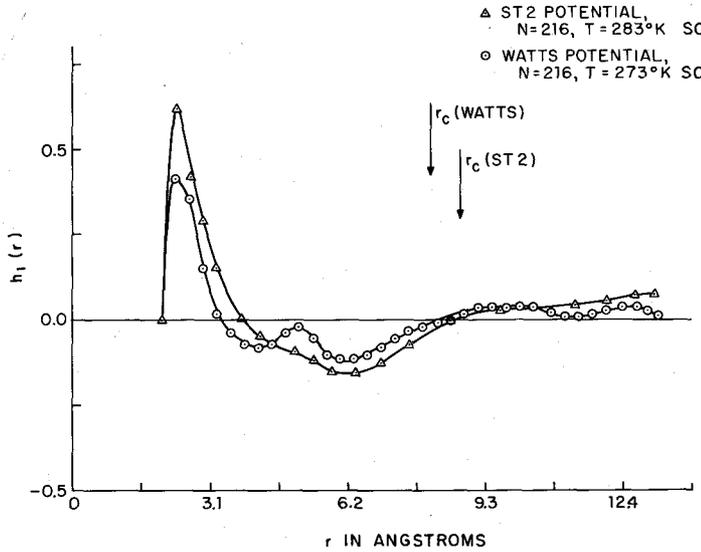
Figure 13. The angular correlation functions $h_1(r)$ comparing ST2 water (triangles) and Watts water (circles).
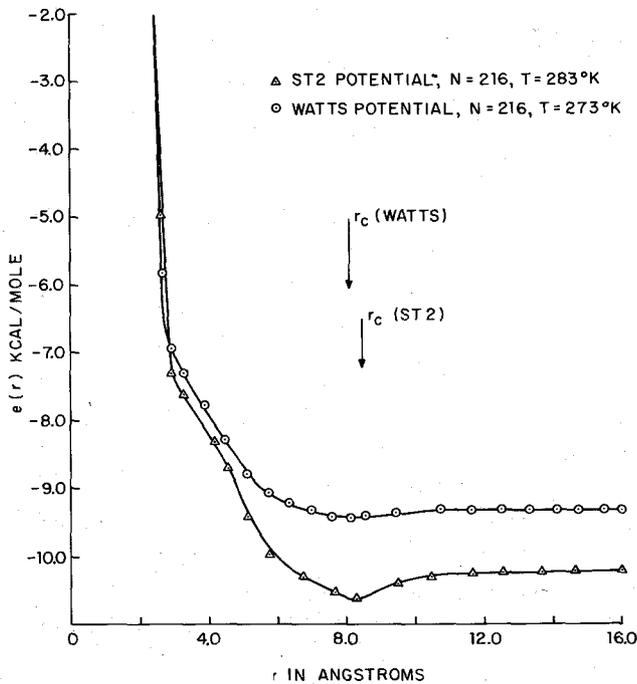
Figure 14. The angular correlation function $e(r)$ comparing ST2 water (triangles) and Watts water (circles).

fluctuations are sensitive to the type of boundary conditions used. Even in the case where there are no observable differences in radial distribution functions, the angular correlations as shown in this paper are considerably different. Although similar results have been observed previously [11] using a different model potential for water, their importance generally has been neglected. This paper re-examines some of the questions raised recently [16, 20] using an efficient Monte Carlo simulation and two different model potentials for water. It would be of interest to see how the Clementi potential for water behaves under such an investigation. It is also important to note that the value of energy $e(r)$ at the cut-off distance $r_c$ is the same for the three different systems ($N = 27$, 125, 216) (compare figure 6).

These observations together with the results on hard dipolar fluids [21] force us to conclude that the orientational correlations are quite sensitive to $r_c$ and the boundary conditions employed. These points lead us to believe that caution should be exercised when studying aqueous solutions, particularly with non-spherical solutes. In addition, there are the problems of estimating errors because of the slow settling to equilibrium. Thus one must take with a 'grain of salt' any estimate of the thermodynamic properties of water either based on short simulation runs or on small system sizes, unless these results are properly corrected to yield their thermodynamic limit.

A note of caution regarding error estimates is in order. Because of the strong correlations between successive configurations generated in the course of the Monte Carlo walk [25] (be it Metropolis or force- bias), often the error estimates are much smaller than are justified. For example, the error in the average energy $\langle e \rangle$ is given by

$$\epsilon_r = \frac{\langle \delta e^2 \rangle}{n},$$

where $n$ is the number of independent blocks used in computing $e$. A block is a section of phase trajectory and is considered independent if it covers a time $\tau$ greater than the correlation time, $\tau_c$, for the property (i.e. energy, in this example) being averaged. The most conservative estimate of $\epsilon_r$ is obtained by setting $n = 1$. Usually, it is a difficult matter to determine $\tau_c$. In [25] we estimate $\tau_c \simeq 5000$ passes using an optimized version of the force bias algorithm on 216 molecules. Thus a 10 000 pass trajectory affords us two independent blocks for estimating $\epsilon_r$. Poor determinations of the errors often lead to over-optimistic estimates of the entropy and free energy.

We are therefore forced to conclude that the properties of simulated water are dependent on the cut-off and on the boundary conditions. How then can one proceed ? One obvious way is to perform a sequence of simulations on systems of larger and larger size with Ewald summation until the properties reach a limiting value. This method although rigorous is impractical because of the enormous expense that it entails. Another possibility is to follow a path similar to that used by Levesque *et al.* [21] for a point dipolar hard sphere fluid. These authors used the results of the computer simulations on small systems in conjunction with the Linearized Hypernetted Chain approximation with great success. Another possibility involves computer simulations on sufficiently large systems that a reaction field approximation can be used. This approach has been applied on the BNS potential by Watts [11]. Recently, however, Van

Grunsteren *et al.* [20] have shown that there are strong differences between a molecular dynamics simulation using the normal reaction field and one using a delayed reaction field [20].   Clearly, a more detailed study along these lines is needed before progress can be made in comparing simulation results with real experiments.

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