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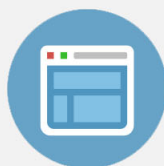
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# Application of a new reverse Monte Carlo algorithm to polyatomic molecular systems. I. Liquid water

Fernando Luís B. da Silva<sup>a)</sup>

*Division of Theoretical Chemistry, Chemical Center, P.O. Box 124, Lund University, S-221 00 Lund, Sweden and Departamento de Física, Fac. de Ciências/Unesp, 17033-360 Bauru, São Paulo, Brazil*

Wilmer Olivares-Rivas<sup>b)</sup>

*Grupo de Química Teórica, Químico-Física de Fluidos y Fenómenos Interfaciales (QUIFFIS), Departamento de Química, Universidad de los Andes, Mérida 5101, Venezuela*

Léo Degève<sup>c)</sup>

*Grupo de Simulação Molecular, DQ/F.F.C.L.R.P, USP 14040-901 Ribeirão Preto, São Paulo, Brazil*

Torbjörn Åkesson<sup>d)</sup>

*Division of Theoretical Chemistry, Chemical Center, P.O. Box 124, Lund University, S-221 00 Lund, Sweden*

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Using a new reverse Monte Carlo algorithm, we present simulations that reproduce very well several structural and thermodynamic properties of liquid water. Both Monte Carlo, molecular dynamics simulations and experimental radial distribution functions used as input are accurately reproduced using a small number of molecules and no external constraints. *Ad hoc* energy and hydrogen bond analysis show the physical consistency and limitations of the generated RMC configurations. © 2001 American Institute of Physics. [DOI: 10.1063/1.1321766]

## I. INTRODUCTION

Water has been exhaustively studied both theoretically and experimentally, because of its fundamental chemical and biochemical importance. Nevertheless, analytical approaches for the description of water are seriously limited by the lack of symmetry and the complexity of the intermolecular interactions in the dense liquid state. It has therefore been more convenient to carry out computer “experiments.” In this approach, an interaction potential is chosen, usually assuming site–site pair interactions, and well-established techniques, like Monte Carlo (MC)<sup>1–3</sup> or molecular dynamics<sup>2,3</sup> methods are then applied.

However, a critical issue is the water model chosen, as is clearly shown in a pioneering paper by Barker and Watts.<sup>4</sup> A number of molecular models are described in the literature, based either on empirical or quantum mechanical methods, including rigid or flexible models, with or without polarizabilities, etc.<sup>4–13</sup> Often, a given model successfully accounts for specific properties, but fails to describe others. A comparative study for pure water models was presented by Jorgensen *et al.*,<sup>6</sup> while Levitt made similar investigations with biological applications in mind.<sup>12</sup>

To obtain a better understanding of water we have basically two alternatives: (a) to develop more accurate interatomic potentials, suitable to both molecular simulations and theoretical applications or (b) to find alternative routes to properly study the system without any need of potentials.

One promising step in the latter direction was given by Kaplow and collaborators 20 years ago<sup>14</sup> and, recently, McGreevy and Pusztai presented a modified and improved version of Kaplow’s work.<sup>15</sup> This so-called reverse Monte Carlo (RMC) method<sup>15–24</sup> is a technique for computer simulations that only needs information from scattering experiments. Basically, the idea is to generate configurations that reproduce a given experimental radial distribution function (rdf) or structure factor. No interaction potential is required, and the simulation is carried out in such a way that the differences between the input (experimental) distribution function and the corresponding calculated function is minimized.

The main purpose of a reverse method is to provide structural properties of the system, e.g., the orientational correlations could be obtained considering the experimental rdf.<sup>25</sup> Also, from a theoretical point of view, it is quite interesting to explore the possibilities that such a technique could offer to extract or improve pair potentials, as was pointed out by McGreevy and Pusztai<sup>15</sup> and later by other authors.<sup>26,27</sup> However, there are still some doubts about the reliability of RMC configurations.<sup>28,29</sup> In fact, the RMC method and similar techniques such as Soper’s empirical potential Monte Carlo<sup>21</sup> have been a matter of continuous discussions and controversies.<sup>28–34</sup> Consequently, methodological aspects need to be reviewed and carefully worked out.

Several successful RMC applications are found in the literature, including some attempts to study bulk water.<sup>18–23</sup> In general, these investigations were made by a RMC version<sup>15</sup> that implemented constraints to avoid overlaps between the particles. Yet deviations of the rdf at short distances are obtained,<sup>16,17</sup> which is a known drawback of that RMC version.<sup>35</sup> Such deviations could cause inconvenience

<sup>a)</sup>Electronic mail: fernando@signe.teokem.lu.se

<sup>b)</sup>Electronic mail: wilmer@ciens.ula.ve

<sup>c)</sup>Electronic mail: leo@obelix.ffclrp.usp.br

<sup>d)</sup>Electronic mail: torbjorn@signe.teokem.lu.se

studying liquids, since the short-range repulsion primarily governs the structure.<sup>24</sup> Often, it is necessary to perform simulations with a large number of particles and, even after adding the mentioned short-range constraints, some differences remain in the produced structure.<sup>16,17</sup>

Convergence problems have also been reported for bulk fluids of spherical particles. These difficulties were satisfactorily eliminated by a new RMC algorithm presented by us elsewhere.<sup>31,36</sup> With that approach, a small number of particles, typically less than 100, is enough to give proper convergence and there is no need for additional constraints. So far, we have successfully applied the new algorithm to hard spheres,<sup>31</sup> continuous and discrete Lennard-Jones,<sup>31,36</sup> and hard-dumbbell systems.<sup>37</sup> No problems within the hard-core range were found and thermodynamic properties, such as the configurational average energy or the excess chemical potential calculated using an *ad hoc* model, were well reproduced. Additionally, for all studied systems, the obtained three-body correlation function was in close agreement with the corresponding MC results.<sup>31</sup>

Besides such methodological questions, RMC results are in general followed by serious reservation<sup>29,32</sup> and often the physical meaning of its generated configurations is questioned.<sup>28</sup> Thus, one may not attempt any further use of the RMC collected configurations before the input radial distribution functions and other thermodynamics properties are reproduced with adequate accuracy, without any additional external constraint.

The aim of this paper is to demonstrate the reliability of the new RMC algorithm,<sup>31</sup> but also to show that it lends itself to liquid water studies. In order to control the system and to avoid interference with experimental errors, RMC tests with rdfs theoretically obtained from model systems are more convenient. This approach also has the advantage that generated RMC configurations can be analyzed in terms of *ad hoc* energies and hydrogen bonding. Nevertheless, in this report a preliminary study with real experimental data is included.

## II. THE RMC METHOD

The RMC method is a relatively recent molecular modeling technique that generates spatial configurations in concordance with the input experimental data, such as rdfs or structure factors, for a given density,<sup>15,31</sup> without needing an interatomic interaction potential. The principle behind RMC is the minimization of the differences between the input rdf and the calculated one by generating particle configurations randomly. The fundamental basis is the equivalence between particles and fields. For pairwise potentials such an equivalence follows from the fact that the radial distribution function is a unique functional of the intermolecular potential.<sup>38,36</sup> Here, a brief description of the new RMC algorithm,<sup>31</sup> adapted for molecular liquids, is given.

In the RMC approach, the water molecules are built up by point atoms, connected according to some geometrical model.  $N$  particles are placed in a simulation box, with the volume,  $V$ , chosen to give the system the desired experimental density,  $\rho$ . The initial configuration could be either randomly created or obtained from a previous simulation. At

each RMC step, a single trial move is made by randomly changing the position of a particle or rotating the molecule. Instead of calculating the potential energy required in Metropolis Monte Carlo simulations (MMC),<sup>1</sup> the  $\chi^2$  parameter for both the new and the old configuration is calculated as

$$\chi_{\text{new}}^2 = \sum_{j=1}^{n_f} \sum_{i=1}^{n_l} \frac{[g_{\text{new}}^j(r_i) - g_e^j(r_i)]^2}{\sigma^2}, \quad (1)$$

$$\chi_{\text{old}}^2 = \sum_{j=1}^{n_f} \sum_{i=1}^{n_l} \frac{[g_{\text{old}}^j(r_i) - g_e^j(r_i)]^2}{\sigma^2}, \quad (2)$$

where  $n_f$  is the number of experimental rdfs,  $n_l$  is the number of layers or ‘bins,’  $g^j(r)$  stands for the distribution function  $j$  and the subscript  $e$  denotes a given experimental function. For example, in the case of water, three rdfs will be used;  $g^{(\text{O-O})}(r)$ ,  $g^{(\text{O-H})}(r)$ , and  $g^{(\text{H-H})}(r)$ . The generated RMC rdfs are constructed from histograms accumulated over all previous observations.<sup>31,34,36</sup>

For the  $k$ th move generating a configuration, a histogram  $h_k$  is constructed over the  $N-1$  distance counts (or observations). After a large number of moves  $k$ , the cumulative histogram  $H_k = \sum_{l=0}^k h_l$  contains the statistical memory of all previous configurations. The rdf for the new and old configurations can be defined as

$$g_k^{\text{new}}(r_i) = \frac{1}{4\pi r_i^2 \Delta r (a_k + b)} [H_{k-1} + h_k] \quad (3)$$

and

$$g_k^{\text{old}}(r_i) = \frac{1}{4\pi r_i^2 \Delta r (a_k + b)} [H_{k-1} + h_{k-1}], \quad (4)$$

where  $a_k = k(N-1)$  and  $b = N(N-1)/2$ . If  $\chi_{\text{new}}^2 \leq \chi_{\text{old}}^2$ , the trial move is accepted. Otherwise, it would be accepted with probability equal to  $\exp(\chi_{\text{old}}^2 - \chi_{\text{new}}^2)$ .

In conventional RMC calculations,  $\sigma^2$  is assumed to correspond to the rdf experimental error. Instead, we have adopted a constant and very small  $\sigma$  (of the order of  $10^{-15}$ ) as previously used for spherical bulk particles.<sup>31</sup> Obviously, the algorithm works purely as a minimization process, where  $\chi^2$  acts as a variational functional.<sup>31,34,36</sup> This simplification together with the absence of *ad hoc* constraints diminishes the number of parameters involved in a RMC calculation. We are basically left with displacement parameters and the simulation length (number of trial moves) as in ordinary MMC runs. For some polyatomic systems, however, it might be useful to adopt different  $\sigma$ 's for each experimental pair correlation function to speed up convergence. We did not find it necessary for the water study presented here.

There might be doubts if a pure minimization criterion of the rdf would lead to unphysical trapping of the system into ‘local minima’ in phase space. That was a problem that previous RMC algorithms suffered from,<sup>32</sup> even if a probability for ‘bad’ moves was given. The present algorithm, however, seems to prevent the system from being trapped by the use of cumulative histogram and from the symmetric treatment of new and old configuration, Eqs. (3) and (4). This can be seen by the results shown in the following sec-

tions. In order to quantify RMC sampling properties, we have suggested<sup>34</sup> two indicators, the mean square displacement of a particle,  $\langle \Delta r^2 \rangle$ , and the so-called “translational order parameter,”  $O(t)$ .<sup>39</sup> From the latter one can determine if the system is in a liquid or solid state. It is defined as

$$O(t) = \frac{1}{3} \sum_{i=1}^N \{ \cos Kx_i(t) + \cos Ky_i(t) + \cos Kz_i(t) \}, \quad (5)$$

where  $t$  corresponds to the RMC step,  $K$  equals  $4\pi(N/V)^{1/3}$ , and  $x_i(t)$ ,  $y_i(t)$ , and  $z_i(t)$  are the coordinates of particle  $i$  at a particular  $t$ . If the system is in the liquid state, oscillations around zero with an amplitude of  $\sim N^{1/2}$  (Ref. 39) is expected.

### III. SIMULATION DETAILS

To critically test the new RMC algorithm<sup>31</sup> we have chosen a strategy, where the rdfs are generated by conventional simulation techniques. To avoid interference with three-body effects a pairwise interatomic potential is chosen. Thus, direct comparisons between the properties obtained from reversed and conventional techniques are feasible. It is important to notice that in such tests, the use of  $r$  space is most appropriate.

In this study, three water models based on the rigid TIP4P and SPC and the flexible SPCFX potentials<sup>6–9</sup> were considered. To produce the intermolecular rdfs of the two former models Metropolis Monte Carlo simulations were carried out in an  $NVT$  ensemble. The volume was adjusted to a mass density of 0.999 kg/l, the temperature,  $T$ , equals 298 K, and  $N=108$ . The O–H distance and the HOH angle were chosen as 0.9572 Å and 104.52°, respectively, for TIP4P and 1.0 Å and 109.47° for SPC. Standard periodic boundary conditions and minimum image convention were used. No special treatment was given to the long-range interactions and no cutoff scheme was applied. The ranges for translation and rotation displacements were  $\pm 0.14$  Å and  $\pm 12^\circ$ . Besides generating the rdf with different layer sizes,  $dr=0.05$  and  $dr=0.01$ , a hydrogen bond (HB) analysis was carried out. Data were collected along 10 000 Monte Carlo cycles (one cycle is an attempt to move  $N$  particles).

For the reversed calculation, referred to as TIP4P-RMC and SPC-RMC, a simulation box identical to the one used in MMC runs was adopted. The displacement parameter was  $\pm 0.06$  Å and the range for rotations was  $\pm 2^\circ$  for the TIP4P-RMC case, and  $\pm 0.15$  Å and  $\pm 5^\circ$  for SPC-RMC simulations. The equilibration criterion was chosen according to Ref. 31. In general, RMC required longer equilibration than the corresponding MMC simulations and it is very sensitive to the choice of displacement parameters. Equilibration runs with 100 000–300 000 cycles were carried out, while the production phase included 10 000 cycles. The acceptance ratio was about 20% for the RMC simulations. Runs starting from different configurations were performed in order to discard a possible dependence on initial parameters.

Another set of simulations, referred to as SPCFX-RMC, was carried out with a flexible SPC water model (SPCFX).<sup>9</sup> The input rdfs were generated by a molecular dynamics simulation ( $T=300$  K) with the MUMOD package.<sup>40</sup> After

100 ps of equilibration the trajectories of 125 molecules were sampled during 50 ps. In the corresponding RMC simulation, however, the rigid SPC model was implemented.

In order to test the applicability of our RMC algorithm to real experimental data, the rdfs obtained by Soper and Philips<sup>41</sup> were used as input for the RMC together with the SPC model. The grid size was chosen according to the finest experimental resolution, 0.10 Å. Since the experimental grid was not uniform, however, some points were obtained by interpolation. For all distances below 2.025, 1.05, and 1.05 Å for  $g_{OO}$ ,  $g_{OH}$ , and  $g_{HH}$ , respectively, we assumed  $g(r)=0$ . For these RMC runs, labeled EXPT-RMC, the number of water molecules was 75 (determined from the largest given distance in the experimental rdf). The displacement parameter was in this case  $\pm 0.10$  Å and the rotation,  $\pm 0.5^\circ$ . Similar equilibration and production runs were performed as in the theoretical tests described previously.

## IV. RESULTS AND DISCUSSION

### A. Liquid water structure

In Fig. 1, we present our results for the intermolecular rdfs of TIP4P water [ $g^{(O-O)}(r)$ ,  $g^{(O-H)}(r)$ , and  $g^{(H-H)}(r)$ ]. In all cases an excellent agreement between RMC and MMC is shown, and the reversed calculations reproduce the rdfs within 0.1%–0.2%. Similar results were obtained with the SPC model and likewise for the flexible SPCFX and the experimental case, as shown in Figs. 2–4.

To the best of our knowledge such an essentially perfect agreement has not been reported before. In Figs. 1–4 the dashed lines represent the corresponding differences [ $g_e^j(r_i) - g^j(r_i)$ ]  $\times 10^3$ . The order of deviations,  $10^{-2}$ – $10^{-3}$ , is rather small and within statistical errors of a simulation. However, it is  $10^2$ – $10^3$  times larger than what has been observed for spherical Lennard-Jones particles.<sup>31,36</sup>

We stress again that in all RMC simulations in this report, the particles were allowed to approach at any distance, i.e., they were not prevented from overlapping. Nevertheless, no deviations were found in the short-range region, which is the case for most RMC simulations presented in the literature. When a similar comparison, reported by Ref. 20, was made for the SPC model, the first peak for  $g^{(H-H)}$  was significantly lower than the corresponding MC value. In the same report, RMC results obtained by fitting experimental data showed the common drawback of previous RMC versions, and  $g^{(H-H)}$  and  $g^{(O-O)}$  exhibited sharp cutoffs at small separations instead of decreasing gradually to zero. Deviations around the first minimum of  $g^{(O-H)}$  were also clearly seen. We did not find any of those discrepancies.

It is also interesting to note that  $g^{(H-H)}$  has smaller deviations than  $g^{(O-O)}$ . The better  $g^{(H-H)}$  statistics could to some extent be a trivial consequence of the fact that four times as many H–H pairs are available. Alternatively, these findings could follow from the associative properties of the liquid in the sense that strong hydrogen bonds are formed. This gives a special feature to the water structure and this information, hidden in the rdfs, could be more difficult to be fully reproduced in the RMC fitting. A revealing test would be to perform similar studies with other three-site molecules.

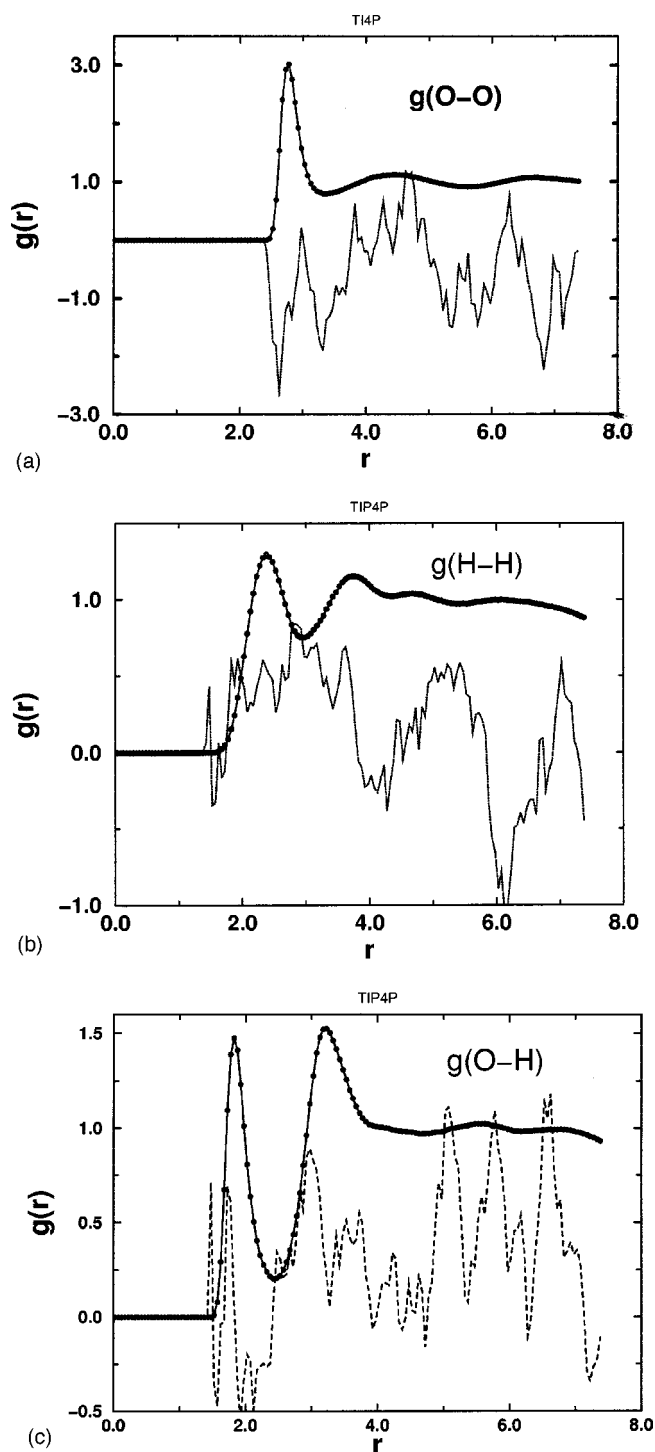


FIG. 1. Comparison between MMC (closed circles) and RMC (solid line) radial distribution functions (rdfs) for the TIP4P water model. The dashed line shows the difference  $[g_{\text{MMC}}^i(r_i) - g_{\text{RMC}}^i(r_i)] \times 10^3$ : (a)  $g^{\text{O-O}}(r)$ , (b)  $g^{\text{H-H}}(r)$ , and (c)  $g^{\text{O-H}}(r)$ .

Liquid hydrogen sulphide would be an appropriate candidate, since it is a molecule with large similarities to water and yet has less tendency to form hydrogen bonds. Such study is in progress.

As shown in Fig. 3 the largest deviations are observed for the flexible SPCFX model rdfs when reproduced by the RMC with a rigid geometry. Even though the rdfs are well fitted, the RMC finds difficulties arranging configurations of

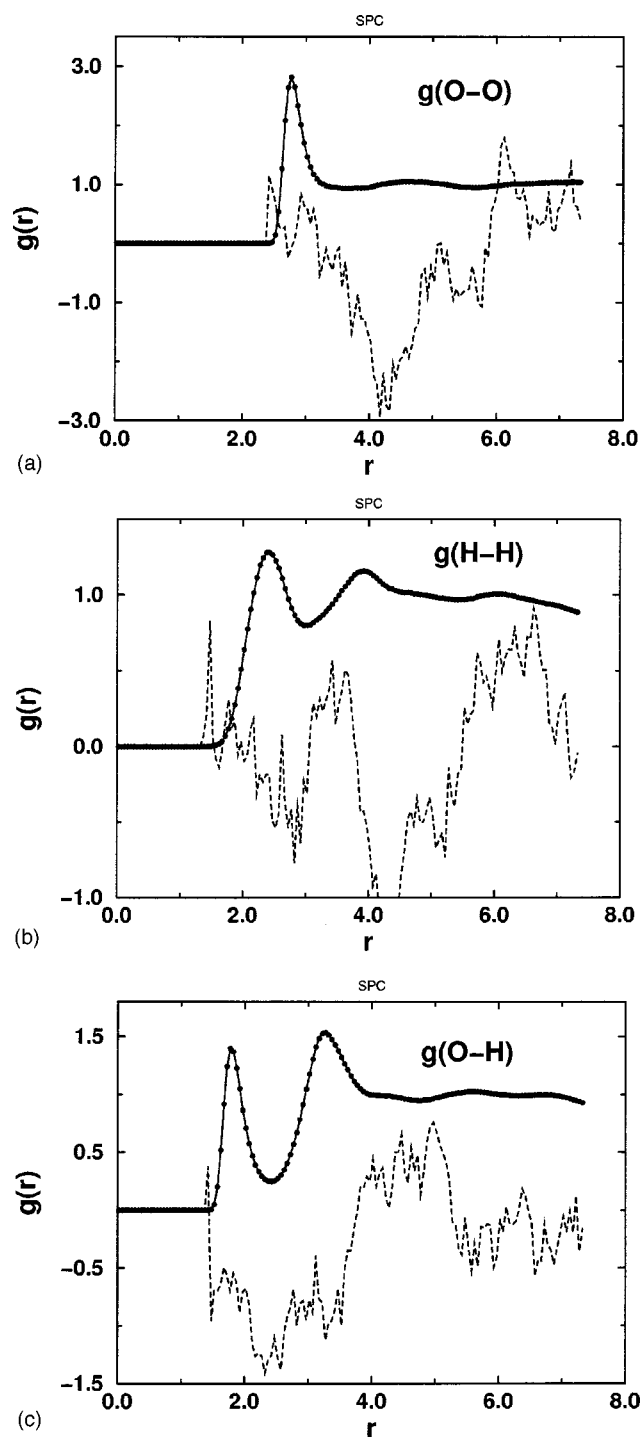


FIG. 2. Comparison between MMC and RMC rdfs for SPC water. Notations are the same as in Fig. 1.

rigid molecules to perfectly fit the structure generated by the flexible water model. One would expect similar differences when using real experimental data as the input for the RMC, as is, in fact, seen in Fig. 4.

In general, the agreement could be improved by decreasing the bin size ( $dr$ ). Discussions regarding the importance of  $dr$  have already been given for spherical particles,<sup>31,36</sup> and it is sufficient to mention some basic aspects. RMC is unable to distinguish positions within the same bin, and within this resolution every point is equivalent. For this reason, layers

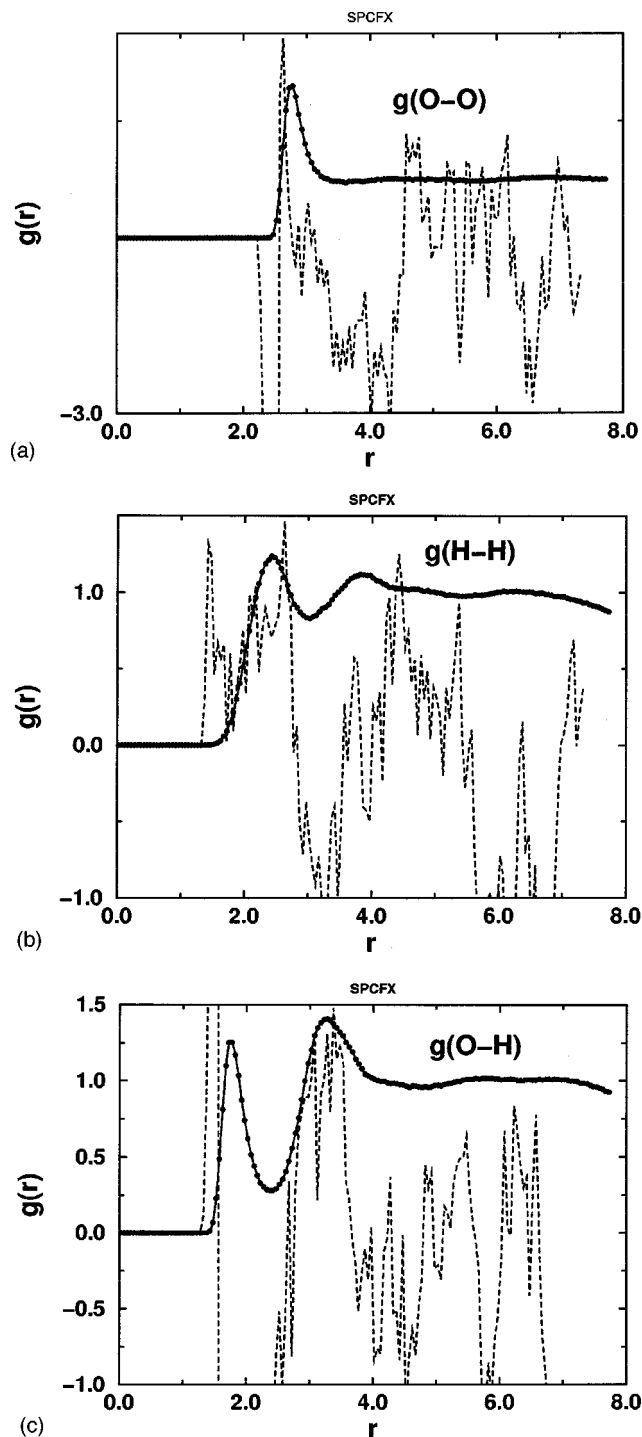


FIG. 3. MMC and RMC rdf's for the flexible water model SPCFX. Notations are the same as in Fig. 1.

between close contact and the first maximum will be overestimated, while layers where the rdf is decreasing will be underestimated. This can be visualized by performing a RMC simulation with the same bin as the experimental one, and then calculating the rdf for the generated RMC configurations with a smaller grid on the analysis phase. With a large experimental grid size, an interpolation of experimental points in order to refine the data and generate appropriate input for RMC is recommended.

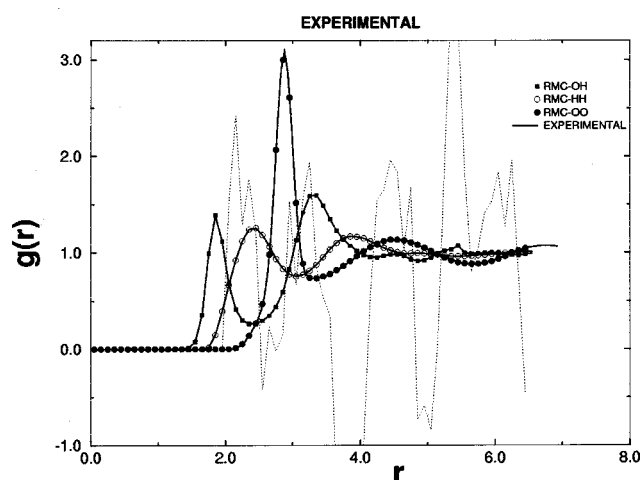


FIG. 4. Comparison between experimental rdfs of real water (closed circles) (from Ref. 41) and RMC rdfs. The dashed line shows the difference  $[\rho_{\text{EXP}}^{O-O}(r_i) - \rho_{\text{RMC}}^{O-O}(r_i)] \times 10^3$ .

### B. Hydrogen bond analysis

Liquid water has the peculiar characteristic of forming strong HB, which is manifested in the rdfs. In the literature, different definitions for HB are found based on geometric and/or energetic criteria.<sup>5</sup> Generally, in RMC applications, where the pair interactions are unknown, only a geometrical criterion could be used. However, for our theoretical studies, the energetic form of Jorgensen *et al.* will be taken.<sup>6</sup> With this definition, one assumes the existence of a hydrogen bond for any pair of molecules whenever they interact with an energy of at least  $-2.25$  kcal/mol. After identifying a HB, the angles formed between the hydrogen donor ( $\phi$ ,  $O-H \cdots O$ ) and acceptor ( $\omega$ ,  $H \cdots O-H$ ) are used to characterize the structure.<sup>6</sup>

Assuming that the particles interact according to the TIP4P model, we were able to calculate for instance the percentage of molecules having  $n_{\text{HB}}$  hydrogen bonds. It should be stressed that the interaction potential was necessary only for the present analysis purposes.

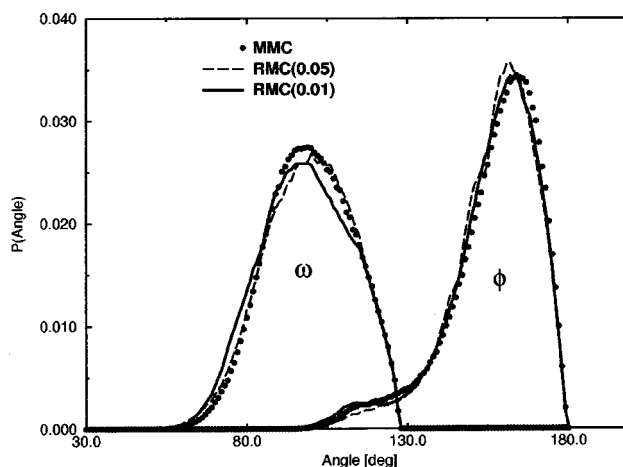


FIG. 5. The angular distribution functions,  $P$ , as a function of  $\phi$  and  $\omega$ . Closed circles represent MMC data, while the solid line is the RMC result with  $dr=0.01$  and the dashed line is the RMC result with  $dr=0.05$ .

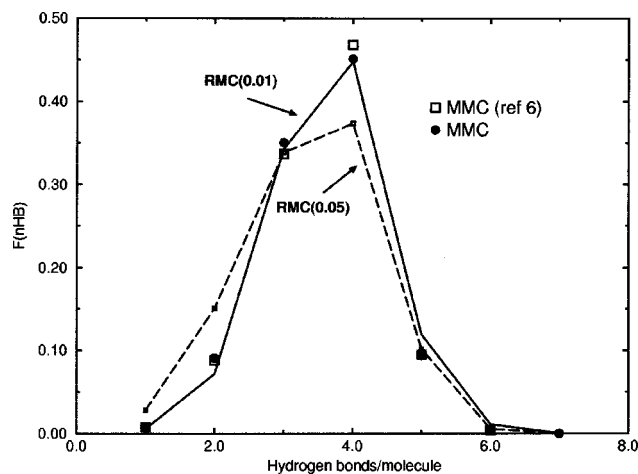


FIG. 6. The percentage of clusters with  $n_{\text{HB}}$  hydrogen bonds. Notations are the same as in Fig. 5.

Figure 5 illustrates how the hydrogen bonds are oriented, while the percentage of clusters having  $n_{\text{HB}}$  hydrogen bonds is plotted in Fig. 6. In general, the RMC data were found to reproduce the MMC results well, particularly when a finer  $dr$  is used both for the input rdf and the RMC simulation.

As shown in Table I, the RMC average number of HB,  $\langle n_{\text{HB}} \rangle$ , and the average energy,  $\langle \epsilon_{\text{HB}} \rangle$ , are within the statistical errors for  $dr=0.01$ . It also seems that the hydrogen bond energy is not particularly sensitive to small structural changes. An analogous reasoning can be applied to the orientation formed by the hydrogen donor ( $\phi$ ,  $\text{O}-\text{H}\cdots\text{O}$ ) and acceptor ( $\omega$ ,  $\text{H}\cdots\text{O}-\text{H}$ ) as shown in Table I.

The agreement between RMC and MMC is surprisingly good, considering that the three-dimensional structure of a pair of water molecules depends on the Euler angles and the distance between the reference points of both molecules. These variables can be reduced to six (five angles and the intermolecular distance).<sup>42</sup> As a consequence, the presented version of the RMC method, which used only three rdFs, i.e., three variables, could be working with an insufficient amount of information to fully reproduce the three-dimensional structure. Nevertheless, the hydrogen bond analysis shows that the main features of the structure are satisfactorily reproduced.

### C. Configurational energy

The criterion of “goodness” for RMC results in terms of energetic analysis was introduced before.<sup>29,31,36,43</sup> For many pair potentials, like Lennard-Jones, small changes in

the rdf may introduce large deviations in the configurational energy,  $U$ , since the dominant contributions come from small separations. For this reason,  $U$  is a sensitive indicator of the reliability of the RMC outcomes.

Table I shows the average energy of the present MMC and RMC simulations together with MC simulations of Jorgensen *et al.*<sup>6</sup> The RMC with small bin size satisfactorily reproduces the MMC energy, although the deviations are larger than one would expect from the excellent agreement found for the rdFs. The relative error is  $\sim 10$  and 17% for  $dr=0.01$  and  $dr=0.05$ , respectively. When compared to Lennard-Jones studies,<sup>31,36</sup> these numbers are at least five times larger. With the TIP4P model the O–O interaction dominates and it is exactly for this pair that we did find higher differences for the rdf.

Our results therefore indicate that even getting a near perfect agreement for all rdFs, as  $g(\text{O}-\text{O})$ ,  $g(\text{H}-\text{H})$ , as  $g(\text{O}-\text{H})$  in liquid water, the three-dimensional structure of complex polyatomic molecules is not completely resolved by the RMC technique. The small angular distortions that we observed in Fig. 5, and also increased as the bin size increased, seem to be enough to produce the observed average energy discrepancies.

### D. Sampling properties

Earlier RMC algorithms have suffered from sampling problems.<sup>32</sup> Therefore it is important to verify that independent configurations have been generated. To check this, one could for instance look at fluctuations of measurable thermodynamic variables or at the acceptance ratio. However, as we have also suggested,<sup>34</sup> two complementary indicators of the sampling properties of the system should be used in a RMC simulation. It is convenient to follow the displacement of the particles and to characterize the physical state of the collected configurations by the order parameter Eq. (5). Indeed, even the acceptance ratio should be analyzed in more detail, e.g., by looking to blocks of the production run.

In Fig. 7, the behavior of the acceptance ratio is shown as a function of the number of RMC cycles ( $N_{\text{cycles}}$ ) at the production phase. The data is for the SPC-RMC system. Each point corresponds to a block average over 100 cycles. New configurations are accepted in this case with an almost constant probability of 23%. There is no indication that the method is sampling the same configuration during the observation time. In contrast, new configurations have been generated at a reasonable ratio. It still remains a question of how much the particles are moving, which can be seen from the

TABLE I. Comparison of the average total configurational energy,  $U$ , and hydrogen bond properties for the TIP4P model, using two different “bin” sizes.  $\langle n_{\text{HB}} \rangle$  and  $\langle \epsilon_{\text{HB}} \rangle$  correspond to the average number of HB and the average energy, respectively. The angles  $\phi$  and  $\omega$  are defined as in the text.

| Simulation  | Jorgensen | MMC               | RMC- $dr=0.01$   | RMC- $dr=0.05$   |
|---|-----------|-------------------|------------------|------------------|
| $\langle U \rangle$ (kcal/mol)                    | -10.07    | $-10.20 \pm 0.14$ | $-9.18 \pm 0.09$ | $-8.46 \pm 0.08$ |
| $\langle n_{\text{HB}} \rangle$                   | 3.57      | $3.55 \pm 0.09$   | $3.64 \pm 0.07$  | $3.39 \pm 0.07$  |
| $\langle \epsilon_{\text{HB}} \rangle$ (kcal/mol) | -4.17     | $-4.13 \pm 0.12$  | $-4.23 \pm 0.08$ | $-4.27 \pm 0.07$ |
| $\langle \omega \rangle$ (deg)                    | 99        | 99                | 98               | 98               |
| $\langle \phi \rangle$ (deg)                      | 158       | 157               | 156              | 155              |

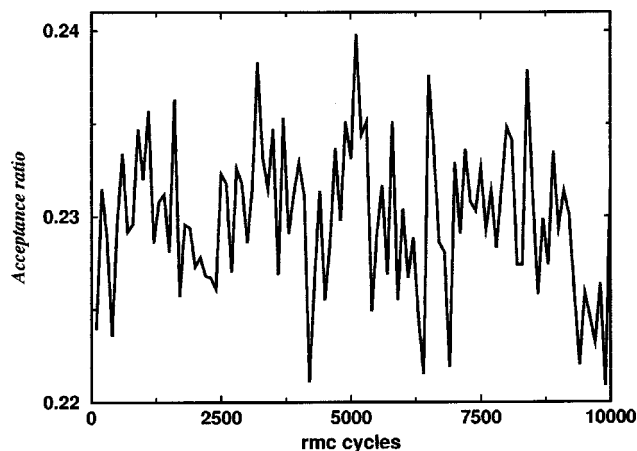


FIG. 7. The acceptance ratio during the production phase as a function of the number of RMC cycles ( $N_{\text{cycles}}$ ). Each point in the graph corresponds to an average over 100 RMC cycles. Data are obtained for the SPC-RMC system.

development of  $\langle \Delta r^2 \rangle$  as a function of  $N_{\text{cycles}}$ . In Fig. 8 the translational displacement of the oxygen atoms is plotted. It is evident from Fig. 8 that the particles are exposed to rational displacements and are not trapped into phase space points that could correspond to local minima. On the contrary, their displacement have similar behavior as found in ordinary MC simulations. Nevertheless, to certify that the system is really in the liquid state, the order parameter,  $O(t)$ , defined in Eq. (5) was also analyzed. In Fig. 9, a plot of  $O(t)$  as a function of RMC  $N_{\text{cycles}}$  is presented. The mean value of  $O(t)$  is  $-0.8$ , which is of the same order as the values reported by Berne and Harp for a Stockmayer fluid.<sup>39</sup> Similar behavior is found for other systems, e.g., the mean value of  $O(t)$  for EXPT-RMC was found to be  $-0.3$  for a RMC simulation with an acceptance ratio of 17%. These values are characteristic for a system in the liquid state. However, we should point out that  $O(t)$  is also sensitive to the choice of translational and rotational displacement parameters. There is a

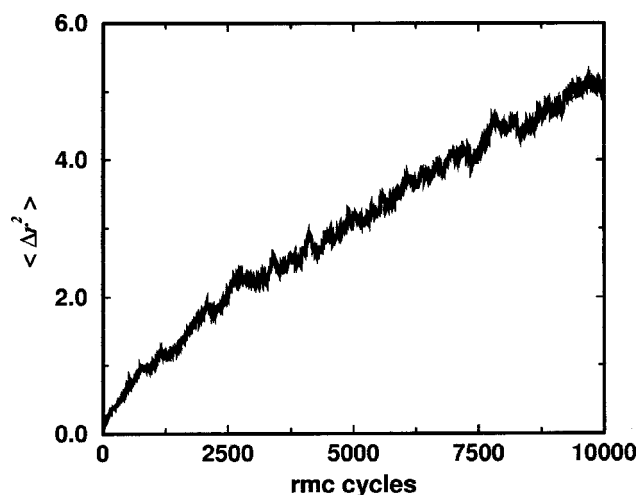


FIG. 8. The mean square translational displacement ( $\langle \Delta r^2 \rangle$ ) of oxygen atoms in units of  $\text{Å}^2$  as a function of the RMC simulation cycles ( $N_{\text{cycles}}$ ). The data are obtained for the SPC-RMC system and collected during the production phase.

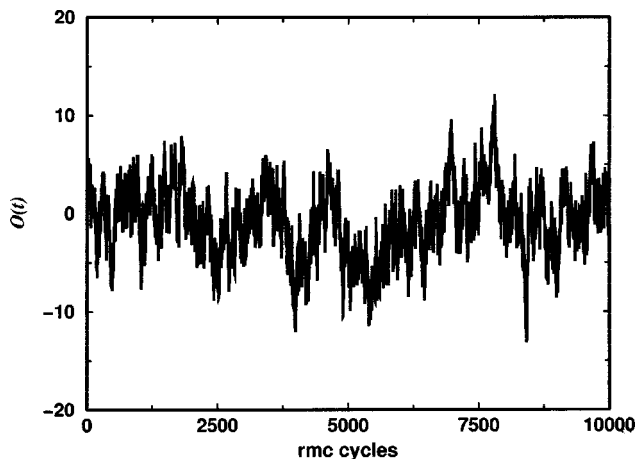


FIG. 9. Translational order parameter [ $O(t)$ ] for the oxygen atoms as a function of the RMC simulation cycles ( $N_{\text{cycles}}$ ). The system and conditions are the same as in Fig. 8.

coupling between these parameters that does not seem to obey a general rule. The only trend already found is that decreasing the translational displacement parameter and increasing the rotational one usually leads to a bit higher acceptance and translational “diffusion coefficients” (the slope of the graphic  $\langle \Delta r^2 \rangle$  as a function of the  $N_{\text{cycles}}$ ). A more systematic and strictly technical study will be addressed in forthcoming works.

## V. CONCLUSIONS

RMC is a novel molecular modeling technique, still under development. One basic problem, the complete reproduction of the input rdfs, was eliminated with the algorithm proposed in this paper. The liquid water structure was successfully reproduced without any *ad hoc* constraints, even when real experimental data were used as the input. With the studied algorithm it is sufficient to have a small number of particles (of the order of 100).

The average energy may be sensitive to small configurational changes. This fact increases the demands on the RMC technique to generate adequate configurations. The simulation tests presented in this report indicate that the new algorithm is successful in this respect, at least with a bin size small enough. Also the hydrogen bond analysis showed quite good agreement between the RMC results and the MC simulations.

On the other hand, we have also seen that an excellent reproduction of the input rdfs, although necessary, is not sufficient to guarantee prediction with the same accuracy for other properties in a polyatomic liquid such as water. This is probably a consequence of the fact that it is not enough to consider only three input variables, namely the available rdfs. However, to neglect small angular corrections seems not to severely affect for instance the configurational energy.

This finding opens up new perspectives for RMC studies of molecular liquids. The present study might be extended to extract fairly accurate angular correlations from experimental water data and to improve existing water pair potentials. This



work has already been started and the results will be presented in a forthcoming paper.

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