

A configuration bias Monte Carlo method for water

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A configuration bias Monte Carlo (CBMC) procedure suitable for the insertion and deletion of water molecules (SPC/E) in grand canonical and Gibbs ensemble Monte Carlo (GEMC) simulations under ambient conditions is presented. This CBMC technique involves sampling a number of orientations of the molecule at the chosen site and selecting one with a probability proportional to its Boltzmann weight. The Swendsen–Wang technique is used to reject improbable insertions or deletions before performing expensive CBMC calculations. This approach yields significant gains in efficiency and should be applicable to many other systems. Water molecules are frequently inserted and deleted in the same locations indicating that the overall acceptance rate for such moves is somewhat misleading. A better measure is to only consider deletions of molecules that have remained in the system for a sufficiently long time. Based upon this measure insertions and deletions should be attempted at least as often as displacements in grand canonical Monte Carlo simulations of water. © 1995 American Institute of Physics.

I. INTRODUCTION

Monte Carlo techniques such as grand canonical Monte Carlo (GCMC) or Gibbs ensemble Monte Carlo (GEMC)^{1–3} provide useful approaches for studying phase diagrams. Also GCMC is useful for the general study of solutions and confined systems. Of the systems that can be studied using these approaches, aqueous solutions are undoubtedly among the most important. For dense aqueous systems near room temperature one of the main difficulties encountered in GCMC or GEMC calculations is that moves which involve adding or removing molecules typically have relatively low acceptance rates.

Two of the methods that have been previously employed to try to overcome this problem in pure water are cavity bias Monte Carlo^{4,5} and rotation bias Monte Carlo⁶ in which one of the three rotational axes is sampled with an effective Boltzmann weighting factor. The latter was implemented in GEMC and involved relatively few switches of molecules between the simulation boxes compared to the number of translational and rotational moves within each box. Cracknell *et al.*⁶ expressed concerns that higher numbers of switching attempts result in frequently switching the same molecules (among essentially the same sites) leading to artificially high acceptance rates and little real improvement in the sampling. Both techniques result in significant gains as compared to simply using straightforward deletions and insertions.^{5,6}

It is evident that one should be able to efficiently optimize all three orientational degrees of freedom for the water molecules using the CBMC technique.^{7–10} It should be possible to combine this approach with the excluded volume mapping technique^{11,12} (which is closely related to the cavity bias approach) for the grand canonical ensemble along with increased numbers of insertion relative to deletion attempts as was suggested in Ref. 6.

The Swendsen–Wang (SW) method^{13,14} provides a mechanism for rejecting insertions and deletions which would have a very low probability of being accepted before

performing expensive CBMC calculations. Since the vast majority of attempts at such moves in ambient water fit into this category, the SW method proves to be very useful indeed.

In this paper we apply CBMC, excluded volume techniques with high rates of insertion attempts, and the SW method in order to increase the effectiveness of GCMC simulations for pure water. The merits of various combinations of these techniques have been systematically explored taking into account the influence of frequent insertions and deletions of water molecules at essentially the same sites. The method presented is directly applicable to water molecules in aqueous solutions and also to a wide range of anisotropic molecules in liquids. Previously, we have applied a related CBMC method to GCMC simulations of ionic solutions at elevated temperatures with considerable success.¹⁵ It seems likely that these techniques or closely related ones could be applied to a wide range of systems and ensembles including the Gibbs, canonical, and semigrand¹⁶ ensembles. In Sect. II a formal outline of the simulation techniques is given. Following that we present the results from a series of simulations and discuss their implications.

II. METHOD

In this section we describe a CBMC method suitable for inserting and deleting water molecules in condensed phases. A number of complementary techniques are also described. While this paper explicitly outlines a method for GCMC calculations for pure water it is directly applicable to any rigid anisotropic molecule in solution. We begin by outlining a formalism for performing straightforward insertions and deletions in the grand canonical ensemble. Next excluded volume techniques, particularly in combination with larger numbers of insertion attempts than deletion attempts, are reviewed. Then we provide the formalism for the SW and CBMC techniques followed by explicit descriptions of CBMC for water molecules. We employ the so-called SPC/E¹⁷ water model. Briefly, this model consists of three

sites that roughly correspond to the oxygen and two hydrogen atoms within a water molecule. The oxygen carries a charge of $-0.8476e$ while each of the hydrogen atoms carries a balancing charge of $0.4238e$. A Lennard-Jones potential centered on the oxygen atom is also used.

Excellent background material for GCMC is available in Refs. 1–3. For reasons of efficiency most Monte Carlo techniques involve moves which modify one aspect of the configuration at a time in a manner that depends only on the configuration itself. A sequence of such moves is called a Markov chain.¹ One condition nearly always imposed on these moves is detailed balance,

$$\pi_{ij} p_i = \pi_{ji} p_j, \quad (1)$$

where p_i and p_j are the probabilities that the system is in state i and state j , while π_{ij} and π_{ji} are the probabilities of a system in state i going to state j and a system in state j going to state i . This condition requires that the probability of making a Monte Carlo move from a particular state i to another state j is equal to the probability of going from j to i for all states i and j of the system.

Typically, in Monte Carlo simulations one has

$$\pi_{ij} = \alpha_{ij} f_{ij}, \quad (2)$$

where α_{ij} is the probability of attempting a certain move and f_{ij} is the probability of accepting that move. Combining Eqs. (1) and (2) and rearranging gives

$$\frac{f_{ij}}{f_{ji}} = \frac{\alpha_{ji} p_j}{\alpha_{ij} p_i}. \quad (3)$$

To insure that Eq. (3) is satisfied, Metropolis *et al.*¹⁸ employed a condition equivalent to

$$f_{ij} = \min\left(1, \frac{f_{ij}}{f_{ji}}\right), \quad (4)$$

which requires that one calculate the ratio of the α 's and p 's for a particular move and for its inverse (i.e., the move that would precisely undo it). If the resulting f_{ij} is greater than or equal to a random number generated on the interval $[0,1]$ then the move is accepted. In the grand canonical ensemble the probability of a state i , assuming that the particles of a species are indistinguishable, is given by¹⁹

$$p_i = \left(\frac{e^{\beta\mu}}{\Omega \Lambda^3}\right)^N d\Omega d\mathbf{R} e^{-\beta U_i} / \Xi, \quad (5)$$

where N is the number of molecules, μ is the chemical potential, $\beta = (k_B T)^{-1}$, where k_B is the Boltzmann constant and T the temperature, Λ is the thermal de Broglie wavelength ($\Lambda = \sqrt{\beta h^2 / 2\pi m}$, where h is Planck's constant and m the mass), U_i is the total potential energy of the i th state of the system, Ω is 1 , 4π , or $8\pi^2$ if the species is spherical, linear, or nonlinear, respectively, $d\Omega$ is the product of all of the solid angle elements of all of the particles in the system, $d\mathbf{R}$ is the product of all of the volume elements of all of the particles in the system, and Ξ is the grand canonical partition function.

A typical grand canonical Monte Carlo simulation involves four types of moves: translations, rotations (if the particles are nonspherical), insertions, and deletions of par-

ticles. Since methods for making translations and rotations are described elsewhere,^{1–3} they are not discussed here.

It is straightforward to determine the expression for accepting or rejecting moves which involve changing the number of particles.^{1–3,19} For instance, for an insertion of a molecule, Eq. (3) becomes

$$\frac{f_{ij}}{f_{ji}} = \frac{V e^{-\beta(U_j - U_i - \mu)} a}{(N+1) \Lambda^3}, \quad (6)$$

where a is 1 for spherical particles and $\sin \theta$ otherwise (θ is the angle between a chosen molecular axis and some arbitrary space fixed axis) and V is the volume of the simulation box.

We now consider methods to improve the sampling for water insertions and deletions. It is appropriate to think of α_{ij} as a product of the form

$$\alpha_{ij} = \alpha_{ij}^p \alpha_{ij}^0 \alpha_{ij}^{\text{SW}} \alpha_{ij}^{\text{CBMC}}, \quad (7)$$

where α_{ij}^p is the probability of attempting a particular move in a particular direction, α_{ij}^0 is the probability that a move from state i to j will be attempted once the type of move has been selected, α_{ij}^{SW} is a factor determined by the SW filters, and $\alpha_{ij}^{\text{CBMC}}$ is the factor that corrects for the bias introduced by the CBMC technique. Similarly,

$$\alpha_{ji} = \alpha_{ji}^p \alpha_{ji}^0 \alpha_{ji}^{\text{SW}} \alpha_{ji}^{\text{CBMC}}. \quad (8)$$

In the following the implementation and effect of each part of the calculation represented by the breakdown of the α 's given above are systematically considered. If SW filters or CBMC are not employed the corresponding α 's are 1.

If making a move in one direction is cheaper than its inverse then one might want to make more moves in that direction and correct for the bias in the corresponding α^p . In grand canonical simulations insertions can often be rejected quite early in the process because of excessive overlap of the molecular cores. By performing more insertion than deletion attempts one can obtain significantly more successful insertions and deletions in a given amount of CPU time. In addition there are efficient methods for rejecting insertions such as cavity bias^{4,5} and the closely related excluded volume mapping techniques.^{11,12} In this work we employ the excluded volume mapping technique. This technique requires that the system be divided up into small cubes. In the current implementation, for each cube there is a character storage location in memory which contains a count of the water molecules which have oxygen atoms that are closer than a specified distance to all points within the cube. This array is initialized at the beginning of the simulation. As the simulation proceeds it is updated when moves are accepted. When one attempts an insertion one first determines what cube the insertion site is in and then checks to see if the corresponding character array element is nonzero. If the element is nonzero then the insertion move may be rejected immediately without introducing any error into the calculation if the specified distance used to construct the array is smaller than the minimum separation ever observed between the molecules. For the current GCMC simulations of liquid water under ambient conditions, unless a large number of insertions are attempted relative to displacement attempts the overhead of maintain-

ing the table outweighs the advantage gained by being able to reject some insertions using the excluded volume mapping technique. However, if many insertions are being attempted compared to the number of displacements significant gains can be attained.

Frenkel provides a very useful description of a scheme¹⁴ developed from the SW method¹³ for rejecting moves in early or intermediate stages provided that one has a predictor for the success of a move. Ideally, one would like to have a property that may be calculated significantly faster than the move itself and that may be reliably used to predict whether an attempted move will fail. Given such a predictor one can reject moves with a probability $1 - \alpha^{\text{SW}}$ at some stage during the move. Since a number of such SW filters may be employed in the same move we have

$$\alpha_{ij}^{\text{SW}} = \prod_{l=1}^{n_{\text{SW}}} \alpha_{ijl}^{\text{SW}}, \quad (9)$$

where $1 - \alpha_{ijl}^{\text{SW}}$ is the probability of immediately rejecting a move with the l th SW filter and n_{SW} is the number of SW filters employed. Note that the filters should be applied at the same stages in the reverse process (i.e., if the filter is being applied at the beginning of insertion attempts then the same filter should be applied at the end of deletion attempts).

There is considerable freedom in choosing the α_{ijl}^{SW} probabilities. Since the success of an attempted move ultimately depends on energetic considerations the SW filters are often based on properties closely related to the energetics of the move. Thus, it is convenient to treat the α^{SW} factors in a manner similar to that employed in Metropolis sampling, namely

$$\alpha_{ijl}^{\text{SW}} = 1 \quad \text{if} \quad \Delta U_{ijl}^{\text{SW}} \leq 0, \\ = e^{-\beta \Delta U_{ijl}^{\text{SW}}} \quad \text{if} \quad \Delta U_{ijl}^{\text{SW}} > 0, \quad (10)$$

where $\Delta U_{ijl}^{\text{SW}}$ is a function that has dimensions of energy and is a predictor for the success of the move being attempted. We also require that $\Delta U_{ijl}^{\text{SW}} = -\Delta U_{jil}^{\text{SW}}$. Combining this requirement with Eq. (10) one finds that

$$\alpha_{jil}^{\text{SW}} / \alpha_{ijl}^{\text{SW}} = e^{\beta \Delta U_{ijl}^{\text{SW}}}. \quad (11)$$

This ratio is implicitly present in Eq. (3). Choices for $\Delta U_{ijl}^{\text{SW}}$ for water are discussed below. Unfortunately such predictors in general depend on the state of the system. As well, biasing techniques such as CBMC require predictors distinct from cases where they are not employed. In this work we ignore the effect of attempting insertions and deletions with different probabilities on the choice of the predictors since the effect is a relatively minor one. Developing and using SW predictors is justifiable if the system will be studied enough to get a useful return. Water under ambient conditions is definitely such a system. Further, it would not be surprising if the same predictors prove to be effective for aqueous systems with somewhat different compositions and temperatures.

Since the ratio f_{ij}/f_{ji} is closely related to the acceptance probability for an attempted move, it is useful to consider it when looking for predictors. Figure 1(a) gives $\ln(f_{ij}/f_{ji})$ for

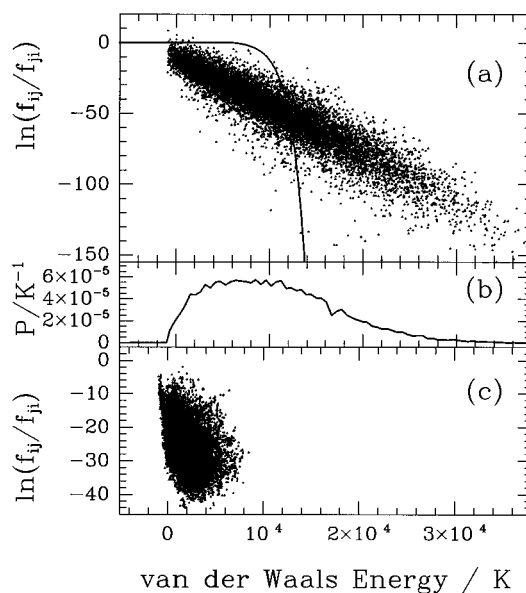


FIG. 1. A demonstration of how a Swendsen–Wang filter for the insertion and deletion of water molecules can be constructed for the total van der Waal's energy of the water molecule for straightforward insertions and deletions. The ratio f_{ij}/f_{ji} is used to determine whether the attempted move will be accepted in the Metropolis scheme. For values of f_{ij}/f_{ji} less than 1 [$\ln(f_{ij}/f_{ji})$ less than 0] this ratio is the probability of accepting the move. Plot (a) gives the $\ln(f_{ij}/f_{ji})$ vs the van der Waal's energy of the water molecule that one is attempting to insert. Insertions which would result in water molecules being closer than 2.3 Å have already been eliminated from consideration. The curve is the $\Delta U_{ijl}^{\text{SW}}$ function used to discern which moves have a chance of being accepted from those that do not. Plot (b) gives the normalized distribution for the van der Waal's energies plotted in (a). Plot (c) gives the $\ln(f_{ij}/f_{ji})$ vs the van der Waal's energy of the water molecule that one is attempting to delete. Note that the regime in which $\Delta U_{ijl}^{\text{SW}}$ differs significantly from 0 lies above the range where deletion attempts have a reasonable chance of success. This is important since the van der Waal's energy and hence $\Delta U_{ijl}^{\text{SW}}$ is a rather poor predictor of the success of deletion attempts.

attempts to create a new molecule as a function of the total van der Waal's energy U_{VDW} , experienced by the molecule. Note that insertions which lead to water molecules with oxygen atoms closer than 2.3 Å, a region never sampled in ambient trajectories, have already been removed and do not appear in the plot. The distribution of these van der Waal's energies is given in Fig. 1(b). One can see that the van der Waal's energy is a good predictor for the success of the insertion and that it should be possible to reject many insertion attempts based on it alone. This is significant since it means that one can terminate the insertion attempt for most insertions after the relatively inexpensive van der Waal's energy calculation and before calculating the more expensive electrostatic energy and, if utilized, the CBMC calculations.

In general, one could take the SW predictor for the success of an insertion, $\Delta U_{ijl}^{\text{SW}}$, to be a linear function of some relevant energy in the system U_l^{SW} , i.e., $k(U_l^{\text{SW}} - U_l^{\text{SW}0})$ where k and $U_l^{\text{SW}0}$ are constants. The van der Waal's energy is not a very good predictor in the region where attempted moves are frequently accepted [see the upper left-hand corner of Fig. 1(a)]. As a result, one would like to avoid having the SW filter based on the van der Waal's energy affect attempts for this range of energies. Therefore, it would be

TABLE I. Parameters for the Swendsen–Wang filters.

CBMC employed	Type of filter	D^a	Parameters		Fraction removed
			$A \cdot 10\,000$ (K^{-1})	U_0 (K)	
No	VDW ^b	Insertion	6.5	6000	0.73
Yes	VDW ^b	Insertion	10	8000	0.48
Yes	VDWEF ^c	Insertion	10	-1000	0.76
Yes	VDWMP ^d	Deletion	-6.5	-6000	0.95

^aThe direction for which D is 1 rather than -1 [see Eq. (12)].

^bThe SW filter with U_l^{SW} given by the total van der Waal's energy of the water molecule.

^cThe SW filter with U_l^{SW} determined from the total van der Waal's energy of the water molecule and the local electric field using Eq. (20).

^dThe SW filter with U_l^{SW} determined from the total van der Waal's energy of the water molecule and gradients of the electrostatic potential using Eq. (21).

necessary to consider using either a k which is rather small in magnitude or a $U_l^{\text{SW}0}$ which is large or some combination thereof. Clearly this would not eliminate as many attempts as should be possible. Therefore we have chosen an alternate approach with

$$\beta\Delta U_{ijl}^{\text{SW}} = D(e^{A_l(U_l^{\text{SW}} - U_l^{\text{SW}0})} - 1),$$

$$\text{for } A_l(U_l^{\text{SW}} - U_l^{\text{SW}0}) > 0,$$

$$= 0, \quad \text{otherwise,} \quad (12)$$

where A_l is a constant. D is 1 for a move in a particular direction and -1 for the inverse move ensuring that $\Delta U_{ijl}^{\text{SW}} = -\Delta U_{jil}^{\text{SW}}$. Equations (10) and (12) indicate that filters constructed in this way have a convenient feature in that they only terminate moves in one direction (insertions in the present case). For the van der Waal's filter for insertions $U_l^{\text{SW}} = U_{\text{VDW}}$ and D is 1. The corresponding SW predictor for the deletion of a water molecule also uses $U_l^{\text{SW}} = U_{\text{VDW}}$ where the U_{VDW} is the van der Waal's energy of the molecule that is being considered for deletion and D is -1 .

The form given in Eq. (12) is, of course, not unique or necessarily optimal but it works well for water. The values of the constants A_l and $U_l^{\text{SW}0}$ can be determined by performing brief simulations in which U_{VDW} and f_{ij}/f_{ji} are monitored for the attempted moves in question. The parameters can then be determined from plots of these results. The values determined for these constants are given in Table I and the resulting curve is plotted in Fig. 1(a). This particular filter results in the immediate rejection of about 75% of the insertion attempts that make it to this stage. Figure 1(c) gives the corresponding plot for the van der Waal's energy of the water molecules for attempted deletions. It can be seen that the van der Waal's energy is a poor predictor for the success of deletions of water molecules. However, the SW filter employed in order to terminate insertions is essentially zero throughout the range of van der Waal's energies for water molecules considered for deletion; hence it has very little affect on these deletion attempts.

Filters based on the same functional form can also be made using the van der Waal's energy plus an estimate of the

electrostatic energy for the water molecule. For deletions the estimate of the electrostatic energy can be made using

$$U_{\text{El}}^{\text{est}} = -\boldsymbol{\mu} \cdot \mathbf{E} - \mathbf{Q} : \nabla \mathbf{E} - \mathbf{O} : \nabla \nabla \mathbf{E}, \quad (13)$$

where \mathbf{E} is the electric field at the location of the water molecule and $\boldsymbol{\mu}$, \mathbf{Q} , and \mathbf{O} are the space fixed dipole, quadrupole, and octapole moments, respectively, for the water molecule. The symbols $:$ and $:$ correspond to the diadic product operators.

For insertions, it is not so clear what orientation of the new molecule should be used for the estimate of the electrostatic energy. We have opted for the simplest approach in which an indication of the size of the electrostatic energy is obtained from the optimal interaction energy between the dipole moment of the water molecule and the local electric field, i.e., $-|\boldsymbol{\mu}||\mathbf{E}|$.

Since the van der Waal's energy is cheap to calculate it can help improve the efficiency of normal insertion and deletion moves. The filters based on the gradients of the electrostatic potential do not significantly improve on the efficiency of normal insertions and deletions, since the calculation of these gradients is essentially as expensive as the calculation of the energy change for the move itself. However, for the expensive CBMC moves described below the gradients of the electric fields are calculated at the start of the move anyway, so these filters can be implemented without significant overhead. The parameters A_l and $U_l^{\text{SW}0}$ for all of the SW filters employed are listed in Table I along with the fraction of the attempts that each eliminates. For the CBMC simulations the combination of these filters eliminates about 90% of the insertion and deletion attempts not including those insertions easily eliminated by excessive overlap.

Before explicitly presenting a CBMC technique for water insertions and deletions a more general formulation that is useful for rigid molecules will be provided. This approach can be regarded as a simple version of the methods developed for polymeric systems⁸⁻¹⁰ and for insertions and deletions of ions.¹⁵ Note that these methods provide more than one way to get from state i to state j , so one must make sure that the simulation still satisfies detailed balance. One way to ensure this is to impose a condition referred to as superdetailed balance.¹⁴ What this boils down to in the present context is that if one uniquely pairs each path from state i to state j with one from state j to state i for all paths between the states, and applies the detailed balance condition for each such pair of paths, then detailed balance is collectively satisfied for all of the paths between the states i and j . In the current work each path is paired with the path that performs the transformation in precisely the reverse manner.

The forward part of the move is constructed by selecting a set of new coordinates $\{\mathbf{u}_n\}_{ij}$, containing n elements, for some part of the system. The subscripts ij are used to differentiate this set from the one for the reverse move (from j to i signified by ji). The probability for choosing any member of this set, g , is determined by its Boltzmann weight within the set, i.e.,

$$p_g^{\text{CBMC}} = \frac{e^{-\beta U_{\mathbf{u}_g}^{\text{CBMC}}}}{\sum_{\{\mathbf{u}_h\}_{ij}} e^{-\beta U_{\mathbf{u}_h}^{\text{CBMC}}}}, \quad (14)$$

where $U_{\mathbf{u}_h}^{\text{CBMC}}$ is the potential energy used in the CBMC scheme. The state actually chosen is used as the final state j for the move so that $\mathbf{u}_j \equiv \mathbf{u}_g$ and $p_j^{\text{CBMC}} \equiv p_g^{\text{CBMC}}$. $\alpha_{ij}^{\text{CBMC}}$ is then given by

$$\alpha_{ij}^{\text{CBMC}} = \frac{p_j^{\text{CBMC}} n!}{(V_c)^n}, \quad (15)$$

where V_c is the number of computer addressable points for the coordinate space being sampled in this stage. The $n!$ and V_c factors take into account the probability of selecting the set $\{\mathbf{u}_h\}_{ij}$.

Similarly one can choose a set of coordinates $\{\mathbf{u}_h\}_{ji}$ (which must include \mathbf{u}_i , the initial coordinates) for the reverse process and calculate the probability for choosing the initial state i from this set using

$$p_i^{\text{CBMC}} = \frac{e^{-\beta U'_{\mathbf{u}_i}}}{\sum_{\{\mathbf{u}_h\}_{ji}} e^{-\beta U'_{\mathbf{u}_h}}}, \quad (16)$$

where U' represents the energy of the original state for the molecule(s) in question. $\alpha_{ji}^{\text{CBMC}}$ is given by

$$\alpha_{ji}^{\text{CBMC}} = \frac{p_i^{\text{CBMC}} n!}{(V_c)^n}. \quad (17)$$

One can then see that

$$\frac{\alpha_{ji}^{\text{CBMC}}}{\alpha_{ij}^{\text{CBMC}}} = \frac{p_i^{\text{CBMC}}}{p_j^{\text{CBMC}}}. \quad (18)$$

In the context of this work the forward process could involve an insertion of a water molecule into the system. The positional coordinates are common to all members of the set and the orientational coordinates are chosen randomly. The reverse process involves creating an ideal gas particle whose orientation coordinates are also chosen from a set containing n elements. Since all n ideal gas samples are equivalent, $p_i^{\text{CBMC}} = 1/n$, and Eq. (18) becomes

$$\frac{\alpha_{ji}^{\text{CBMC}}}{\alpha_{ij}^{\text{CBMC}}} = (np_j^{\text{CBMC}})^{-1}. \quad (19)$$

One could also select the sets $\{\mathbf{u}_h\}_{ij}$ and $\{\mathbf{u}_h\}_{ji}$ using techniques such as force bias or gradient bias^{20–22} in order to reduce n and thus the CPU time needed for the CBMC calculations. Since the CBMC method in this work does not add a significant amount of CPU time to the simulation when combined with SW techniques such approaches have not been pursued.

For the insertion of a water molecule, calculating the electrostatic energy with all of the molecules in the system for each different trial orientation of the new molecule is expensive. Instead we have chosen to calculate the first three gradients of the local electrostatic potential at the site of the new water molecule. The gradients are calculated without including the contributions from the images of the new water molecule. The electrostatic energy can then be estimated (with an error of $\sim 10\%$) relatively quickly by using the

space fixed multipolar moments of the water molecule in Eq. (13) for each of the trial orientations used in the CBMC calculation.

An explicit description of a CBMC water insertion is as follows.

- (1) Randomly select a position for the new water molecule.
- (2) Check the excluded volume array for the new position if this option is being used.
- (3) If the SW filter for van der Waal's energy is on, calculate the van der Waal's energy of the new water molecule. Consider rejecting the move with the probability $1 - \alpha_{ijl}^{\text{SW}}$, where α_{ijl}^{SW} is given by Eqs. (10) and (12), using this energy.
- (4) Calculate \mathbf{E} , $\nabla \mathbf{E}$ and $\nabla \nabla \mathbf{E}$ at this location (not including contributions from the new water molecule and its images).
- (5) If the SW filter for van der Waal's energy and the electric field,

$$U_{\text{VDWEF}}^{\text{SW}} = U_{\text{VDW}} - |\boldsymbol{\mu}| |\mathbf{E}|, \quad (20)$$

is on, use Eqs. (10) and (12) to determine if the move is to be rejected.

- (6) Perform the CBMC insertion of the water molecule. This is accomplished by trying n orientations for the water molecule and choosing one of them, g , with a weight given by Eq. (14) with $U_{\mathbf{u}_g}^{\text{CBMC}}$ given by the estimate of the electrostatic energy of the water molecule U_E^{est} obtained using Eq. (13). The ratio $\alpha_{ji}^{\text{CBMC}}/\alpha_{ij}^{\text{CBMC}}$ is calculated from Eq. (18).
- (7) If the SW filter for the van der Waal's energy plus the multipolar energy,

$$U_{\text{VDWMP}}^{\text{SW}} = U_{\text{VDW}} + U_E^{\text{est}}, \quad (21)$$

is on, use Eqs. (10) and (12) to determine α_{ijl}^{SW} .

- (8) Calculate the true change in the energy (i.e., not using the gradients), $U_j - U_i$, for inserting the water molecule.
- (9) Accept or reject the entire move using Eqs. (3) and (4) with f_{ij}/f_{ji} given by

$$\frac{f_{ij}}{f_{ji}} = \frac{\alpha_{ji}}{\alpha_{ij}} \frac{p_j}{p_i} = \frac{V e^{-\beta(U_j - U_i - \mu)} \alpha_{ji}^{\text{SW}} \alpha_{ji}^{\text{CBMC}} \alpha_{ji}^p}{(N+1) \Lambda^3 \alpha_{ij}^{\text{SW}} \alpha_{ij}^{\text{CBMC}} \alpha_{ij}^p}, \quad (22)$$

where

$$\alpha_{ji}^{\text{SW}}/\alpha_{ij}^{\text{SW}} = \exp \left[\beta \left(\sum_{l=0}^{n_{\text{SW}}} \Delta U_{ijl}^{\text{SW}} \right) \right], \quad (23)$$

and $\Delta U_{ijl}^{\text{SW}}$ for each filter is given by Eq. (12) with the coefficients from Table I.

The procedure for deleting a water molecule is very similar except that a randomly chosen water molecule is removed and the electric field \mathbf{E} and its gradients are calculated without contributions from this molecule and its periodic images. As well, the SW filters are applied at the same stages in the reverse process.

Many variations of the method given above were attempted; however, none were more effective for insertions and deletions of water. Notable examples of these are:

(1) The water molecule being inserted was translated using a CBMC procedure based solely on its van der Waal's energy prior to conducting the procedures outlined above.

(2) Using a scheme similar to that given in Ref. 15, nearby water molecules were rotated while the new water molecule was slowly inserted. This approach does lead to an increase in the acceptance rate of about a factor of 3 over those presented in this paper, but the final technique even with SW filtering requires more than three times the CPU time. This approach might prove useful for other systems or for water in a different state.

III. APPLICATIONS AND DISCUSSION

Our test system for this work consisted of roughly 216 water molecules in a cubic box with sides L 18.644 Å long. Ewald periodic boundary conditions were used to eliminate surface effects while taking into account the long-range nature of the Coulombic interactions.^{2,23} We used $\alpha L = 5.6$, $\epsilon_s = \infty$, and 586 k vectors.²³ The Lennard–Jones potentials were truncated at half the box length and the corresponding potential energy corrections¹ were applied. We employed combined translational and rotational moves of the water molecules (referred to as displacement moves), with frequent adjustments of the size of the maximum changes for each of these coordinates to ensure that the acceptance rate for displacements was close to 0.5.

A number of simulations were performed to determine the excess chemical potential for SPC/E at 298.15 K and a density of about 0.997 g/cc. From a simulation with an average density of 0.9952 g/cc the excess chemical potential was noted to be -29.2 kJ/mol (no correction for the self-polarization of the water molecule has been used) in agreement with a value of -29.1 kJ/mol given in the literature for the SPC/E model.²⁴ For all runs a common equilibrated starting configuration containing 216 molecules was used. The type of move to attempt at any particular time (e.g., a deletion vs a displacement move) was chosen with a probability given by the desired number of attempts divided by the total number of attempts per pass requested in the input data file. A number of test runs were performed from which it was determined that a $40 \times 40 \times 40$ (about 7 boxes across a water molecule) grid for the excluded volume mapping was essentially optimal. All boxes that lie completely within 2.25 Å of any water molecule were considered occupied. Further, all insertion attempts which placed water molecules within 2.3 Å of another water molecule were rejected based on direct distance calculations since water molecules were not observed to approach each other closer than this in canonical simulations.

For the CBMC calculations 500 trial orientations for the water molecules were used. Experience has shown that this value is large enough to ensure adequate sampling of the orientational degrees of freedom. Smaller numbers of trial states may prove to be sufficient. This possibility was not explored since SW procedures are so effective in the current

study that the overall CPU time is not affected much by a reduction of this number.

A pass in the reference run is composed of 216 attempts to displace a water molecule, 216 attempts to insert a new water molecule, and 216 attempts to delete a water molecule. To learn more about the issue raised by Cracknell *et al.*⁶ concerning the effect of a higher number of insertion or deletion moves (in their case switches) a run with only 22 insertion and deletion attempts per pass was also carried out. A number of runs with a higher number of the computationally cheaper insertion attempts while maintaining the number of deletion attempts at 216 were conducted. The optimal ratio of the number of insertion to deletion attempts is in the range of 10 to 100. A ratio of 25 was employed in this work. Excluded volume techniques were used with this higher ratio resulting in a reduction in the CPU time of about a factor of 2. SW techniques were implemented with the non-CBMC run where the higher number of insertions was used and in combination with CBMC with and without increased insertion attempt rates. All runs consisted of 5000 passes except for the reference run and the run with a reduced number of insertion and deletion attempts for which the run lengths were 10 000 and 20 000 passes, respectively.

The results obtained are presented in Table II. Since the primary goal of this paper is to describe a more effective method for performing GCMC simulations of water the results presented are largely confined to those which characterize the effectiveness of the various methods. However, the total potential energies, electrostatic energies, and densities are also included. The values obtained are consistent within 3% for the various runs. This variation is in the range expected for the run lengths employed.

The program maintains the molecules in the lowest entries of the data arrays. When a molecule is deleted the entries in the upper portions of the arrays are moved down to fill the gap. New molecules are added to the end of the arrays. One useful side effect of this procedure is that molecules which have existed in the system the longest tend to eventually evolve into the lower numbered elements of the arrays. This provides a convenient way to distinguish between molecules that have been recently inserted and those which have been in the system longer. By monitoring the position in the arrays of the molecules being deleted it is possible to learn about the extent of the rapid insertion and deletion of molecules in essentially the same location. The number of successful deletions per 1000 passes, N_D , is listed in Table II. In Fig. 2 the distribution of the array entry numbers for the water molecules that were successfully deleted is given for the reference run and for the run with the highest rate of deletions (i.e., the CBMC run involving an insertion/deletion ratio of 25:1). The large peak at around 215 indicates that in both runs most of the deletions occur among the more recently inserted molecules, as pointed out in Ref. 6. This problem is somewhat more pronounced in the system with the higher rate of insertion attempts. These plots suggest an alternate measure for determining the effectiveness of a given simulation. Below array entries of about 150 the distributions in Fig. 2 are fairly flat suggesting that such molecules have existed in the system long enough to become

TABLE II. Parameters, properties, acceptance rates, and execution times for various types of runs.

	Runs							
	216	22	5400	5400	216	216	5400	5400
Insertions/pass	216	22	5400	5400	216	216	5400	5400
Deletions/pass	216	22	216	216	216	216	216	216
Excluded volume	No	No	Yes	Yes	No	No	Yes	Yes
CBMC	No	No	No	No	Yes	Yes	Yes	Yes
SW	None	None	None	VDW ^a	None	All ^b	None	All ^b
\bar{U} (kJ/mol) ^c	-46.53	-47.08	-46.65	-46.58	-46.51	-46.53	-47.02	-47.09
\bar{U}_{el} (kJ/mol) ^d	-55.39	-56.28	-55.24	-55.23	-55.25	-55.28	-56.11	-55.92
ρ (g/cc)	1.01	0.997	1.01	0.989	1.01	0.999	1.02	0.995
N_D^e	17.4	2.2	80.2	160.6	103.6	120.6	512.8	465.2
N_D^{*f}	1.00 ^g	0.2	3.6	4.2	3.6	4.0	10.4	7.8
t_r^h	1.00	0.76	2.16	1.96	2.26	1.13	4.29	1.99
$gain^i$	1.00	0.17	2.13	4.71	2.63	6.13	6.87	13.4
$gain^{*j}$	1.00	0.26	1.67	2.14	1.59	3.54	2.42	3.92

^aVDW means that the Swendsen–Wang filter for non-CBMC runs (the first filter listed in Table II) was used.

^bAll means that all three Swendsen–Wang filters for CBMC runs listed in Table II were used.

^c \bar{U} is the average potential energy.

^d \bar{U}_{el} is the average electrostatic potential energy.

^eNumber of successful deletions for every 1000 passes.

^fNumber of successful deletions for every 1000 passes where the molecule number is less than 100.

^gThis value is 1.00 by coincidence.

^hExecution time per 1000 passes relative to the reference run which employed 216 normal insertion and deletion attempts per pass (7649 s on an IBM R6000 model 370 workstation).

ⁱAn estimate of the gain achieved relative to the reference run which employed 216 normal insertion and deletion attempts per pass.

^jAn estimate of the gain achieved relative to the reference run which employed 216 normal insertion and deletion attempts per pass based upon deletions where the molecule number is less than 100.

“typical” water molecules. Monitoring the number of deletions of such molecules should provide a more reliable measure of the effectiveness of various simulation techniques. The relative value of this quantity is fairly insensitive to the

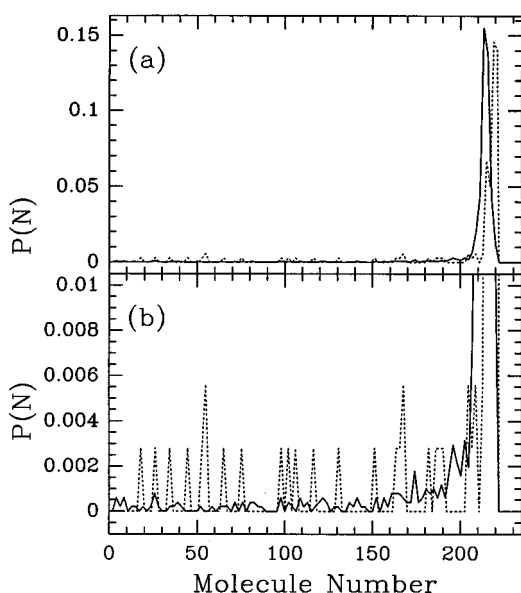


FIG. 2. The normalized distributions of the molecule number of water molecules that were successfully deleted. The dashed line is for the reference run while the solid line is for the run combining CBMC with insertion/deletion ratios of 25:1. Plot (a) presents the full distributions while plot (b) has an expanded vertical scale to illustrate the differences in the distributions. The large peak at about 215 in the distributions for both runs demonstrates that most of the deletions are of molecules that have recently been inserted.

maximum array element considered for values of the cutoff less than 150. To have an additional safety margin a cutoff of 100 was used. The number of successful deletions of water molecules that meet this criterion per 1000 passes, N_D^* , is also given in Table II.

The runs that employed SW filters had acceptance rates comparable with those that did not, indicating that the filters have been properly implemented. The simple SW filter used for normal insertion and deletion attempts based on the van der Waal's energy alone resulted in a reduction of the CPU time of only $\sim 10\%$. For CBMC moves the SW filters reduce the CPU time to a value only slightly larger than the corresponding non-CBMC runs.

Other values given in Table II include the ratio of the CPU time for each simulation to that for the reference run t_r and the $gain$. The $gain$ is the most useful measure of the relative efficiencies of the runs and is defined as

$$gain = \frac{N_D/t_r}{N_D^{ref}/t_r^{ref}}. \quad (24)$$

Two measures of gain are given in Table II, $gain$ and $gain^*$ which are calculated using N_D and N_D^* , respectively.

From Table II one can see that the N_D^* results are more consistent than the N_D ones between nearly equivalent runs. For instance, the third and fourth runs are the same except that one employed a SW filter. N_D for these runs differs by a factor of 2 while N_D^* differs by only 20%. As well, the ratio N_D/N_D^* ranges from 5 to 50 with the highest ratios obtained for those runs that employed increased numbers of insertion attempts. These results indicate that a significant fraction of the N_D accepted deletions represent molecules that are being

repeatedly inserted and deleted. Such changes do not result in significant improvement in the sampling. The real gain lies somewhere between $gain$ and $gain^*$ and is likely closer to the $gain^*$ value.

Based primarily upon $gain^*$, our results indicate that if the number of insertion and deletion moves are kept the same the optimal number of such attempts is close to and likely moderately higher than the number of displacement moves. Employing 5400 normal insertions and 216 normal deletions combined with excluded volume mapping is about twice as effective as simply using 216 insertions.

The best results are obtained for CBMC runs that employ SW filters, excluded volume mapping, and 25 times more insertion attempts than deletion attempts. However, using CBMC and SW filters with the same number of insertion and deletion attempts (i.e., 216) is only slightly less effective.

IV. CONCLUSIONS

We have explored a number of ways of improving the efficiency of GCMC simulations of water. Since Gibbs ensemble simulations are most effective when the phases being compared have significantly different densities, most of the lessons learned from the GCMC work would carry over directly to the Gibbs ensemble if properly implemented. Even the idea of using more insertions than deletions (combined with excluded volume mapping) in the grand ensemble is roughly equivalent to attempting more moves from the less dense to the more dense phase and should yield useful gains. Since this method is easy to implement it should not be overlooked. The optimal ratio for the number of insertion to deletion attempts is likely less than 25. As far as the gross number of insertions and deletions are concerned there is little reason to use reduced levels of such moves in GCMC simulations of ambient water. One would expect that the same would also be true for the dense phase in GEMC simulations of water. However, from the current study we cannot comment on the fluctuations in the gas phase density noted at high switching rates in GEMC studies.⁶

The conventional approach to estimating the efficiency of a particular method by counting the number of successful insertions or deletions when passes involve roughly the same number of insertion, deletion and displacement attempts is demonstrated to be misleading because of the rapid insertion and deletion of the water molecules at the same location as previously noted.⁶ A better approach is to count only insertions or deletions involving those molecules that have been in the system for a sufficient number of passes. CBMC moves particularly in conjunction with SW filters are of great use and improve the efficiency by more than a factor of 3 (or 6 if the more conventional measure is used). If this approach

is combined with using 25 times more insertions than deletions, then the improvement in the efficiency approaches 4 (or 13 for the conventional measure). Neither of these strategies involves significant CPU overhead as compared to equivalent non-CBMC approaches.

The methods presented in this paper will be used in studies of inhomogeneous aqueous systems. In addition, we are continuing to develop means to study complex systems using open ensembles and are currently working on methods for inserting and deleting ions in water. These CBMC techniques as they are or possibly combined with those already in the literature^{7-10,15} should greatly extend the range of systems that can be productively simulated.

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¹M. P. Allen and D. Tildesley, *Computer Simulations of Liquids* (Clarendon, Oxford, 1987).

²*Computer Simulations in Chemical Physics*, edited by M. P. Allen and D. Tildesley, NATO ASI Series C (Kluwer Academic, Dordrecht, 1992), Vol. 397.

³*Computer Simulations in Material Science*, edited by M. Meyer, and V. Pontikis, NATO ASI Series E (Kluwer Academic, Dordrecht, 1991), Vol. 205.

⁴M. Mezei, *Mol. Phys.* **40**, 901 (1980).

⁵M. Mezei, *Mol. Phys.* **61**, 565 (1987).

⁶R.F. Cracknell, D. Nicholson, and N.G. Parsonage, *Mol. Phys.* **71**, 931 (1990).

⁷J. I. Siepmann, *Mol. Phys.* **70**, 1145 (1990).

⁸J. I. Siepmann and I. R. McDonald, *Mol. Phys.* **75**, 255 (1992).

⁹D. Frenkel and B. Smit, *Mol. Phys.* **75**, 983 (1992).

¹⁰J. J. De Pablo, M. Laso, and U. W. Suter, *J. Chem. Phys.* **96**, 6157 (1992).

¹¹G. L. Deitrick, E. Scriven, and H. T. Davis, *J. Chem. Phys.* **90**, 2370 (1989).

¹²M. R. Stapleton and A. Z. Panagiotopoulos, *J. Chem. Phys.* **92**, 1285 (1990).

¹³R. H. Swendsen and J.-S. Wang, *Phys. Rev. Lett.* **58**, 86 (1987).

¹⁴D. Frenkel, in *Computer Simulations in Chemical Physics*, edited by M. P. Allen and D. Tildesley, NATO ASI Series C (Kluwer Academic, Dordrecht, 1992), Vol. 397, p. 93.

¹⁵J. C. Shelley and G. N. Patey, *J. Chem. Phys.* **100**, 8265 (1994).

¹⁶D. A. Kofke and E. D. Glandt, *Mol. Phys.* **64**, 1105 (1988).

¹⁷H. J. C. Berendsen, J. R. Grigera, and T. P. Straatsma, *J. Phys. Chem.* **91**, 6269 (1987).

¹⁸N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. H. Teller, and E. Teller, *J. Chem. Phys.* **21**, 1087 (1953).

¹⁹J. P. Valleau and L. K. Cohen, *J. Chem. Phys.* **72**, 5935 (1980).

²⁰C. S. Pangali, M. Rao, and B. J. Berne, *Chem. Phys. Lett.* **55**, 413 (1979).

²¹M. Rao, C. S. Pangali, and B. J. Berne, *Mol. Phys.* **37**, 1779 (1979).

²²P. J. Rossky, J. D. Doll, and H. L. Friedman, *J. Chem. Phys.* **69**, 4628 (1978).

²³W. Smith, *CCP5 Q.* **5**, 13 (1982).

²⁴J. Hermans, A. Pathiaseril, and A. Anderson, *J. Am. Chem. Soc.* **110**, 5982 (1988).