

ON A NOVEL MONTE CARLO SCHEME FOR SIMULATING WATER AND AQUEOUS SOLUTIONS*

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The usual Metropolis Monte Carlo algorithm, when applied to highly associated liquids like ST-2 water is shown to be very slow in establishing equilibrium, and often leads to bottlenecks in configuration space. A new algorithm is presented in which the Monte Carlo moves are biased in the direction of the forces and torques acting on the individual molecule. Comparison with the Metropolis scheme shows that this new method is much more rapidly convergent.

1. Introduction

In this note we introduce a novel rapidly convergent Monte Carlo technique and apply it to the study of water where the common Metropolis procedure is very slowly convergent and often leads to bottlenecks in configuration space.

In the Monte Carlo method [1,2], various configurations of the system are sampled according to the Boltzmann distributions

$$\exp[-\beta V(R_1, \dots, R_N)] dR_1 \dots dR_N, \quad (1)$$

where R_j is a vector specifying both the positions and orientations of molecule j . For rigid linear molecules R_j is a five component vector whereas for rigid non-linear molecules R_j is a six component vector. dR_j is the appropriate volume element.

To generate a set of configurations that are distributed according to eq. (1), Metropolis et al. [1,2], devised a scheme according to which a new configuration $R' = (R'_1, \dots, R'_N)$ is generated from an old configuration $R = (R_1, \dots, R_N)$ by sampling a prescribed transition probability, $T(R'|R)$, and this new configuration is accepted with probability

$$p = \text{Min} \left[1, \frac{T(R|R')}{T(R'|R)} \frac{\exp[-\beta V(R')]}{\exp[-\beta V(R)]} \right] \quad (2)$$

and rejected with probability $q = 1 - p$. In this way a random walk over configuration space is generated. Averages over the distribution (1) are obtained by weighting old configurations with q and new configurations by p [3].

Up to this point the method is quite general. Usually the configuration is changed by single particle moves. First particle 1 is moved and this move is either accepted or rejected according to eq. (2), then this is repeated for particle 2, 3 ... N . The full cycle of moves is then repeated. Thus all that need be specified is the transition probability for a single particle move. For atomic fluids, particle j is displaced from R_j to R'_j where R'_j is randomly sampled between $R_j - \frac{1}{2}\Delta R_0$ and $R_j + \frac{1}{2}\Delta R_0$. The maximum value of the move is $\frac{1}{2}\Delta R_0 = (\frac{1}{2}\Delta x_0, \frac{1}{2}\Delta y_0, \frac{1}{2}\Delta z_0)$ and the larger this parameter the larger the region of configuration space sampled in a fixed number of iterations, but ΔR_0 cannot be made arbitrarily large because most of the moves will then be rejected. The transition probability for the single particle move is then

$$T(R'_j|R_j) = (\Delta x_0 \Delta y_0 \Delta z_0)^{-1}, \quad \delta R_j \in D; \\ = 0, \quad \delta R_j \notin D. \quad (3)$$

Here δR_j denotes the particular choice of δx , δy , and δz and D denotes the domain defined by the above inequalities. Similarly for molecules, the translational and rotational moves are sampled randomly from

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some domain D . For uniform sampling the ratio of the transition probabilities in eq. (2) is unity.

This procedure, correct though it is, does not converge rapidly when applied to strongly angle dependent potentials like the water potential where it leads to bottlenecks in configuration space. In fact, previous Monte Carlo and molecular dynamics studies on water do not agree [4]. A little thought shows that the moves in molecular dynamics are usually biased in the direction of the intermolecular forces, and torques, whereas the moves sampled according to eq. (4) by the usual Metropolis prescription gives equal weight to moves parallel to the forces as to those antiparallel to those forces. It occurred to us that if we built this bias into $T(R'_j|R_j)$, rapid convergence might result[‡].

We propose to modify the standard Metropolis scheme by biasing the moves to be along the forces and torques. If $T(R'_j|R_j) \propto e^{-\beta V(R')}$ is substituted into eq. (2) it is readily seen that the acceptance probability will be unity. Of course this procedure is not feasible since it presupposes knowledge of the very distribution required. Expansion of $V(R')$ around R , gives for the one particle move

$$T(R'_j|R_j) = c \exp[-\beta[\nabla_{R_j} V(R)] \cdot \delta R_j], \quad \forall \delta R_j \in D; \\ = 0, \quad \text{otherwise,} \quad (4)$$

where c is the normalization constant and where ∇_{R_j} is the gradient operator with respect to the positions and angles. For monatomic fluids, $-\nabla_{R_j} V(R_1, \dots, R_N)$ is the force F_j on particle j . T then simplifies to $c \exp(\beta F_j \cdot \delta R_j)$. This clearly shows that displacements are more often made in the direction of the force than otherwise. Detailed balance however is still satisfied.

For polyatomic molecules $T = c \exp \beta(F_j \cdot \delta r_j + N_j \cdot \delta \omega_j)$ where F_j , N_j , δr_j and $\delta \omega_j$ are respectively the total force, torque, center of mass displacement

and angular displacement of molecule j . The precise form of $N_j \cdot \delta \omega_j$ depends, of course, on the particular angles used to define the molecular orientations. In a more extensive paper we show how to apply eq. (3) to a wide variety of representations including simulations involving reshaping using holonomic constraints [7], and simulations involving Euler angles. Here we restrict our attention to a more straightforward procedure.

Our new *force-bias method* is applied to the study of ST-2 water molecules [8]. First an axis $\hat{n}$ is chosen at random from one of the three orthogonal spaced fixed axes ($\hat{x}$, $\hat{y}$, $\hat{z}$). Then the molecule is rotated around this axis by an angle, $\delta \theta_j$. $\delta \theta_j$ and the translational displacement $\delta r_j = (\delta x_j, \delta y_j, \delta z_j)$ are sampled according to the distributions

$$T(R'_j|R_j) = c \exp \beta(F_j \cdot \delta r_j + (N_j \cdot \hat{n}) \delta \theta_j), \quad \delta R_j \in D; \\ = 0, \quad \delta R_j \notin D, \quad (5)$$

where c is the normalization constant, F_j and N_j are the force and torque acting on molecule j before it is moved (when it is at R_j). The domain D is defined such that the translational and angular displacements must be written $-\frac{1}{2}\Delta \leq \delta x_j, \delta y_j, \delta z_j \leq \frac{1}{2}\Delta$ and $-\frac{1}{2}\Delta\theta_0 \leq \delta \theta_j \leq \frac{1}{2}\Delta\theta_0$. In the following simulations we take $\frac{1}{2}\Delta = 0.1\sigma$ and $\frac{1}{2}\Delta\theta_0 = 0.1047$ radians where σ is the Lennard-Jones parameter in ST-2 water ($\sigma = 3.1 \text{ \AA}$).

It is important to recognize that if uniform sampling were made in this domain this procedure would be identical to the one introduced by Watts in his Monte Carlo study of water using the Ben-Naim–Stillinger potential [9]. We have been calling this uniform sampling the Metropolis scheme and to avoid ambiguity we shall continue to call it this. We now compare the force-bias scheme to the Metropolis scheme for ST-2 water.

2. Results and discussion

The efficiency of the new method is demonstrated in fig. 1. Starting from a lattice configuration with 216 H₂O molecules with random orientations and interacting with an ST-2 potential, a Monte Carlo run was made using the standard Metropolis walk appropriately tailored to water using the Watts prescription and a temperature of 283 K. After 500 000 attempted

[‡] In several previous papers, various attempts have been made to improve the efficiency of the Monte Carlo technique. In the study of many-body quantum system [5] a force biasing technique was used. Because T was chosen to be linear in $F \cdot \delta r$, and because N particle moves were made, the acceptance ratio decreased by a factor of ten, and the method was not pursued. The transition probability has also been modified in various attempts to use importance sampling (see ref. [2]) and to simulate the gas–liquid interface (see ref. [6]).

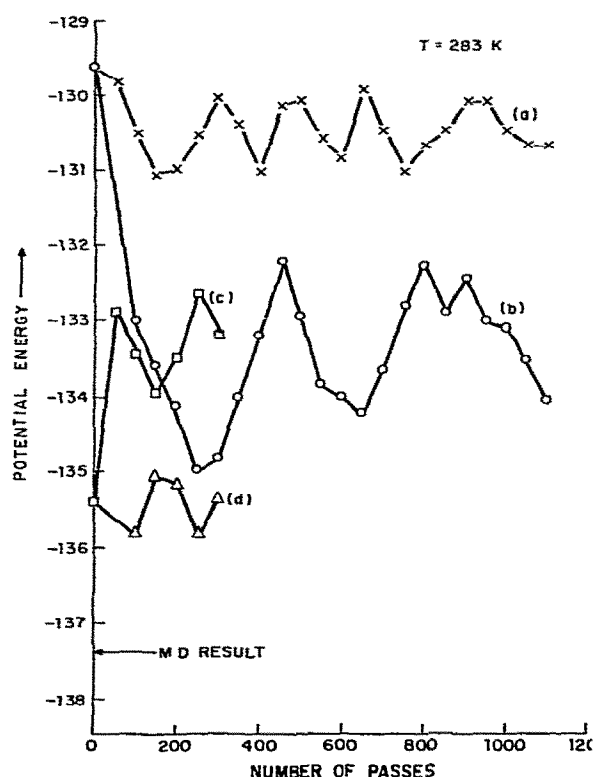


Fig. 1. The average potential energy (in units of ϵ) as a function of the number of attempted moves (1 pass = 216 attempted moves) at $T = 283$ K. The points denote averages over 5 passes. Curves (a) and (b) correspond respectively to the Metropolis scheme and the force-bias scheme starting from the same high energy configuration. Curves (c) and (d) correspond respectively to the force-bias scheme and the Metropolis scheme starting with a configuration from equilibrated molecular dynamics run at 283 K.

moves with an acceptance ratio of 0.43 the average potential energy per particle $\langle V \rangle$, settled down to a value of $-130.5 \epsilon \pm 0.2 \epsilon$ ($\epsilon = 5.31 \times 10^{-15}$ erg). Starting with the final configuration of this run ($V = -129.6 \epsilon$) two Monte Carlo runs were made. One of these runs was carried out using the standard Metropolis scheme (curve a of fig. 1) whereas the other was carried out using our force-bias scheme (curve b of fig. 1). The standard scheme generated a walk in configuration space (with acceptance ratio 0.43) that fluctuated around a "bottleneck" with a mean potential energy per particle $\langle V \rangle = -130.5 \epsilon \pm 0.2 \epsilon$. Our force-bias scheme generated a quite different walk (with acceptance ratio 0.65). First V rapidly decreased and

then fluctuated around a steady value of $-133.5 \epsilon \pm 0.4 \epsilon$ which is considerably lower in energy than that given by the standard method.

Rahman and Stillinger [8] have studied 216 H_2O molecules interacting with an ST-2 potential at the temperatures $T = 270$ K, 283 K, 391 K by molecular dynamics. At $T = 283$ K, their potential energy per particle fluctuates around the average $\langle V \rangle = -137.4 \epsilon$. This is indicated in fig. 1. It is clear from this that the force-bias Monte Carlo is much closer to molecular dynamics than the standard Metropolis technique. Nevertheless the two methods do not seem to agree. The same behavior was observed at the lower temperature $T = 270$ K where molecular dynamics gives $\langle V \rangle = -141.25 \epsilon$ and the force-bias technique gives $\langle V \rangle = -136.2 \epsilon \pm 0.5 \epsilon$.

Further comparison between the two Monte Carlo methods gives a very striking result. Starting with a configuration generated by molecular dynamics at 283 K with $V = -135.5 \epsilon$, the standard Metropolis technique at $T = 283$ K generates a walk in configuration space (curve d) which fluctuates around $-135.0 \epsilon \pm 0.2 \epsilon$. Starting with the same configuration, the force-bias technique (curve c) at $T = 283$ K generates a walk that very rapidly returns to equilibrium and fluctuates around the same average potential energy per particle that it reached starting from a higher energy configuration (curve a). It is clear that the force-bias method rapidly generates a unique equilibrium state independent of initial configuration whereas the standard technique either gets stuck in bottlenecks or equilibrates so slowly that a drift towards equilibrium is not even perceived over the run lengths studied here.

Comparison of curves a and b of fig. 1 shows that the amplitude of potential energy fluctuations is greater for the force-bias scheme, than for the Metropolis scheme. It is an interesting consequence of this that the predicted heat capacity will be smaller in the Metropolis scheme than in the force-bias scheme. Care must therefore be exercised in drawing any conclusions about heat capacity from standard Monte Carlo studies of water.

It is well known that for temperatures greater than 323 K water behaves like a normal liquid. Thus at high temperatures we expect that the hydrogen bond network will be disordered. It is interesting to compare molecular dynamics and the two Monte Carlo

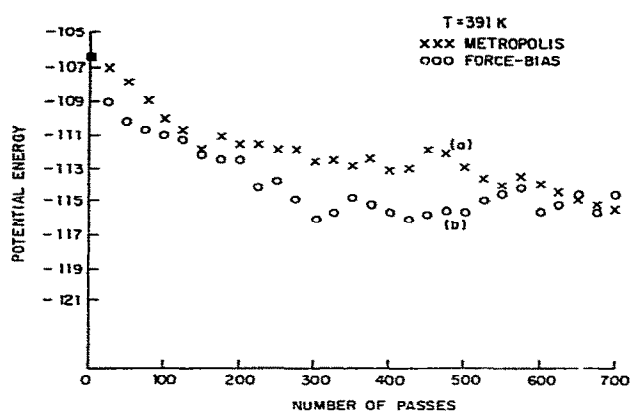


Fig. 2. The average potential energy (in units of ϵ) at $T = 391$ K, plotted as a function of the number of attempted moves. The points denote averages over 5 passes (1 pass = 216 attempted moves). Curve (a) corresponds to the force-bias scheme and curve (b) to the Metropolis scheme.

methods at the high temperature, $T = 391$ K. In fig. 2 curve a corresponds to the force-bias scheme and curve b corresponds to the Metropolis scheme. All methods go to the same equilibrium state with statistically indistinguishable average potential energies; $\langle V \rangle_{\text{MD}} = -115.9 \epsilon$, $\langle V \rangle_{\text{Metropolis}} = -115.5 \epsilon \pm 0.3 \epsilon$ and $\langle V \rangle_{\text{force bias}} = -115.5 \epsilon \pm 0.4 \epsilon$. It is clear from fig. 2 that the force-bias scheme converges much more rapidly than the standard Metropolis scheme even for temperatures where the hydrogen bond network is substantially broken. Thus for both low and high temperatures this is the method of choice.

Several questions emerge from the preceding discussion. First and foremost is why do the force-bias simulation and the molecular dynamics simulation disagree at low temperatures? It is important to recognize that in molecular dynamics the pair force is set equal to zero when the pair separation exceeds a certain distance r_0 . The trajectories that are generated correspond to a shifted potential $\phi(r) - \phi(r_0)$. Unfortunately, in the molecular dynamics simulations the potential at the cut-off, $\phi(r_0)$, varies with orientation. In certain orientations $\phi(r_0)$ can be positive (where the hydrogens in both molecules point towards each other) and in other orientations it can be negative. Where it is positive, the shifted potential has a deeper well depth than would the unshifted potential and therefore leads to a lower average poten-

tial energy $\langle V \rangle$. In the Monte Carlo technique, we deal with a truncated but unshifted potential. Thus we are really comparing two different systems and should not really expect agreement.

This prompted us to study a droplet of water at low temperatures with the infinite range ST-2 potential. Molecular dynamics and the force-bias Monte Carlo give identical results when applied to a droplet containing 27 molecules at $T = 283$ K. However further studies are required using larger droplets to shed light on this problem.

The main thrust of this paper is to present a new Monte Carlo procedure — the force-bias method — which is more efficient than the usual Metropolis scheme. The extra computational burden is more than offset by the increased efficiency of the simulation. This paper shows that Monte Carlo studies on highly structured fluids can be very misleading. It appears that at low temperatures, these procedures can get trapped into configurational bottlenecks. Although the force-bias method is preferable to the standard Metropolis scheme it is very important that any sampling method be explicitly tested to see that a unique equilibrium state has been achieved.

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