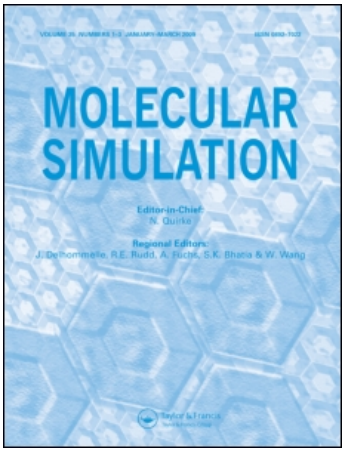

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Preliminary Communication

ON THE SAMPLING METHOD FOR GRAND CANONICAL MONTE CARLO SIMULATIONS

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A bulk Lennard-Jones fluid was simulated using the grand canonical Monte Carlo method. Three different sampling methods were used in the transition matrix, namely the Metropolis, Barker and a third novel method. While it can be shown that the Metropolis method will give the most accurate ensemble averages in the limit of an infinitely long run, the new method termed "Modified Barker Sampling" (MBS), is shown to be superior for the runs of practical length for the particular system studied.

KEY WORDS: Grand canonical Monte Carlo, modified Barker sampling, Lennard-Jones fluid

1 INTRODUCTION

Monte Carlo computer simulation in the grand ensemble (GCMC) is an established technique for studying both bulk and confined fluids [1], [2]. The chemical potential of each component, and the temperature and volume of the system are specified in advance; a GCMC algorithm consists of three types of trial: attempts to move particles within the simulation box, attempts to create new particles, and attempts to delete particles. A major disadvantage of GCMC is that the rate of acceptance for the creation of new particles may be extremely low, leading to a slow convergence of ensemble averages; the problem is particularly acute for insertion into dense fluids. Methods have been developed to bias the position [3] and orientation [4] of trial insertions so that acceptance is more likely, however scant attention has been paid to which sampling procedure is optimal for GCMC simulations. In this work, the efficiency of three sampling methods are compared for a GCMC simulation of a dense Lennard-Jones fluid; the conventional Metropolis (asymmetric) algorithm is compared with the Barker (symmetric) algorithm and a new sampling method is introduced.

2 SAMPLING METHODS

I have adopted the same nomenclature as is found in the book by Allen and Tildesley [1], whereby the transition matrix is denoted by π and π_{mn} is the transition probability of going from state m to state n in a particular Monte Carlo step. The limiting probability of state m is denoted ρ_m.

In the Metropolis (or asymmetric) sampling method [5]:

$$\pi_{mn} = \alpha_{mn} \qquad \frac{\rho_m}{\rho_n} \leq 1 \tag{1a}$$

$$\pi_{mn} = \alpha_{mn}\frac{\rho_n}{\rho_m} \qquad \frac{\rho_m}{\rho_n} > 1 \tag{1b}$$

In the Barker (or symmetric) sampling method [6]:

$$\pi_{mn} = \alpha_{mn}\frac{\rho_n}{\rho_n + \rho_m} \tag{2}$$

Both prescriptions require that $\alpha_{mn} = \alpha_{nm}$ in order to satisfy the condition of microscopic reversibility. I present an alternative method to the above two, which I have termed "Modified Barker Sampling" (MBS). The transition probabilities are given by:

$$\pi_{mn} = \alpha_{mn}\beta\frac{\rho_n}{\rho_n + \rho_m} \qquad \frac{\rho_m}{\rho_n} \geq (\beta - 1) \leq \frac{\rho_n}{\rho_m} \tag{3a}$$

$$\pi_{mn} = \alpha_{mn}\frac{\rho_n}{\rho_n + \rho_m} \qquad \frac{\rho_m}{\rho_n} < (\beta - 1) \quad \text{or} \quad \frac{\rho_n}{\rho_m} < (\beta - 1) \tag{3b}$$

β is defined as a real number in the interval [1, 2]. For a choice of β greater than 2 the method reduces to the Barker method since the inequality in (3a) can not be satisfied. A choice of β between zero and unity is likely to lead to slower convergence than Barker sampling. We can write the MBS step for a transition from state n to state m as

$$\pi_{nm} = \alpha_{nm}\beta\frac{\rho_m}{\rho_n + \rho_m} \qquad \frac{\rho_n}{\rho_m} \geq (\beta - 1) \leq \frac{\rho_m}{\rho_n} \tag{4a}$$

$$\pi_{nm} = \alpha_{nm}\frac{\rho_m}{\rho_n + \rho_m} \qquad \frac{\rho_m}{\rho_n} < (\beta - 1) \text{ or } \frac{\rho_n}{\rho_m} < (\beta - 1) \tag{4b}$$

It can be seen that the inequalities in (3a) and (4a) are the same, thus either both equation (3a) and (4a) are valid or both (3b) and (4b). Thus the relation

$$\rho_m \pi_{mn} = \rho_n \pi_{nm} \tag{5}$$

is always true and microscopic reversibility is shown to be obeyed provided $\alpha_{mn} = \alpha_{nm}$. This is a sufficient condition for correct convergence of the Markov chain.

If in a simulation, averages of a quantity A are taken over n successive states

of the Markov chain and denoted M_n^A, the size of the variance of M_n^A, (ie the variance of the average over n states, not the variance of A) gives an indication of the degree of convergence of the simulation, and provides a method of discriminating between simulation techniques, specifically in this case the different sampling methods. The quantity V_n^A is defined

$$V_n^A = n \quad \text{var} \quad (M_n^A) \tag{6}$$

and its limit as n tends to infinity is called the asymptotic variance,

$$V_\infty^A = \lim_{n \to \infty} V_n^A \tag{7}$$

The asymptotic variance is closely related to another quantity called the statistical inefficiency which has been used by other workers for this kind of analysis [1]. Peskun [7] has determined an important relationship between the off diagonal elements of transition matrix $\boldsymbol{\pi}$ and V_∞. For two different sampling schemes, labelled 1 and 2, if

$$\pi_{mn}^{(1)} \geq \pi_{mn}^{(2)} \tag{8}$$

then

$$V_\infty^{(1)} \leq V_\infty^{(2)} \tag{9}$$

For the Metropolis, Barker and MBS sampling schemes, it is straightforward to show that

$$\pi_{mn}^{MET} \geq \pi_{mn}^{MBS} \geq \pi_{mn}^{BARK} \tag{10}$$

for all the possible conditions in equations 1–3, thus

$$V_\infty^{MET} \leq V_\infty^{MBS} \leq V_\infty^{BARK} \tag{11}$$

On this basis, one might conclude that the Metropolis transition matrix is superior because it has a lower asymptotic variance; however as Valleau and Whittington point out [8], one must consider that Markov chains are of finite length and it is not necessarily clear which method is best for normal simulation purposes. The simulations which were conducted to make such a comparison are described below.

3 GCMC SIMULATION

Grand Canonical Monte Carlo simulations were run for a bulk Lennard-Jones fluid with the potential cut and shifted at 2.5 times the Lennard-Jones σ parameter. The simulations were run in a cubic box of width 8σ. We chose a state point corresponding to a liquid in order to compare the algorithms – it is for dense fluids that optimisation of the algorithm is most important. The particular state point was $z\sigma^3 = 0.06$ (where z is the absolute activity equal to $\exp(\mu/kT)/\Lambda^3$) and reduced temperature $kT/\varepsilon = 1.0$. Simulations were run using the Metropolis, Barker and MBS transition matrices in the acceptance/rejection part of the algorithm. The Metropolis algorithm was used for particle displacements. For the MBS simulation, two values of the parameter β were tried, $\beta = 1.25$ and $\beta = 1.75$. In order to accurately determine the variance of averages taken over particular block lengths in

the simulation, long runs were necessary, 4×10^7 configurations required approximately 6 days of CPU on and Intel i860 processor. The ensemble averages over the whole runs are given in table 1. Another shorter run (not shown) was conducted at a state point corresponding to a Lennard-Jones vapour in order to verify that all three methods converged to the same density.

Mean values of N, the number of particles in the box were taken over blocks of n configurations, the averages are denoted M_n^N. Figure 1a shows the quantity V_n^N (defined in (6)), plotted against n. In the limit of n to infinity one would anticipate that it would be the Metropolis algorithm with the lowest variance, however for blocks of lengths up to 50000 configurations, the MBS method with a β of 1.75 has the lowest variance. The curves for all three methods have a very similar shape with a maximum in all four curves at $n = 35000$. It is likely that $n = 35000$ corresponds to half the period of a particular statistical fluctuation (it can be shown that if a sine function $f = \sin(x)$ (or $f = \cos(x)$) is divided into segments along the x direction of a given length and the mean of the function taken within that segment, then the variance of those means as a function of segment length will be a maximum for $x = \pi$); thus it may be asserted that all three sampling methods produce the same statistical fluctuations since all four curves have this maximum.

Figure 1b shows the difference between V_n^N for each transition matrix relative to the corresponding quantity for the Metropolis sampling method. It can be seen that for n greater than 20000, even the Barker method is superior to the Metropolis method, while the MBS method ($\beta = 1.75$) is clearly superior. Longer simulations would be required to extend the curve to higher values of n, clearly as n increases, the number of blocks of n in a run of 40 million configurations decreases accordingly, thus reducing the statistical accuracy with which the variance of the means can be computed. It is to be expected that V_n^N will reach a limiting value and that the Metropolis method will have the lowest asymptotic variance, however it also clear that this limit is of little practical interest in a computationally viable Grand Canonical Monte Carlo scheme.

4 CONCLUSIONS

Despite having a lower asymptotic variance, the Metropolis transition matrix may not necessarily give the most accurate ensemble averages for runs of a practical length. While one would not advocate abandoning the Metropolis method for GCMC on the basis of this preliminary study, it is clear that the MBS sampling method is worthy of further investigation.

Table 1 Simulation averages for bulk Lennard-Jones fluid cut and shifted at 2.5σ. $z\sigma^3 = 0.06$, $kT/\varepsilon = 1.0$, box volume $512\sigma^3$.

TRANSITION MATRIX	β	$\langle N \rangle$	$\langle U \rangle / kT$ *per particle*
METROPOLIS	-	331.06	−3.842
BARKER	-	330.83	−3.835
MBS	1.25	330.10	−3.825
MBS	1.75	330.48	−3.834

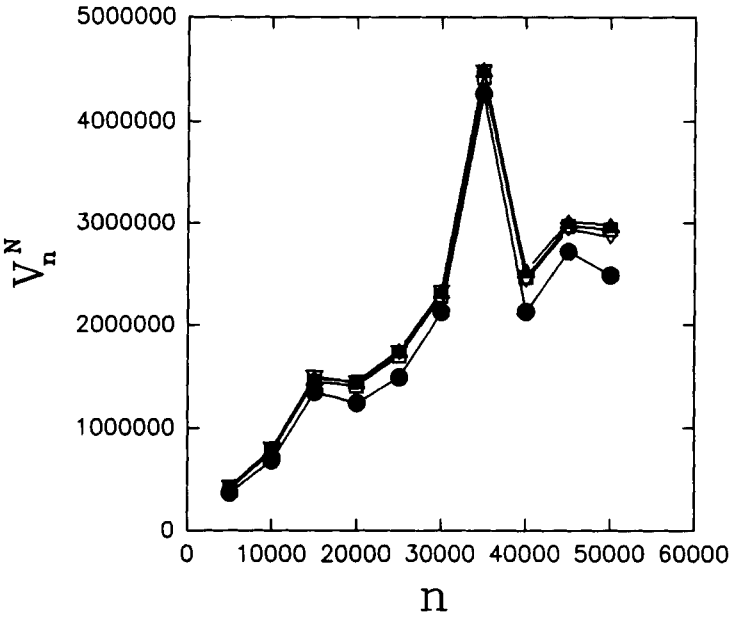

Figure 1a Results from GCMC simulation of Lennard-Jones fluid. $z\sigma^3 = 0.06$, $kT/\varepsilon = 1.0$. V_n^N plotted against n for three sampling methods [▲: Metropolis; ▽: Barker; □: MBS ($\beta = 1.25$); ●: MBS ($\beta = 1.75$)].

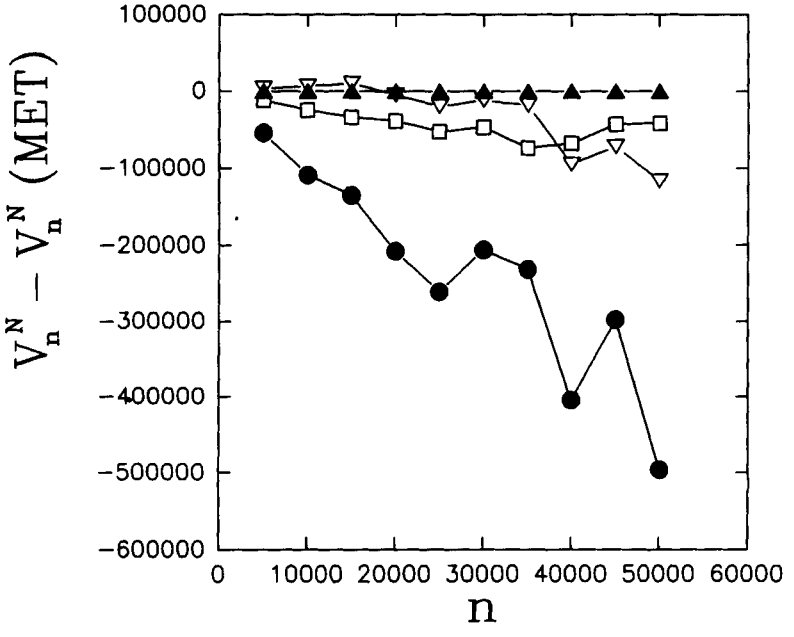

Figure 1b $V_n^N - V_n^N$ (METROPOLIS) plotted against n. The legend is as for figure 1a.

Acknowledgements

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