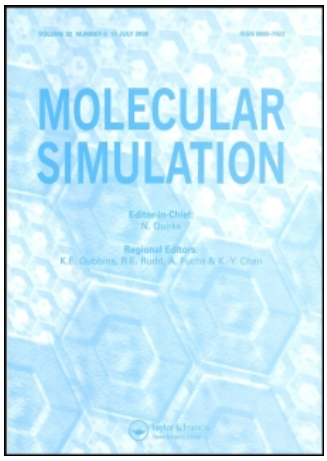

Molecular Simulation
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

The Detailed Balance Energy-scaled Displacement Monte Carlo Algorithm

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Online Publication Date: 01 November 1987
To cite this Article: Mezei, M., Bencsath, K. A., Goldman, S. and Singh, S. , (1987) 'The Detailed Balance Energy-scaled Displacement Monte Carlo Algorithm', Molecular Simulation, 1:1, 87 - 93
To link to this article: DOI: 10.1080/08927028708080933
URL: http://dx.doi.org/10.1080/08927028708080933

Molecular Simulation, 1987, Vol. 1, pp. 87–93
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THE DETAILED BALANCE ENERGY-SCALED DISPLACEMENT MONTE CARLO ALGORITHM

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(Received October 1986; in final form March 1987)

The Detailed Balance Energy-scaled Displacement Monte Carlo method that stems from the previously published Energy Scaled Displacement Monte Carlo method is presented. The results of tests performed on a dense Lennard-Jones liquid and on two particles in one dimension are reported.

KEY WORDS: Monte Carlo, detailed balance, energy-scaled displacement, Lennard-Jones.

INTRODUCTION

The Metropolis Monte Carlo algorithm (MMC) [1] forms the basis of several liquid state computer simulation studies. The substantial computational effort it requires inspired numerous attempts at improving its efficiency. In general, these efforts involve replacing a random process in the algorithm by a more "informed" one based on the knowledge of some aspect of the system under study. Examples of this are the Force-Biased MMC (FBMC) of Rao, Pangali and Berne [2], and the Smart Monte Carlo of Rossky, Doll and Friedman [3] where moves along the force acting on the particle are sampled more frequently; the preferential sampling of Owicki and Scheraga [4, 5] where particles in an inhomogeneous system are perturbed with a frequency dependent on location; the method of Noguti and Go [6] where the stepsize varies with the direction to reflect the anisotropy of the system; the cavity-biased (T, V, μ) ensemble method of Mezei [7, 8] where particle insertions are attempted only into existing cavities and the virial-biased (T, P, N) ensemble method of Mezei [9] that extends the idea of FBMC to the changes in volume. Although several of these techniques involve significant additional computational expense, the overall saving is usually still significant.

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A recent idea of Goldman [10] sought to improve the MMC by varying the stepsize for the displacement as a function of the energetic environment of the molecule to be moved. The procedure is based on the observation that, while for a particle in a low energy position only small displacements are likely to be accepted, in a high-energy environment the acceptance of larger steps may be more likely. The implementation of this idea, the Energy-scaled Displacement Monte Carlo method (ESDMC), modified the MMC by making the stepsize a function of the total interaction energy of the particle to be moved. Numerical examples on the Lennard-Jones (LJ) fluid and the ST2 water models [11] showed that the inclusion of energy-scaled displacements into MMC resulted in significant convergence improvements. Also, the asymptotic values computed from MMC, FBMC and ESDMC were in agreement for several calculations (i.e. they fell within each other's uncertainties) [12]. With some other calculations, however, significant discrepancies were found between the results of ESDMC and those of MMC and FBMC [13]; these were attributed to insufficient equilibration in Ref. 10. From subsequent work, however, it became clear that, because ESDMC violated detailed balance, the self-correction presumed in Ref. 10 could not be expected [14].

The purpose of this paper is to present the Detailed Balance Energy-Scaled Displacement Monte Carlo method (subsequently to be referred to as the detailed balance method for brevity). This method generates attempted moves for the particles according to the ESDMC prescription, but modifies the acceptance probability expression in order to maintain detailed balance. The convergence characteristics of the method are demonstrated by application to a LJ fluid near its triple point. The manifest effect of ESDMC's violation of detailed balance is also examined by studying a system of two particles in one dimension where high-precision results can be obtained by numerical integration.

THE DETAILED BALANCE METHOD

Following the general ideas of the Metropolis Monte Carlo method, the detailed balance method selects particles to be moved one at a time, but sets the maximum displacement along any of the coordinate axes to be

$$\Delta = \begin{cases} \Delta_0 \exp\left[A(e_p - \langle \bar{e} \rangle)/kT\right] & \text{if } A(e_p - \langle \bar{e} \rangle)/kT)/kT < E_{max} \\ \Delta_0 \exp\left(E_{max}\right) & \text{otherwise} \end{cases} \tag{1}$$

where k is the Boltzmann constant, T is the absolute temperature and $\langle \bar{e} \rangle$ is the ensemble average of the total energy per particle that is continually updated during the run (since, in general, its value is not known a priori). The total energy of the moved particle is obtained from

$$e_p = \left(\sum_{q=1}^{N} u_{pq}\right)/2 \tag{2}$$

where u_{pq} is the interaction energy between particles p and q.

We also examined the prescription

$$\Delta = \Delta_0\{1 + B \tan^{-1}[A/(e_p - \langle \bar{e} \rangle)]/(\pi/2)\} \tag{3}$$

for the displacement, designed to eliminate some of the extreme step sizes that can be

generated by Equation (1), and to make the variation in step size more nearly symmetrical around a value of Δ_0 for which the acceptance rate is approximately 0.5. From Equation (3), clearly $\Delta_0(1 - B) \leqslant \Delta \leqslant \Delta_0(1 + B)$.

The rules governing the acceptance of a trial configuration are established from the condition for detailed balance. This requires that if i and j represent two system states then the number of systems in the ensemble making the transition from i to j be equal to the number of those making the reverse transition from j to i. Thus, if f_i is the normalized limit (equilibrium) distribution, and p_{ij} is the probability of the system undergoing the transition from state i to state j, detailed balance requires that

$$f_i p_{ij} = f_j p_{ji}. \tag{4}$$

Writing p_{ij} as the product of an a prior normalized transition probability p_{ij}^* and the acceptance probability a_{ij}, gives the condition

$$f_i p_{ij}^* a_{ij} = f_j p_{ji}^* a_{ji}. \tag{5}$$

Considering only single particle moves means that the two states i and j differ only in the location of one particle. Equations (1) and (2) restrict the new location of the moved particle to be within a cube of edge length 2Δ centered at the old position. Since the constraining cubes drawn around a particular particle in states i and j usually differ in size, there are, in principle, three possibilities for their overlap. These correspond to the conditions: (1) $p_{ij}^* > 0$ and $p_{ji}^* > 0$ (complete overlap); (2) either $p_{ij}^* > 0$ and $p_{ji}^* = 0$ or $p_{ji}^* > 0$ and $p_{ij}^* = 0$ (partial overlap); and (3) $p_{ij}^* = p_{ji}^* = 0$ (zero overlap). Each of these conditions will lead to a rule in the algorithm for determining the acceptance probability a_{ij}.

Note that the partial overlap occurs when the constraining cube around the particle in the trial location is too small to encompass the center of the cube around that same particle in the initial state. Also, the zero overlap case does not arise operationally, but its introduction is necessary if one were to construct the full transition matrix of the system.

To satisfy Equation (5) for the case of complete overlap we rearrange it to the form:

$$\frac{a_{ij}}{a_{ji}} = \frac{f_j}{f_i}\frac{p_{ji}^*}{p_{ij}^*} \tag{6}$$

and use the fact that

$$\frac{p_{ji}^*}{p_{ij}^*} = \frac{V_i}{V_j} \tag{7}$$

where V_i and V_j are the volumes of the constraining cubes in states i and j, respectively. Combining Equations (6) and (7) results in

$$\frac{a_{ij}}{a_{ji}} = \frac{f_j}{f_i}\frac{V_i}{V_j} = R. \tag{8}$$

This leads to the following rule: if $R > 1$, accept the new state, i.e. set $a_{ji} = R^{-1}$ and $a_{ij} = 1$; if $R < 1$, accept the new state with probability R, i.e. set $a_{ji} = 1$ and $a_{ij} = R$.

For partial overlap, we always reject the new state and count the initial state again in the averaging process, i.e. we satisfy Equation (5) by setting $a_{ij} = a_{ji} = 0$. Finally, the zero overlap condition automatically satisfies detailed balance.

CALCULATIONS AND RESULTS

(a) Lennard-Jones Fluid near its Triple Point

We applied the detailed balance method, using both Equation (1) and Equation (3), to a dense Lennard-Jones system at $T^* = 1.5$ and $\varrho^* = 0.85$. Face-centered cubic periodic boundary conditions were applied. The cutoff on the potential was 2.5σ and no contributions from interactions beyond the cutoff distance were estimated. For comparison, we also performed MMC, FBMC and ESDMC calculations on the same system. In each case we started from the same equilibrated configuration. Our results for the various algorithms are collected in Table 1. We found that all the algorithms, except ESDMC, converge to the internal energy value -4.89 within 0.2%. The ESDMC algorithm results in an internal energy that is about 1% above this value. Except for ESDMC, all the pressure results were within 1% of 4.99, while the ESDMC runs fell within 0.4% of 5.14. We also found that both the MMC and FBMC converge to the reduced heat capacity value of 0.9 within 1%. The ESDMC algorithm converges to values that are approximately 20% above this, while all the calculations

Table 1 Excess reduced energies and heat capacities and the pressure from various Monte Carlo algorithms for a 100-particle Lennard-Jones fluid at $T^* = (kT/\theta) = 1.5$, $p^* = \varrho\sigma^3 = 0.85$.

	Unscaled displacement			*Energy scaled displacement*						*Run len.*
				With detailed balance				*No detailed balance*		
				Eq. (1)		*Eq. (3)*				
E_{max}				2.0	1.0			3.0	2.0	
A				0.35	0.35			0.35	0.35	
B						0.50	0.75			
λ	0.0	0.50	1.0	0.0	0.0	0.0	0.0	0.0	0.0	
Δ_0	0.12	0.135	0.125	0.12	0.12	0.12	0.12	0.12	0.12	
$-\langle E\rangle$	4.895	4.884	4.876	4.918	4.891	4.878	4.864	4.865	4.827	4
	4.888	4.884	4.895	4.915	4.889	4.881	4.872	4.860	4.837	8
	4.892		4.892	4.894	4.895	4.879	4.876	4.853	4.840	12
	4.886		4.891	4.886	4.893	4.882	4.881	4.846	4.839	16
					4.894	4.883				20
					4.896	4.884				24
$\langle P\rangle$	4.949	5.006	5.036	4.821	4.977	5.040	5.092	5.051	5.209	4
	4.982	5.003	4.984	4.860	4.890	5.020	5.054	5.060	5.169	8
	4.969		4.963	4.957	4.956	5.031	5.035	5.091	5.158	12
	4.995		4.971	4.998	4.958	5.013	5.011	5.127	5.159	16
					4.953	5.012				20
					4.941	5.006				24
$\langle C_v$	0.997	0.879	0.879	0.947	0.802	0.758	1.085	1.013	1.075	4
	0.898	0.900	0.901	0.935	0.815	0.765	0.990	1.044	1.106	8
	0.893		0.909	0.989	0.829	0.800	0.987	1.082	1.105	12
	0.897		0.909	0.984	0.868	0.812	0.993	1.085	1.096	16
					0.856	0.823				20
					0.873	0.828				24
P_{acc}	0.43	0.66	0.64	0.34	0.35	0.39	0.39	0.45	0.45	

E_{max}: defined in Equation (1); A: defined in Equation (1); B: defined in Equation (3); λ: the force-bias parameter[2] ($\lambda = 0$ is the MMC); Δ_0: the step-size parameter; P_{acc}: the average acceptance rate; run length: number of attempted moves $\times 10^{-5}$.

with our detailed balance algorithms produced heat capacities within $\sim 10\%$ of the MMC–FBMC value, depending on the choice of the biasing parameters A and B. This spread indicates that they converge slowly in this application. As for comparing the use of Equation (1) and Equation (3) for the determination of the stepsize, despite Equation (3) yielding higher acceptance rates, the corresponding heat-capacity calculation converges slower.

(b) Two Particles in One Dimension

We carried out calculations for this simple system to get around the two uncertainties that almost always arise in many-particle Monte Carlo simulations – namely, not knowing the exact results and not knowing whether an algorithm has run long enough to converge to the equilibrium distribution. Our system here consisted of two particles interacting through the continuous, soft, repulsive potential $u(x) = x^{-2}$. We took the sample size to be of unit length, $kT = 1$, and applied the usual periodic boundary conditions. Unlike the calculations on the Lennard-Jones fluid, all these calculations used the true ensemble-averaged energy taken from the quadrature for $\langle \bar{e} \rangle$ in Equation (1). E_{max} and Δ_0 in Equation (1) were 2 and 0.1, respectively, giving acceptance rates of approximately 0.6. For this system the total reduced configurational energy and heat capacity, found by one-dimensional quadratures, were 4.783 and 0.647, respectively.

Figure 1 displays the computed internal energy ($\langle E \rangle$) and constant-volume heat capacity ($\langle C_v \rangle$) as functions of the scaling parameter A for both the detailed balance method (with Equation (1)) and ESDMC; $A = 0$ represents the MMC method. Calculations with 10^5, 10^6, 5×10^6 trial steps at acceptance rates of 0.6 all gave essentially the same results, a fact indicating convergence with each algorithm at each point. It is clear from Figure 1 that for this system both MMC and the detailed balance method give the same correct $\langle E \rangle$ and $\langle C_v \rangle$ values, while the ESDMC results oscillate around the exact value as A is varied. Furthermore, the non-zero values of A at which the ESDMC results for the energy and the heat capacity agree with the exact ones are different, dashing all hope of finding a single non-zero A value that would give the correct result with ESDMC. Extensions of these calculations to systems of several particles in one dimension gave similar results, although the discrepancy with ESDMC tended to decrease as the number of particles increased. The reason for this remains unclear.

DISCUSSION AND SUMMARY

Using long runs on different systems, we have tested the detailed balance energy-scaled Monte Carlo algorithm that is designed to produce convergence to the correct limiting distribution function. The additional computational expense incurred by the use of the algorithm in a conventional Metropolis program is negligible; thus, the potential benefits were expected to be significant. Disappointingly, however, for a dense Lennard-Jones fluid slower convergence was found than with the conventional MMC algorithm. Since the ESDMC algorithm, while not exact, produces only small errors and since it is efficient in the early part of a walk, we feel there is still some advantage in using the original ESDMC algorithm to speed up the initial phase of a

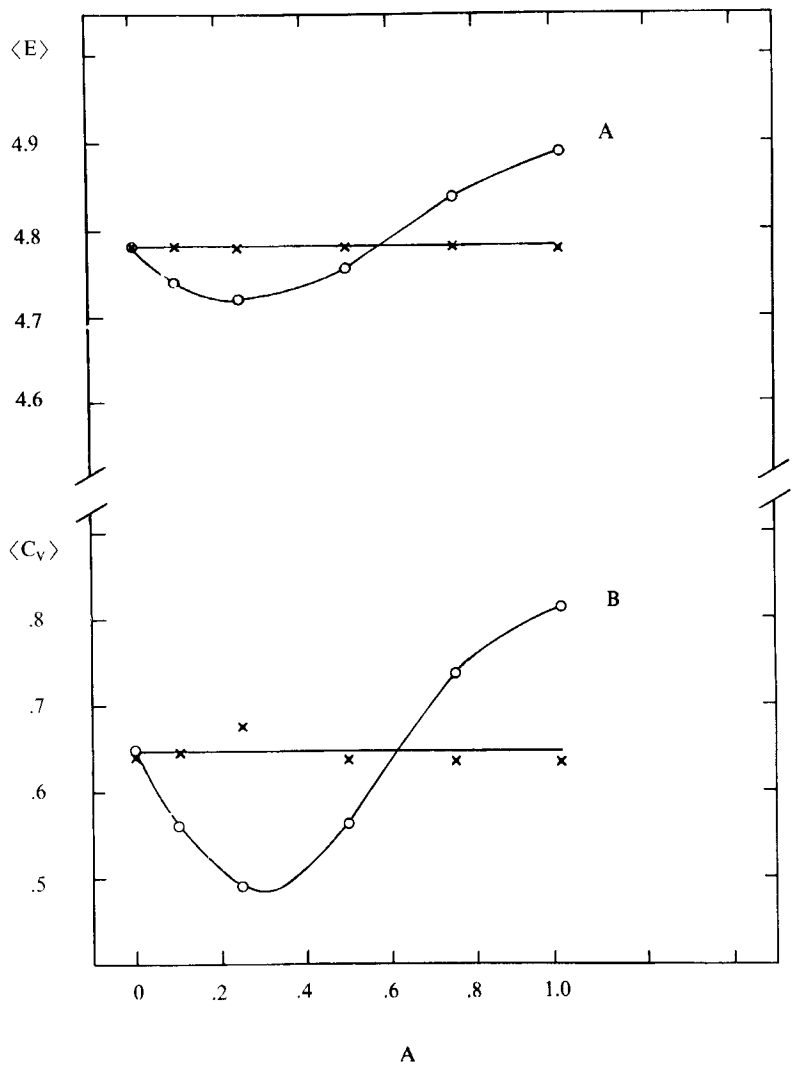

Figure 1 (A) Internal energy of 2-particles in one dimension on a unit length interacting through the potential $u(x) = x^{-2}$. A is the scaling parameter in Equation (1). The horizontal line is the quadrature result. × = detailed balance method; ○ = ESDMC. Each point is the result of 10^6 trials. (B) As for Figure 1A, C_v is the system heat capacity.

simulation. Of course, the final phase, during which the actual equilibrium results are collected, should be run with another algorithm that satisfies detailed balance.

Acknowledgements

One of us (SG) would like to thank Bernie Nickel for his very helpful discussions. We are also grateful to the Natural Sciences and Engineering Research Council of Canada

for financial assistance, to the University of Guelph and its Computing and Communications Services department for their continuing support of the Special Computing Project and the Array Processor. This research was also supported by NIH Grant GM-24149 and NSF Grant CHE-8203501.

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[12] See, for example, the energies and heat capacities entered in Tables III and IV of Reference 10.

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