Brownian dynamics as smart Monte Carlo simulation

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A new Monte Carlo simulation procedure is developed which is expected to produce more rapid convergence than the standard Metropolis method. The trial particle moves are chosen in accord with a Brownian dynamics algorithm rather than at random. For two model systems, a string of point masses joined by harmonic springs and a cluster of charged soft spheres, the new procedure is compared to the standard one and shown to manifest a more rapid convergence rate for some important energetic and structural properties.

I. INTRODUCTION

The Monte Carlo procedure of Metropolis *et al.* [1-3] is widely used to estimate the equilibrium properties of a many-particle system with a specified Hamiltonian. However, the quality of the results obtained is often limited by the fact that simulations of such systems typically consume large amounts of computation time. Since the statistical signficance of the results tends to improve only as the square root of this time, the investment involved in performing increasingly longer simulations is only slowly reflected in improved accuracy. Hence, it is worthwhile to explore the possibility that other simulation procedures may be more rapidly convergent.

In one recent study of a quantum many-body system, [4] a Monte Carlo method was introduced in which gradients of the configurational weight function (in the quantum case, the wavefunction squared) were employed to bias the particle moves in the direction of higher statistical probability. However, in the context employed, the new method was unsuccessful in producing improvement over standard approaches. While the present work was in progress, an extension of this gradient biasing method was introduced[5] and demonstrated to produce improved convergence, compared to standard methods, for a model of liquid water.

Here we describe a new modification of the Metropolis procedure which is expected to give a substantial improvement in efficiency compared to the standard approach. As described below, this modification is suggested by the simulation procedure called Brownian Dynamics, [6-9] but the simulation algorithm itself can be verified rather directly. We report preliminary results in which the new Monte Carlo procedure is compared with the standard one for two model systems: a string of point masses joined by springs and a cluster of charged soft spheres. These model results support the expectation of improved efficiency.

In Sec. II, we develop the new Monte Carlo procedure for canonical ensemble sampling and show that it is expected to lead to a high acceptance probability for trial moves. In Sec. III, the new method and the standard one are applied to the model systems. In Sec. IV, the conclusions are presented and the new method is compared to other recent developments.

II. DEVELOPMENT OF THE METHOD

We consider a system of N particles with the Hamiltonian

$$H_N = K_N + U_N \,, \tag{1}$$

where K and U are the kinetic and potential parts, respectively, and recall that for classical systems the equilibrium configurational averages [e.g., U_N, C_v, $g(r)$] are functionals of U_N but not of K_N. Thus, to calculate these equilibrium averages we may choose K_N strictly on the basis of convenience. Here we choose a K_N characteristic of an N-particle system in a viscous medium; K_N corresponds to each particle obeying not Newton's law but the Langevin equation

$$\ddot{\mathbf{r}} = -\dot{\mathbf{r}}/\tau + (\mathbf{F} + \mathcal{F})/m \,, \tag{2}$$

where m is the particle's mass, τ^{-1} its frictional coefficient, $\mathbf{F} = -\nabla U_N$ is the force on the particle due to all of the others, and $\mathcal{F}$ is the corresponding random force. For N particles in a real viscous medium there are also hydrodynamic interaction force terms in the Langevin equation (alternatively written in terms of off-diagonal elements of the diffusion tensor[9]), but for the present purposes, we choose a hypothetical viscous medium in which these complications are absent.

Under the assumptions that the particle momentum relaxation is much more rapid than the system configurational relaxation and that the spatial gradients of the phase space distribution function are relatively smooth, the Brownian motion of particles governed by the Langevin equation [Eq. (2)] can be approximated by a Smoluchowski equation description. [6,9] The Brownian dynamics can then be simulated using the integration algorithm[6]

$$\Delta\mathbf{r} = D\beta\mathbf{F}\Delta t + \mathbf{R} \,, \tag{3}$$

where $\Delta\mathbf{r}$ is the change of $\mathbf{r}$ in a time step Δt, $\mathbf{F}$ is the force on the particle at the beginning of the step, $\beta = 1/k_B T$, D is the diffusion constant in the absence of interparticle interactions, and $\mathbf{R}$ is the random displacement corresponding to the random force $\mathcal{F}$. We assume that $\mathbf{R}$ is a Gaussian random variable; i.e., it is distributed according to

$$W(\mathbf{R}) = (4A\pi)^{-3/2}\exp(-\mathbf{R}^2/4A) \,, \tag{4}$$

where $A = D\Delta t$; Eq. (3) is then simply

$$\Delta\mathbf{r} = \beta A\mathbf{F} + \mathbf{R} \,. \tag{5}$$

Just as the elements of the diffusion tensor need not be the same for each degree of freedom, the corresponding values of A may also be different from one another. In the following, we assume for simplicity that A is a single constant.

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It is interesting to note that this algorithm can be derived from a molecular dynamical viewpoint if we assume that at the beginning of each time step the velocity $\mathbf{V}$ of each particle is chosen anew from a Maxwell–Boltzmann distribution. This implies

$$\Delta\mathbf{r} = \mathbf{F}\Delta t^2/2m + \mathbf{V}\Delta t \ , \tag{6}$$

which may be rearranged to the form in Eq. (5), with $A = \Delta t^2/2m\beta$.

Equation (5) differs from the standard Monte Carlo algorithm for a tentative step[10]

$$\Delta\mathbf{r} = \mathbf{R}' \ , \tag{7}$$

where each Cartesian component of $\mathbf{R}'$ is uniformly distributed between $-L$ and L for some chosen L. As noted elsewhere,[5] the particle displacements in the exact molecular dynamics are biased in the direction of the force while in the standard Monte Carlo method they are not. The displacements given by Eq. (5) follow directly from a dynamic description and hence the force enters in a natural way; the force term tends to guide the exploration of the configuration space along the trajectory of the natural motion of the system. The quasidynamic algorithm for particle displacements employs a knowledge of both the potential energy and the potential surface gradient; hence we refer to the application of Eq. (5) for a tentative Monte Carlo step as a "smart" Monte Carlo (SMC) procedure. It remains to be seen whether SMC is efficient compared to standard Monte Carlo (MC) in actual computations.

If A is chosen small enough, the trajectories generated from Eq. (5) are expected to provide accurate estimates for equilibrium averages just as in the analogous case of molecular dynamics with a sufficiently small incremental particle displacement; indeed, this has been demonstrated in some Brownian dynamics simulations.[6,7] But if our aim is to generate only equilibrium averages, we may use arbitrary A and still guarantee the correctness of the averages by an appropriate modification of the step algorithm as follows.

Equation (5) defines a Markovian transition probability T^*_{ij} for the transition to a new state j from a state i of the N-particle system. As in the preceding considerations, this may be thought of in terms of a change in locations of all N particles in the time step, but may equally be considered as a change in location of just one particle. For simplicity of notation, we consider the latter case explicitly; the results for the case in which the positions of all particles change in the transition follow by a direct generalization. For a given distribution function $W(\mathbf{R})$, which need not be that given in Eq. (4), the form of T^*_{ij} follows directly from Eq. (5), namely,

$$T^*_{ij} = \frac{\int d\mathbf{R}\, W(\mathbf{R})\delta(\Delta\mathbf{r} - \beta A\mathbf{F}_i - \mathbf{R})}{\int d(\Delta\mathbf{r}) \int d\mathbf{R}\, W(\mathbf{R})\delta(\Delta\mathbf{r} - \beta A\mathbf{F}_i - \mathbf{R})} \ , \tag{8}$$

where $\Delta\mathbf{r} = \mathbf{r}_j - \mathbf{r}_i$; $\mathbf{F}_i$ is the force on the particle in the state i; and $\delta(\mathbf{x})$ is the Dirac delta function.

Except in the limit of small A [see Eq. (5)], these transition probabilities do not exactly satisfy all of the conditions for generating equilibrium averages.[3] However, the modified transition probabilities T_{ij} defined by

$$T_{ij} = \begin{cases} T^*_{ij} & \text{if } T^*_{ji}\pi_j \geq T^*_{ij}\pi_i \ ; \quad j \neq i \qquad (9a) \\ T^*_{ji}\,\dfrac{\pi_j}{\pi_i} & \text{if } T^*_{ji}\pi_j < T^*_{ij}\pi_i \ ; \quad j \neq i \ , \qquad (9b) \end{cases}$$

$$T_{ii} = 1 - \sum_{j \neq i} T_{ij} \ , \tag{9c}$$

where π_i is the Boltzmann probability for state i,

$$\pi_i = \exp[-\beta U_N(i)]\left(\int d(i) \exp[-\beta U_N(i)]\right)^{-1} \ , \tag{10}$$

are consistent with the necessary conditions[3] for the generation of equilibrium canonical ensemble averages.[4,11] As noted above, it is not necessary to assume that in the transition to state j from state i only one particle of an N particle system is moved; Eq. (9) applies equally to simulation by N-particle moves.[4] In the present context, an N-particle move is made by applying Eq. (5) to each of the N particles to change to state j from state i; one interprets each vector in Eq. (5) and Eq. (8) as a set of N vectors.

To generate a Markov chain with transition probabilities T_{ij} we may proceed as follows in each step:

(1) Select at random a value of $\mathbf{R}$ from the distribution $W(\mathbf{R})$.

(2) Calculate the tentative new state j from the old one i using Eq. (5).

(3) Accept the new state with probability

$$P_{\text{SMC}} = \min(1, T^*_{ji}\pi_j/T^*_{ij}\pi_i) \ . \tag{11}$$

(4) If the tentative step is rejected the old state i is counted again before trying another move.

For the distribution $W(\mathbf{R})$ given in Eq. (4), we find from Eq. (8) the explicit form of T^*_{ij}, namely,

$$T^*_{ij} = C \exp[-(\Delta\mathbf{r} - \beta A\mathbf{F}_i)^2/4A] \ , \tag{12}$$

where the normalization constant C depends only on the parameter A and cancels in the evaluation of the ratio in Eq. (11).

To discuss the critical comparison of the SMC acceptance probability P_{SMC} [Eq. (11)] with the corresponding Metropolis probability[3] P_{MC},

$$P_{\text{MC}} = \min(1, \pi_j/\pi_i) \ , \tag{13}$$

we write each in the form

$$P = \min\{1, \exp[\beta Q(j \leftarrow i)]\} \tag{14}$$

and compare the alternative expressions for Q.

Expanding $U_N(\mathbf{r}_j)$ about $\mathbf{r}_i$ and $U_N(\mathbf{r}_i)$ about $\mathbf{r}_j$, and assuming that third and higher derivatives of the potential are negligible in the region of interest, we find

$$Q_{\text{MC}}(j \leftarrow i) = \left(\frac{\mathbf{F}_i + \mathbf{F}_j}{2}\right) \cdot \Delta\mathbf{r} \ . \tag{15}$$

Substituting Eq. (12) into Eq. (11) yields, under the same assumptions,

$$Q_{\text{SMC}}(j \leftarrow i) = -\frac{\beta A}{2}\left(\frac{\mathbf{F}_i + \mathbf{F}_j}{2}\right) \cdot \nabla\mathbf{F}_i \cdot \Delta\mathbf{r} \ . \tag{16}$$

Comparing Eq. (15) and Eq. (16), we conclude that for a given rms displacement of the particles per move we may expect $\langle P_{\text{SMC}} \rangle$, the average value of P_{SMC}, to be sub-

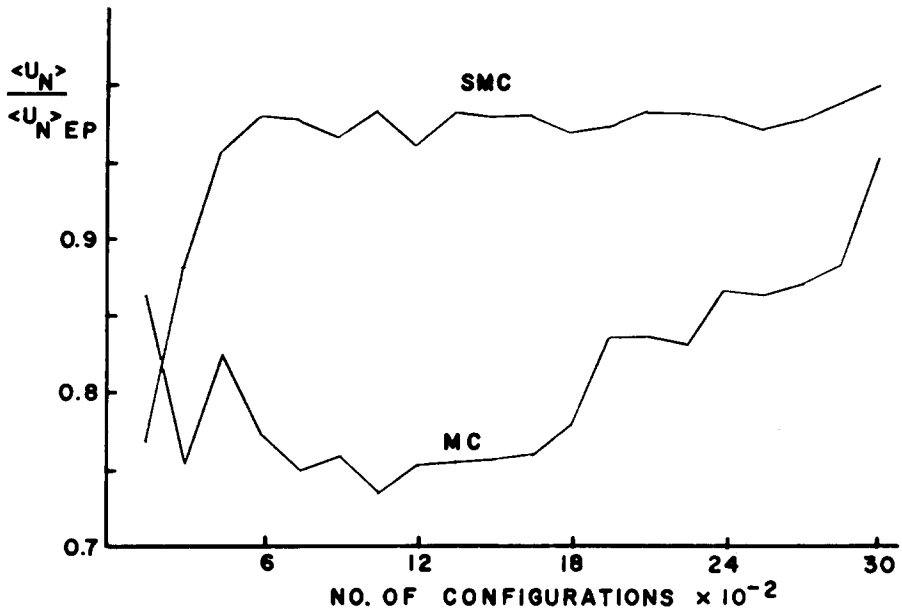

FIG. 1. Average potential energy relative to equipartition value $\langle U_N \rangle_{E.P.}$ for oscillator model. The SMC configurations are for 10-particle moves; for MC they are 1-particle moves.

stantially larger than $\langle P_{MC} \rangle$. Correspondingly, we expect the SMC method to generate trajectories that cover a larger part of the configuration space for a given computational effort.

III. APPLICATION TO MODEL SYSTEMS

The standard Metropolis (MC) and "smart" Monte Carlo (SMC) methods have been applied to simulations of two model systems.

In one series of tests, the SMC technique was applied to a model system consisting of 11 point masses in a linear array connected by springs of force constant k. The particle at one end was taken to be infinitely massive, while the others were of mass m. Starting with all particles in their equilibrium positions sequences of configurations were generated, both according to the usual Metropolis procedure[1-3] and by N-particle moves based on Eq. (6). Shown in Fig. 1 are the average potential energies (compared with the equipartition value) as a function of the number of configurations included in the averages. The system parameters utilized were $T = 500\,°\mathrm{K}$, $m = 200$ proton masses, $\Delta t = 1100$ a.u., and k is chosen so that $\hbar\omega/k_B T = 0.3$, where $\omega = (k/m)^{1/2}$. The Metropolis 1-particle procedure produced an acceptance probability of 0.54, while the SMC acceptance probability for the parameters above was 0.81 even with N-particle moves. As shown in Fig. 1, quite satisfactory convergence is found for N-particle simulation.

In another series of tests, we have studied an assembly of 13 ions of each sign with the pair potential

$$u_{ab}(r) = B_1(r^*/r)^9 + z_a z_b B_2/r\,, \tag{17}$$

where $z_a = \pm 1$ is the charge on ion a. The parameters $B_1 = 2.22758$ kcal/mole, $r^* = 3.65$ Å, and $B_2 = (18.2223)^2$ kcal-Å/mole were chosen so that the system corresponds closely to a cluster of Cs^+ and Cl^- ions in the gas phase. Starting from a cubic lattice configuration, with neighbors separated by r^*, the system was equilibrated with 1-particle SMC moves ($A = 0.02$ Å^2) at 1000 °K; the observed $\langle P_{SMC} \rangle$ was 0.86.

A series of comparative trials, each at 1000 °K and beginning with the equilibrated configuration, were carried out. In the MC (Metropolis) simulations,[3] the distribution of each Cartesian component of $\Delta\mathbf{r}$ is uniform in the range from $-L$ to L, so that the MC parameter L is of similar significance to $(6A)^{1/2}$ in the SMC simulations. The observed rms step size (a rejected tentative step contributes $\Delta\mathbf{r} = 0$)

$$\bar{s} \equiv \langle \Delta\mathbf{r}^2 \rangle^{1/2} \tag{18}$$

has the same significance in the two methods.

In Fig. 2, we show the results for $\langle P \rangle$ and $\bar{s}$ obtained using both the MC and SMC methods with single particle moves [2(a) and 2(b)] and with SMC N-particle ($N = 26$) moves [2(c)]. As expected from Eqs. (15) and (16), the

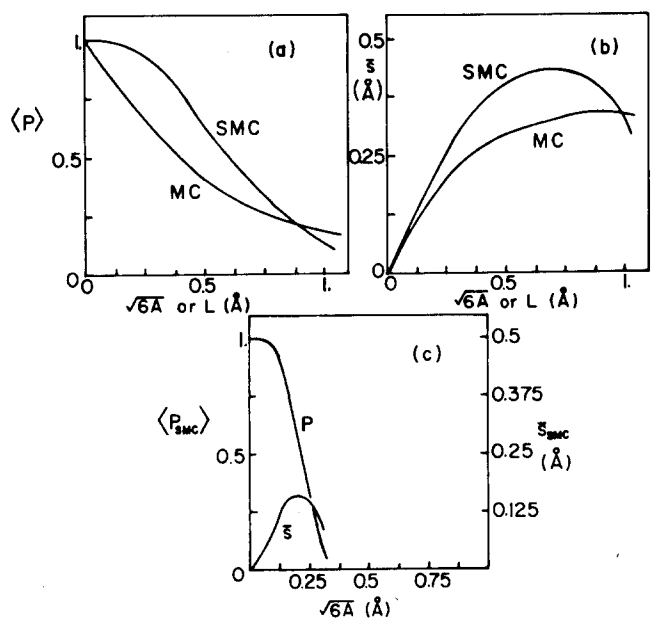

FIG. 2. Acceptance probabilities $\langle P \rangle$ and rms step size $\bar{s}$ for ion cluster: (a) and (b), single-particle moves; (c), 26-particle moves.

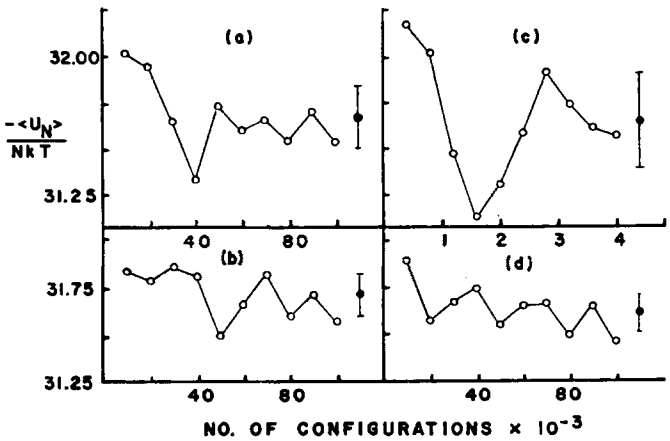

FIG. 3. Potential energy control charts for ion cluster simulations (see Table I). The subaverages are for 10 000 single-particle move [for (c), 400 26-particle move] configurations. Error bars correspond to one standard deviation.

acceptance probability for SMC is much higher than that for MC unless the step length parameter is unreasonably large. For the smaller values of A, $\langle P_{\rm SMC} \rangle$ is nearly unity and the departure from unity is quadratic, in marked contrast to the MC result. For MC, with $\langle P_{\rm MC} \rangle = 0.5$, the usual choice, one has $\bar{s}_{\rm MC} = 0.27$ Å, while for SMC with $\langle P_{\rm SMC} \rangle = 0.5$ we have $\bar{s}_{\rm SMC} = 0.43$ Å. Correspondingly, when $\bar{s}_{\rm SMC} = 0.27$ Å ($A \simeq 0.01$ Å^2), we find $\langle P_{\rm SMC} \rangle = 0.93$.

It is interesting to compare the mean acceptance probability $\langle P^N \rangle$ for N-particle moves with the quantity $\langle P^1 \rangle^N$. For uncorrelated moves, as is the case for the MC method, we expect $\langle P^N \rangle \cong \langle P^1 \rangle^N$. The results in Fig. 2(c) show that $\langle P^N_{\rm SMC} \rangle$ is consistently higher than $\langle P^1_{\rm SMC} \rangle^N$ [see Fig. 2(a)]. For $A = 0.001$ Å^2, $\langle P^1_{\rm SMC} \rangle = 0.998$, $\langle P^1_{\rm SMC} \rangle^{26} = 0.949$, and $\langle P^N_{\rm SMC} \rangle = 0.974$. (For the same value of $\bar{s}$, 0.077 Å, MC gives $\langle P^1_{\rm MC} \rangle = 0.88$ and $\langle P^1_{\rm MC} \rangle^{26} = 0.036$.) There is, in addition, an intrinsic gain of at least a factor of 2 in efficiency in N-particle moves compared to 1-particle moves which is associated with the minimum computational effort required to compute the changes in pair interactions. Hence, it is important to examine the effectiveness of such N-particle moves.

Based on the results in Fig. 2, several relatively long simulations were carried out (Table I). In trials (b) and (d) the SMC method is used with single particle moves; in (b), the parameter A is chosen so that $\langle P \rangle \sim 0.5$ as in the MC trial (a) while in trial (d) A is chosen so that $\bar{s}$ is close to that in trial (a). For the N-particle move SMC trial, (c), we choose a rather small value for A. Assuming that behavior parallel to that shown in Fig. 2(a) and 2(c) is manifest for systems with a larger number of particles, such a value for A would lead to a satisfactory N-particle move acceptance rate even for typical studies with $N \sim 300$; i.e., $\langle P^1_{\rm SMC} \rangle^{300} > 0.5$ for the given A.

The basic results of these trials are given in Part B of the table and in Figs. 3, 4, and 5. Figure 3 shows control charts[2] for the potential energy using 10 000 configuration subaverages. The results in Fig. 3 and Table I B indicate that the SMC 1-particle moves [trials (b) and (d)] outperform the MC (Metropolis) method, although the N-particle trial, (c), does not. Although the variances do not differ greatly, the differences between them suggest that the SMC simulation is more rapidly convergent. For example, applying the variance ratio test (F test)[12] to the variances obtained in trials (a) and (d) yields the conclusion at the 93% confidence level that the true variance ratio for MC compared to SMC simulation using the parameters in these trials is, in fact, greater than unity.

A more sensitive test is provided by the excess heat capacity

TABLE I. Simulations for a cluster of 13 ion pairs.

A. Parameters

Trial[a]	Length (configurations × 10^{-3}) × no. ions moved per configuration	Method	Step size parameter
(a)	100×1	Metropolis (MC)	$L = 0.40$ Å
(b)	100×1	SMC	$A = 0.06$ Å^2
(c)	4×26[b]	SMC	$A = 0.001$ Å^2
(d)	100×1	SMC	$A = 0.01$ Å^2

B. Results

			50 000 configurations[c]		100 000 configurations[c]	
Trial	$\langle P \rangle$	$\bar{s}$(Å)	$-\langle U_N \rangle / NkT \pm \sigma$[d]	$C_v^{\rm ex}/Nk$[e]	$-\langle U_N \rangle / NkT \pm \sigma$[d]	$C_v^{\rm ex}/Nk$[e]
(a)	0.494	0.264	31.74 ± 0.21	2.99	31.67 ± 0.17	2.65
(b)	0.492	0.419	31.76 ± 0.14	2.15	31.71 ± 0.12	1.99
(c)	0.974	0.077	31.62 ± 0.37	5.00	31.65 ± 0.26	3.05
(d)	0.942	0.244	31.68 ± 0.10	2.02	31.62 ± 0.10	1.90

[a]The initial configuration is that derived by equilibration from a lattice as described in the text.
[b]4000 N-particle moves ~ 26×4000 = 104 000 single particle moves.
[c]For trial (c), the entries are for 2000 and 4000 26-particle move configurations.
[d]Standard deviation based on 10 000 configuration subaverages; see Fig. 3.
[e]See Eq. (19).

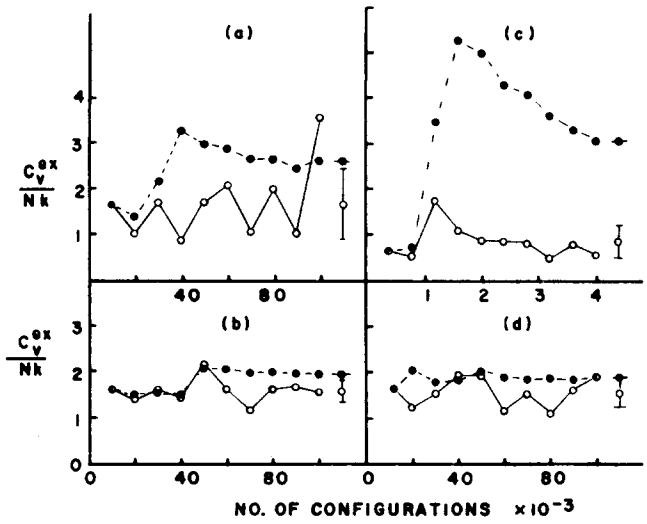

FIG. 4. Heat capacity [Eq. (19)] for ion cluster simulations (Table I). Solid symbols: running average; open symbols: 10 000 configuration subaverage estimates. The error bar indicates the standard deviation of the subaverage estimates.

$$C_v^{ex} = \frac{d\langle U_N\rangle}{dT} = \frac{\langle U_N^2\rangle - \langle U_N\rangle^2}{k_B T^2} \quad . \tag{19}$$

In Fig. 4, we show the results for the accumulated estimate of C_v^{ex} as solid symbols and the *individual* estimates from each successive 10 000 configuration segment as open symbols. The average for the whole simulation is not the average of these estimates; the nearness of the two is, however, a very good indicator of the convergence rate of the simulation.[2] The results in Fig. 4 reflect in an amplified manner the trends seen in Fig. 3. The convergence rate of C_v^{ex} is poor for the MC method and N-particle SMC but quite good for the large step SMC trial, (b), and excellent for the moderate $\bar{s}$ SMC trial, (d).

As a final comparison we consider the spatial distribution of particles in the cluster. Given $\mathcal{N}_{+-}(r)$, the average number of negative ions in a spherical volume of radius r around any positive ion, we define the distribution function

$$\rho_{+-}^{(2)}(r) = \frac{1}{4\pi r^2}\,\frac{d\mathcal{N}_{+-}(r)}{dr} \quad . \tag{20}$$

Figure 5 shows tests of the convergences of $\rho_{+-}^{(2)}(r)$ using two simulation methods. After only 5000 one-particle moves, both give distribution functions in reasonable agreement with the result from 100 000 moves, but the noise appears to be somewhat smaller for SMC than for MC.

IV. CONCLUSIONS

Clear conclusions can be drawn from the model system results presented. The SMC method, embodied in Eqs. (5), (11), and (12), leads to a much more rapidly convergent simulation than the standard Metropolis method. This advantage appears to be most pronounced for the choice of a moderate step size, comparable to that appropriate for a Metropolis (MC) simulation, but for which the SMC acceptance probability is substantially higher. Although in the current trial, using a very small step size, the N-particle moves do not lead to good results, this possibility (prohibited for the traditional MC method by the low value of $\langle P\rangle$) should not be discarded without further examination. In particular, with N-particle moves the close similarity to real Brownian dynamics makes the trajectory more susceptible to intuitive analysis.

The present approach can be compared to other recent developments in the methodology of Monte Carlo sampling.[4,5] Pangali *et al.*[5] employ an algorithm with the transition probability [cf. Eq. (12)]

$$T_{ij}^{*} = C(\mathbf{F}_i, L)\exp(\beta \mathbf{F}_i \cdot \Delta\mathbf{r}) \, . \tag{21}$$

The transition probability of Ceperley and co-workers[4] corresponds directly to a linearization of the exponential in Eq. (21). The presence of $\mathbf{F}_i$ in T_{ij}^{*} in Eq. (21) has qualitatively the same effect as the $\beta A \mathbf{F}_i$ term in Eq. (12), in that trial particle displacements are biased in the direction of the force. However, employing Eq. (21) for T^{*} in Eq. (11) shows that only partial cancellation of the $\mathbf{F}_i \cdot \Delta\mathbf{r}$ (linear) term in Eq. (15) results. Consequently, the acceptance probability using Eq. (21) will generally be lower than that using SMC. It would seem that a higher acceptance probability for a given rms step size should lead to more effective sampling and hence more rapid convergence, although this conclusion must be speculative in the absence of comparative trials. Based on Eqs. (11) and (15), it appears that the modification obtained by substituting $\beta/2$ for β in Eq. (21) should substantially increase the acceptance probability obtained by the method of Ref. 5.

The extra computational effort involved in applying SMC compared to standard methods will depend on the

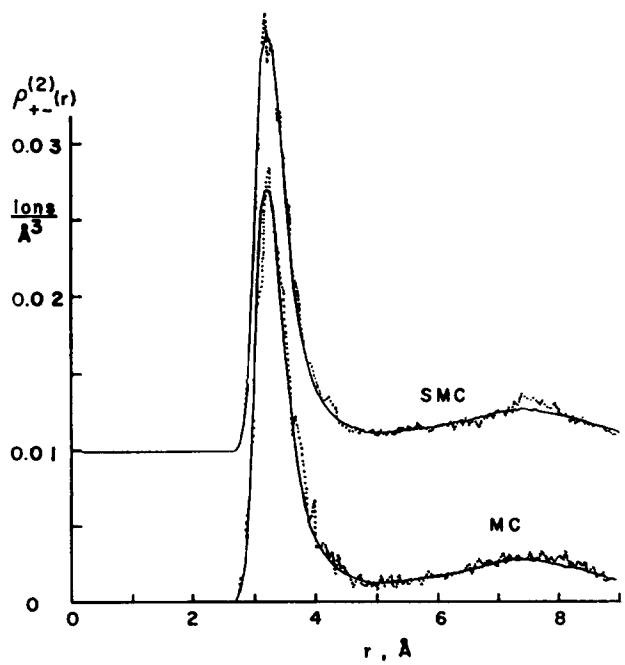

FIG. 5. Distribution function $\rho_{+-}^{(2)}(r)$. The dotted lines result from 5000 1-particle moves, with $L = 0.40$ Å for MC and $A = 0.01$ Å^2 for SMC (shifted upward by 0.01 ions/Å^3). The solid lines show the result of 100 000 1-particle moves with SMC using $A = 0.01$ Å^2.

problem of interest as well as considerations of execution speed and storage facilities in the particular machine application. However, typically one expects that the computation of the force will dominate the increase in execution time; for many potential functions of interest, such as the charged soft sphere interaction, this increase amounts to only a few percent.

Finally, it should be noted that in certain situations where the rate of convergence is dominated by the ability to escape from local energetic minima, SMC may not be as effective as standard methods. Energetic trapping may be very important, for example, in relatively low density molten salts.[13] Since SMC trial moves tend toward the local minimum, escape from the minimum may be made more difficult. We are currently investigating this aspect of Monte Carlo simulation.

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