Stochastic Potential Switching Algorithm for Monte Carlo Simulations of Complex Systems

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This paper describes a new Monte Carlo method based on a novel stochastic potential switching algorithm. This algorithm enables the equilibrium properties of a system with potential \( V \) to be computed using a Monte Carlo simulation for a system with a possibly less complex stochastically altered potential \( \tilde{V} \). By proper choices of the stochastic switching and transition probabilities, it is shown that detailed balance can be strictly maintained with respect to the original potential \( V \). The validity of the method is illustrated with a simple one-dimensional example. The method is then generalized to multidimensional systems with any additive potential, providing a framework for the design of more efficient algorithms to simulate complex systems. A near-critical Lennard-Jones fluid with more than 20000 particles is used to illustrate the method. The new algorithm produced a much smaller dynamic scaling exponent compared to the Metropolis method and improved sampling efficiency by over an order of magnitude.

I. INTRODUCTION

Simulations of complex molecular systems are generally carried out using either the molecular dynamics (MD) or the Monte Carlo (MC) method. Each method has its own merits. The MD method \([1, 2]\), based on the integration of the classical equations of motion of the particles, is conceptually the simpler of the two. With currently available computer power, MD simulations generally cannot be carried out for very long time scales for very large systems, making the extraction of true equilibrium properties often difficult. The MC method \([3, 4]\), on the other hand, relies on stochastic dynamics to generate members of the desired ensemble. MC has the ability to execute non-physical large-scale transitions that are impossible in MD and has the potential to reach equilibrium much faster. However, devising these large-scale transitions that have reasonable acceptance probabilities is not always straightforward.

To search for ways to enable large-scale transitions to be carried out with higher probability in MC simulations, one must tackle the core problem, which is the complexity of the interactions among the particles in the system. If there were no interactions among these particles, any transition, regardless of its scale, would always be accepted. When a move is made in MC, the interactions involving those particles that are being moved will change. In general, the larger the scale of the move and the more complicated the interactions are, the larger the change in the potential becomes. Consequently, large-scale MC moves are very unlikely to be accepted.

A natural question arises: Is it possible to reduce the complexity of the interactions among the particles, for instance, by replacing the actual potential \( V \) by a less complex potential \( \tilde{V} \)? One possibility is proposed in this paper. With this method, it is indeed possible to replace the original potential \( V \) by an arbitrary \( \tilde{V} \). But the procedure has to follow a carefully constructed algorithm to guarantee that detailed balance with respect to the original potential is maintained, so that the correct statistics are produced. An idea similar to this has been exploited in a number of previously proposed Monte Carlo methods, such as J-walking \([5, 6, 7]\), simulated tempering \([8, 9]\), parallel tempering \([10, 11, 12, 13]\), catalytic tempering \([14]\), multicanonical J-walking \([15]\), and the approximate potential method \([16]\). But we will show that when generalized to multidimensional systems, the present method provides flexibilities and potential advantages that are not available with these previous methods and establishes a theoretical framework for the design of possibly more efficient algorithms for simulating complex systems.

II. THE SPS IDEA

Let \( x \) be the configuration of a \( N \)-dimensional system and \( V(x) \) the potential energy divided by the Boltzmann constant \( k_B \). The statistical weight of each member of the canonical ensemble is \( \exp(-V(x)/T) \), \( T \) being the absolute temperature. A MC algorithm that generates configurations consistent with their statistical weights can be constructed from any set of transition rules, as long as the transition probabilities \( W \) between every pair \( x \) and \( x' \) satisfy the detailed balance condition:

\[
e^{-V(x)/T}W(x \to x') = e^{-V(x')/T}W(x' \to x). \tag{1}
\]

The new MC algorithm we propose proceeds as follows:

1. First, consider changing the system potential \( V \) to an arbitrary potential \( \tilde{V} \). This “potential switching” decision is carried out with a stochastic switching probability

\[
S(x) = e^{(\Delta V(x) - \Delta V^*)/T}, \tag{2}
\]

with \( \Delta V(x) = V(x) - \tilde{V}(x) \) and \( \Delta V^* \) is a constant greater than or equal to the maximum value
of $\Delta V(x)$ over all $x$. By incorporating $\Delta V^*$ into Eqn. (2), we ensure that $S(x)$ is between 0 and 1. Note that if $\Delta V^*$ is very large, the resulting $S(x)$ will be small, making switching very infrequent. For systems with a $V$ that is bounded from above, it is always possible to choose a $V$ which yields a finite $\Delta V^*$. Systems with an unbounded $V$ will be addressed in Sect. V.

2. If the switch is made, the configuration of the system is moved from $x$ to $x'$ with transition probability $W(x \rightarrow x')$ chosen to satisfy detailed balance on the switched potential $\tilde{V}$, i.e.,

$$e^{-\tilde{V}(x)/T}W(x \rightarrow x') = e^{-\tilde{V}(x')/T}W(x' \rightarrow x). \quad (3)$$

Any $\tilde{W}$, such as Metropolis, may be used here as long as it satisfies Eqn. (3).

3. If the switch is unsuccessful, the configuration of the system is moved from $x$ to $x'$ with transition probability $\tilde{W}(x \rightarrow x')$ chosen to satisfy detailed balance on a pseudopotential

$$\tilde{V}(x) = V(x) - T \ln[1 - S(x)], \quad (4)$$

Similar to step 2, any $\tilde{W}$ may be used here as long as it satisfies detailed balance on $\tilde{V}$.

After the move from $x \rightarrow x'$ is made (accepted or rejected), the cycle is over and the algorithm returns to step 1. This stochastic potential switching (SPS) idea, with the relevant potential switching and subsequent MC transition probabilities, is illustrated schematically in Fig. 1. Obviously, the SPS algorithm can be used alone in a simulation (if the moves are ergodic) or mixed with other MC moves.

With the algorithm defined above, it is easy to prove that the composite transition probability:

$$W(x \rightarrow x') = S(x)\tilde{W}(x \rightarrow x') + [1 - S(x)]\tilde{W}(x \rightarrow x'), \quad (5)$$

when substituted into Eqn. (1), indeed satisfies detailed balance with respect to the original potential $V$. Therefore, the MC trajectory generated by this SPS idea will produce a sequence of configurations $\{x\}$ that is consistent with the canonical ensemble for a system with potential $V$. It is important to emphasize that the choice of $\tilde{V}$ is completely arbitrary — the proof works for all $\tilde{V}$.

In a real application, one can exploit this arbitrariness to select a $\tilde{V}$ that may be either less complex than the original $V$ or less costly to compute. For a system where the potential is a sum of additive terms $V = \sum_i V_i$, often the case for many-particle systems, the switching decision can be applied to each $V_i$ separately. This generalization will be described in Sect. V.

In form described above, the SPS idea is conceptually related to J-walking [6, 7], parallel tempering [10, 11, 12, 13], and the “approximate potential” method [10]. In J-walking, the simulation is stochastically switched to a configuration sampled from a higher-temperature ($T'$) simulation of the same potential with properly chosen transition probabilities. This is essentially the same as using a potential that is attenuated by a factor $T/T'$ as $\tilde{V}$ in SPS. Similarly, in parallel tempering, the exchange of replicas between two different temperatures is equivalent to having one switched to an attenuated potential and the other to a higher potential.

In the approximate potential method, the simulation is switched to an approximate potential, and the new configuration produced on the approximate potential is accepted or rejected at the end with a “correction” rate that is designed to maintain detailed balance with respect to the original potential; whereas in SPS, the switching decision is made before the move, so that the subsequent update on $\tilde{V}$ will always be accepted. Even though SPS is conceptually akin to these other methods, we will show in Sect. V that when SPS is generalized to multidimensional systems, its offers flexibilities and potential advantages that are not currently available in these related methods.

III. EXAMPLE: A ONE-DIMENSION MODEL

We use a simple one-dimensional example to illustrate the basic SPS idea. The model we selected was a harmonic potential $V(x) = \frac{1}{2}x^2$, with $x$ confined to within the range $[-1, 1]$. We used five different $\tilde{V}(x) = \frac{1}{2}x^n$, with $n = 0, 1, 2, 3$ and 4 to demonstrate that the ensemble averages were indeed invariant with the choice of $\tilde{V}$ and the choice of $\tilde{V}$ is hence arbitrary. For each of the five $\tilde{V}$, we sampled $x$ according to the SPS algorithm using simple Metropolis moves on both $\tilde{V}$ and $\tilde{V}$. $n = 2$ is a special case, because for $n = 2$, $\tilde{V} = V$, so the switch is made with unit probability. The SPS algorithm for $n = 2$ is thus equivalent to the normal Metropolis (i.e. non-SPS) algorithm.

The moments $\langle x^m \rangle$ at $T = 0.2$ for $m = 1$ to 10 are shown in Table I for the five different $\tilde{V}$. The results are clearly invariant with the choice of $\tilde{V}$ to within statistical errors, showing that detailed balance is strictly satisfied with respect to $\tilde{V}$ for any $\tilde{V}$. The switching rate $R_S$ is
also shown for each $\tilde{V}$. $R_S$ is in general lower for those $\tilde{V}$ (particularly $n = 1$ and 3) that are very different from the original potential $V$. Notice also that $n = 0$ corresponds to a flat potential. In this case, if the switch is made, the potential is completely turned off.

IV. RELATIONSHIP TO ISING-TYPE CLUSTER ALGORITHMS

A MC method that is capable of executing large-scale moves with high probability was proposed by Swendsen and Wang [18] for the Ising model in 1987. This method later led to the discovery of a class of methods now collectively known as “cluster algorithms” [19]. These cluster algorithms can be shown to be special cases of the SPS algorithm. Whereas these cluster algorithms permit large-scale MC moves, they are largely restricted to discrete models and are not generally applicable to molecular simulations. The SPS method provides a way to transfer the ideas behind these cluster algorithms to continuous systems.

In the original Swendsen-Wang algorithm, the interaction between each pair of Ising spins $\sigma_i$ and $\sigma_j$ is stochastically deleted with a probability $p_d = \exp[-J(\sigma_i\sigma_j - 1)]$, where $J$ is the Ising interaction. When an interaction is successfully deleted, it has no effect on the subsequent MC move. On the other hand, if an interaction is not deleted, it is frozen such that the value of this interaction is constrained to remain constant in the subsequent MC move. After all the interactions have been either deleted or frozen, the spins break up into clusters of spins having frozen interactions. Each cluster can be flipped independently of the others. Swendsen and Wang showed that this cluster algorithm satisfies detailed balance and it produces much faster equilibration compared to the conventional Metropolis algorithm [17].

The Ising model has potential $V = \sum_{ij} V_{ij}$, where $V_{ij} = -J\sigma_i\sigma_j$ and the sum goes over all nearest-neighbor pairs. It is easy to show that the Swendsen-Wang algorithm can be derived from the SPS algorithm by making the special choice $\tilde{V}_{ij} = 0$. As such, the SPS algorithm can be considered as a “generalized” cluster algorithm. However, we choose not to use this terminology because calling SPS a generalized cluster algorithm would improperly imply some geometric origin. Whereas in discrete systems such as the Ising model there is an obvious geometric interpretation for the SPS algorithm, there may not be any in more general continuous systems.

V. GENERALIZATION TO SYSTEMS WITH ADDITIVE POTENTIALS

While the validity of the SPS algorithm is clear for the basic case considered in Sect. III, the utility of the SPS algorithm in this form is rather limited. There are several reasons why this formulation of the SPS algorithm may not be very practical. (1) The choice of a good $\tilde{V}$ is not obvious. (2) Because $S(x)$ in Eqn. 2 is scaled by $e^{-\Delta V^*/T}$, unless $V$ is close to $V$ everywhere, the switching frequency will be in general small. (3) For a $V$ that is not bounded from above (as in systems with repulsive interactions), there may not be a way to choose a $\tilde{V}$ that keeps $\Delta V^*$ finite.

To make the SPS algorithm more useful, we must first generalize it to an additive potential $V$ that can be written as a sum of two or more terms. Any $V$ can be decomposed into an arbitrary sum. Some systems, such as those with pairwise interactions, have potentials that break up naturally into a sum of terms. In other situations, the potential may have two or more distinct parts that are responsible for different physical phenomena, such as the repulsive and attractive part of a Lennard-Jones potential [20]. We will see that the usefulness of the SPS algorithm is related to how $V$ is decomposed. Our formulation here is inspired by the ideas of Kandel et al. [21] who have provided a generalization of the Swendsen-Wang algorithm [18] for discrete-state (Ising) models.

To illustrate the generalization of the SPS algorithm to a continuous system with an additive potential, we consider a potential with just two terms $V(x) = V_1(x) + V_2(x)$. Extension to more than two terms is straightforward. We can apply the SPS algorithm in Sect. III to each of the terms separately, attempting to switch $V_1$ to a new $\tilde{V}_1$ and $V_2$ to another $\tilde{V}_2$ with switching probabilities $S_1(x) = e^{(\Delta V_1(x) - \Delta V_1^*)/T}$ and $S_2(x) = e^{(\Delta V_2(x) - \Delta V_2^*)/T}$, respectively. Since the potential terms are additive, the switching of $V_1$ and $V_2$ are independent of each other and can be performed in any order.

For two terms in the potential, there are four possible outcomes of the switching decision. For each one, the next part of the simulation will proceed on a different potential: (1) if both $V_1$ and $V_2$ are switched, the new potential becomes $\tilde{V}_1 + \tilde{V}_2$; (2) if both $V_1$ and $V_2$ are not switched, the new potential becomes $\tilde{V}_1 + \tilde{V}_2$; (3) if $V_1$ is switched but $V_2$ is not, the new potential becomes $\tilde{V}_1 + \tilde{V}_2$; (4) if $V_1$ is not switched but $V_2$ is, the new potential becomes $\tilde{V}_1 + \tilde{V}_2$, where $\tilde{V}_1$ and $\tilde{V}_2$ are defined as in Eqn. 4. After the switch is made, the system can be moved from configuration $x \rightarrow x'$ on the new potential. At the end of the move, the original potential can be restored to restart the switching process anew. One can easily show that with this algorithm, detailed balance with respect to the original potential is strictly obeyed along any one of the four pathways. This is a direct result of the additivity of $V_1$ and $V_2$. The sum over all four pathways therefore also obeys detailed balance.

In the above, we have considered switching both terms in $V$, but this needs not be. In fact, we can apply the switching to an arbitrary subset of terms. For example, we may consider switching only $V_1$ to $\tilde{V}_1$ and keeping $V_2$ “alive”. If the switching is successful, the new potential becomes $\tilde{V}_1 + V_2$; otherwise, it is $V_1 + V_2$. This scenario is equivalent to using a $\tilde{V}_2 = V_2$ and thus also satisfies detailed balance. This strategy may be useful, for example,
TABLE I: MC results for the model system \( V(x) = \frac{1}{2}x^2 \) at \( T = 0.2 \) using 5 different \( \tilde{V} = \frac{1}{2}x^n \). \( \langle x^m \rangle \) are the \( m \)-th moments measured by SPS-MC. \( R_S \) are the observed switching rate for each \( \tilde{V} \). The uncertainty of the last digit is shown in parentheses.

| \( n \) | \( n = 0 \) | \( n = 1 \) | \( n = 2 \) | \( n = 3 \) | \( n = 4 \) |
|-------|--------|--------|--------|--------|--------|
| \( \langle x^1 \rangle \) | 0.0003(8) | -0.0009(8) | 0.0008(8) | 0.0004(8) | 0.0010(8) |
| \( \langle x^2 \rangle \) | 0.1698(4) | -0.169(4) | 0.1702(4) | 0.1701(4) | 0.1701(4) |
| \( \langle x^3 \rangle \) | -0.0001(4) | -0.0005(4) | -0.0001(4) | 0.0001(4) | 0.0003(4) |
| \( \langle x^4 \rangle \) | 0.0716(3) | 0.0723(3) | 0.0720(3) | 0.0720(3) | 0.0721(3) |
| \( \langle x^5 \rangle \) | -0.0000(3) | -0.0004(3) | -0.0001(3) | 0.0000(3) | 0.0001(3) |
| \( \langle x^6 \rangle \) | 0.0416(2) | 0.0424(2) | 0.0418(2) | 0.0419(2) | 0.0420(2) |
| \( \langle x^7 \rangle \) | -0.0000(2) | -0.0003(2) | -0.0001(2) | -0.0000(2) | 0.0000(2) |
| \( \langle x^8 \rangle \) | 0.0283(2) | 0.0291(2) | 0.0285(2) | 0.0286(2) | 0.0287(2) |
| \( \langle x^9 \rangle \) | -0.0000(2) | -0.0002(2) | -0.0001(2) | -0.0000(2) | -0.0000(2) |
| \( \langle x^{10} \rangle \) | 0.0211(2) | 0.0218(2) | 0.0213(2) | 0.0214(2) | 0.0215(2) |
| \( \Delta V^* \) | 0.5 | 1.0 | 0.0 | 1.0 | 0.125 |
| \( R_S \) | 0.151 | 0.030 | 1.000 | 0.020 | 0.699 |

in the case of a \( V \) that is not bounded from above. In this case, we can decompose the potential into the repulsive (unbounded) and attractive (bounded) parts, but apply the switching only to the attractive part.

It should now be clear why decomposing \( V \) into many additive terms makes the SPS algorithm more practical. In the original formulation of the SPS algorithm in Sect. II, the entire \( V = \sum_i V_i \) is switched to \( \tilde{V} \). The probability for the simultaneous switching of all \( V_i \) is \( \prod_i S_i \). If the potential contains a large number of terms, the total switching probability will be small even if each individual \( S_i \) is close to unity. Therefore, switching the entire \( V \) is almost impossible, but individual terms in \( V \) can be switched with a much higher probability.

Coupled with good physical insights, the additivity of \( V \) can be exploited to devise efficient SPS algorithms that may be more optimal than others. Some systems, such as those with pairwise interactions, have a natural decomposition for \( V \). This may be used to guide the search for an optimal breakup. On the other hand, there may be a totally unphysical breakup that affords higher efficiency. The additivity of \( V \) offers immense possibilities. In the next section, we will illustrate this using a non-trivial many-particle example.

In fact, crude elements of the basic SPS idea have already appeared in one of our recent studies on the Monte Carlo simulations of imaginary-time path integrals, and these ideas have been proven useful for accelerating the sampling of stiff paths. The strategy proposed there was later implemented in a large-scale path integral simulation of superfluid molecular H\(_2\) clusters. These studies motivated us to refine the crude ideas contained in those two papers and formulate the more general theoretical framework for the SPS algorithm that has been presented in this section.

VI. EXAMPLE: A LENNARD-JONES FLUID NEAR ITS CRITICAL POINT

The correlation length of a system diverges near the critical point. Small local fluctuations of the system at large separations become correlated with each other, making Monte Carlo simulations extremely sluggish. This so-called “critical slowing-down” problem leads to extremely long equilibration time for Monte Carlo simulations that employ only local updates, such as the conventional Metropolis algorithm. Nonlocal moves can also be made using the Metropolis algorithm, but such moves are almost always rejected because of the reason given in the last section.

We will demonstrate how the SPS method can be used to deal with the critical slowing-down problem in a Lennard-Jones fluid. The simulations were carried out in a cubic box with periodic boundary condition. A Lennard-Jones potential \( u(r) = 4\epsilon \left[ (\sigma/r)^12 - (\sigma/r)^6 \right] \) that is truncated but unshifted at \( r_c = 2.5\sigma \) was used for the calculations. Previously, the critical temperature \( T_c \) and density \( \rho_c \) for this system were found to be \( k_B T_c = 1.1853\epsilon \) and \( \rho_c\sigma^3 = 0.3197 \). To check scaling, we vary the box length \( L \) from \( L/\sigma = 10 \) to 40, using up to 20464 particles to maintain a fixed density. Since the heat capacity is expected to diverge as \( |T - T_c|^\alpha \), the slowing-down problem should be manifested in the energy measurement. We compared the scaling of the autocorrelation time for the energy estimator with the box length \( L \) of the SPS method against the Metropolis algorithm and found a much smaller dynamical scaling exponent for the SPS method.

To implement the SPS method, we break up the total potential \( V = \sum_{i<j} u(r_{ij}) \) into the individual pair interactions \( u(r_{ij}) \). Next, for each of the pair interactions, we can further decompose it into its positive and neg-
ative parts, \( u = u_+ + u_- \), such that \( u_+(r) \) is everywhere zero except for \( r < \sigma \) where \( u_+(r) = u(r) \), and \( u_- \) is its complement. With this, the total potential becomes \( V = \sum_{i<j} u_+(r_{ij}) + u_-(r_{ij}) \). (We have also tried to decompose \( u \) according to the WCA prescription but found no major difference in the efficiencies of the two breakups.) With this decomposition, \( u_+ \) is a purely repulsive potential, whereas \( u_- \) is bounded from above by zero. We apply the SPS algorithm to each of the \( u_-(r_{ij}) \) terms to try to switch it to \( \tilde{u}_- = 0 \) but keep all the \( u_+(r_{ij}) \) alive. Since \( u_-(r) \leq \tilde{u}_- \) for all \( r \), \( \Delta u_- \) can be simply set to 0.

The SPS algorithm, when applied to the Lennard-Jones fluid, proceeds as follows. Starting from the current configuration \( \{\vec{r}\} \), we attempt to switch off each of the \( u_-(r_{ij}) \) one by one. After the switching decision has been completed for every \( u_-(r_{ij}) \), the particles now interact with a modified potential in which some pairs of particles interact with \( \tilde{u}_- \) while the rest have zero attraction between them. Since \( u_+ \) have been kept alive, every pair of particles also interact through the purely repulsive \( u_+ \). At this point, one can employ any Monte Carlo move to update the system on this stochastically modified potential. One simple possibility is to apply a Metropolis algorithm with a local update to the SPS modified potential, just like on the original potential. But as we will see, doing this alone will not improve the dynamical characteristics of the sampling.

The autocorrelation time \( \tau \) in MC pass for the total energy measurement is shown in Fig. 2 for different box sizes \( L \), comparing the conventional Metropolis algorithm with a local update applied to the original potential (square) against the same Metropolis update applied to the SPS modified potential (triangles). In both simulations, one MC pass is defined as having attempted one move for each particle in the system. Not surprisingly, the dynamic scaling behaviors of the two are identical to each other. Since both simulations are based on the same local update method and they both satisfy detailed balance, the dynamical characteristics of the two sampling methods ought to be the same. To improve sampling efficiency, nonlocal moves must be used.

In a near-critical system, the slowing-down problem is related to the divergence of the correlation length. Update methods that employ only local moves will therefore have poor dynamical scaling, since they are unable to effect large-scale rearrangements of the system. SPS provides a basis for designing possibly more efficient alternative update schemes. The system potential can be significantly simplified using SPS, enabling large-scale moves to be performed with much higher acceptance ratio compared to the original potential.

To perform large-scale moves in the near-critical Lennard-Jones fluid on the SPS modified potential, we employed a simple scheme based on an algorithm originally proposed by Dress and Krauth to treat hard sphere systems. We changed the method to suit the present situation, and our algorithm is illustrated in Fig. 3 and proceeds as follows.

1. For every pair of particles interacting with \( \tilde{u}_- \), we freeze their distance by placing a rigid “bond” between them.
2. For every pair of particles that have a nonzero \( u_+ \) between them, we consider them to be “overlapping” and also freeze their distance.
3. Based on the bonds and overlaps, we break the particles up into disjoint clusters. Two clusters are disjoint if there is no bond or overlap between them. This constitutes the “background” configuration in Fig. 3(a).
4. To move the clusters, a point inside the simulation box is randomly selected to be the pivot (illustrated by the cross in Fig. 3(a)), and all particles in the box are reflected across the pivot to obtain the “foreground” configuration in Fig. 3(b).
5. When the foreground is overlaid on the background, the clusters from the foreground and background form additional overlaps (but no additional bonds). The foreground and background positions of the same particle are also by default considered to be in the same cluster. Overlapping clusters can then be broken up into disjoint superclusters as in Fig. 3(c).
6. Since there is no overlap between any particles (either foreground or background) from two disjoint superclusters, we can choose randomly to accept either the foreground or background positions inside...
FIG. 3: Illustration of the cluster reflection algorithm. (a) Particles connected by frozen $u_- (4-7$ and $9-10)$ are bonded, shown in the figure connected by think lines. Particles that have a nonzero $u_+$ between them $(3-4, 5-6$ and $8-10)$ are shown as overlapping. Bonded and overlapping particles break up into disjoint clusters. In this example, there are six disjoint clusters. This forms the “background” configuration. The cross indicates the position of the pivot, which for this illustration is near the center of the cell. (b) All particles in the background are reflected across the pivot to generate the “foreground” configuration shown in grey. The new position of each particle $i$ in the foreground is labeled $i'$. (c) Overlaying (b) on (a) generates superclusters from overlapping foreground and background clusters. In addition, foreground and background positions of the same particle are in the same cluster by default. In this example, there are three disjoint superclusters: $(1', 1, 11', 11), (5', 5, 6', 6)$, and a third encompassing the rest. (d) For each supercluster, either all the foreground or all the background positions are accepted into the new configuration. In this example, two superclusters take on the background positions and one supercluster takes on the foreground positions.

This completes one pass in our SPS simulation. At this point, the simulation can start over with another cluster move from step 1, or we can carry out a Metropolis sweep before going back to 1. Notice that since the switching is done stochastically, a different cluster structure would be generated every time even if the switching is applied to the same configuration.

In is easy to show that the cluster reflection algorithm above satisfies detailed balance in a trivial way, because the move conserves the nonzero part of the total potential of the system by fixing all the bonds and overlaps and the reflection clearly produces symmetric transition probabilities. However, by itself the cluster reflection algorithm is nonergodic, because particles that have no overlap with each other in the configuration before the move will have no overlap either after the move. To have an ergodic Monte Carlo simulation, this cluster reflection algorithm must be mixed with another ergodic move, such as Metropolis using a local update. In our simulations, we performed one Metropolis move for every 10 cluster updates, which adds minimal costs to the CPU time.

Autocorrelation times $\tau$ in MC pass for the total energy measurement is shown in Fig. 2 for the SPS algorithm using the cluster reflection update (circles). For the SPS algorithm, one MC pass is defined as having made one cluster reflection move plus one-tenth of a Metropolis move (needed for ergodicity). In actual CPU time, a SPS MC pass is about 20% faster than a Metropolis MC pass. Near the critical point, the autocorrelation time is expected to scale with system size as $\tau \sim L^\eta$, and the dynamical scaling exponent $\eta$ is a measure of the efficiency of the MC method. Clearly, the SPS method has a much smaller dynamical exponent. In terms of absolute efficiency, the SPS algorithm is more than ten times better for the largest simulations considered ($L/\sigma = 40$ with 20464 particles), and accounting for CPU time difference, the SPS algorithm is actually 13 times better.

A generalized geometric cluster algorithm that is also based on the Dress and Krauth cluster move has also been proposed recently by Liu and Luijten. In their approach, the energies of the configuration before and after the cluster move have to be computed to determine the transition probabilities; whereas in our SPS algorithm, only the energy before the move has to be computed in order to determine the switching probabilities. In cases where the potential is complicated and costly to compute, the SPS algorithm here will offer CPU time savings compared to the method of Liu and Luijten, but it may suffer from lower switching rates.

VII. CONCLUSIONS

In summary, we have presented a new Monte Carlo method that is based on a stochastic potential switching algorithm. This new algorithm enables the equilibrium properties of a system with potential $V$ to be computed using a Monte Carlo simulation for a system with a possibly less complex stochastically altered potential $\tilde{V}$. Generalization of this method to systems with additive potentials provides for an efficient scheme for simulating complex systems. The validity of the method is illustrated with a simple one-dimensional example, and its practical utility in alleviating the critical slowing-down problem is illustrated with a Lennard-Jones fluid near its critical point.
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[1] M.P. Allen and D.J. Tildesley, Computer Simulation of Liquids, (Oxford, New York, 1987).
[2] B.J. Alder and T.E. Wainwright, J. Chem. Phys. 27, 1208 (1957).
[3] J.P. Valleau and S.G. Whittington, in: Statistical Mechanics, Part A, B.J. :Berne, Eds., (Plenum, New York, 1977).
[4] K. Binder, Monte Carlo Methods in Statistical Physics, Topics of Current Physics, Vol. 7, (Springer, Berlin, 1986).
[5] D.D. Frantz, D.L. Freeman and J.D. Doll, J. Chem. Phys. 93, 2769 (1990).
[6] D.D. Frantz, D.L. Freeman and J.D. Doll, J. Chem. Phys. 97, 5713 (1992).
[7] E. Curotto, D.L. Freeman and J.D. Doll, J. Chem. Phys. 109, 1643 (1998).
[8] E. Marinari and G. Parisi, Europhys. Lett. 19, 451 (1992).
[9] M.C. Tesi, E.J.J. van Rensburg, E. Orlandini and S.G. Whittington, J. Stat. Phys. 82, 155 (1996).
[10] M. Falcioni and M.W. Deem, J. Chem. Phys. 110, 1754 (1999).
[11] Q.L. Yan and J.J. de Pablo, J. Chem. Phys. 111, 9509 (1999).
[12] Q.L. Yan and J.J. de Pablo, J. Chem. Phys. 113, 1276 (2000).
[13] R. Faller, Q.L. Yan and J.J. de Pablo, J. Chem. Phys. 116, 5419 (2002).
[14] G. Stolovitzky and B.J. Berne, Proc. Natl. Acad. Sci. 97, 11164 (2000).
[15] H. Xu and B.J. Berne, J. Chem. Phys. 110, 10299 (1999).
[16] J. Gelb, J. Chem. Phys. 118, 7747 (2003).
[17] N. Metropolis, A.W. Rosenbluth, M.N. Rosenbluth, A.H. Teller and E. Teller, J. Chem. Phys. 21, 1087 (1953).
[18] R.H. Swendsen and J.-S. Wang, Phys. Rev. Lett. 58, 86 (1987).
[19] H.W.J. Blote, J.R. Heringa and E. Luijten, Comp. Phys. Comm. 147, 58 (2002).
[20] D. Chandler, J.D. Weeks and H.C. Andersen, Science 220, 787 (1983).
[21] D. Kandel, E. Domany, D. Ron, A. Brandt and E.,Jr. Loh, Phys. Rev. Lett. 60, 1591 (1988).
[22] C.H. Mak and S. Zakharov, J. Phys. Chem. B 108, 6760 (2004).
[23] C.H. Mak, S. Zakharov and D.B. Spry, J. Chem. Phys. 122, (in press, 2005).
[24] N.B. Wilding, Phys. Rev. E 52, 602 (1995).
[25] S.-K. Ma, Modern theory of critical phenomena, (Benjamin/Cummings, New York, 1976).
[26] C. Dress and W. Krauth, J. Phys. A 28, L597 (1995).
[27] J.W. Liu and E. Luijten, Phys. Rev. Lett. 92, 035504 (2004).