Rejection-Free Geometric Cluster Algorithm for Complex Fluids

Jiwen Liu and Erik Luijten*

Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, USA

(Received 23 September 2003; published 23 January 2004)

We present a novel, generally applicable Monte Carlo algorithm for the simulation of fluid systems. Geometric transformations are used to identify clusters of particles in such a manner that every cluster move is accepted, irrespective of the nature of the pair interactions. The rejection-free and nonlocal nature of the algorithm make it particularly suitable for the efficient simulation of complex fluids with components of widely varying size, such as colloidal mixtures. Compared to conventional simulation algorithms, typical efficiency improvements amount to several orders of magnitude.

DOI: 10.1103/PhysRevLett.92.035504 PACS numbers: 61.20.Ja, 05.10.Ln, 64.60.Ht, 82.70.Dd

The Monte Carlo (MC) method constitutes an important simulation technique in many areas of physics and chemistry [1,2]. One of its central aspects is the possibility to introduce nonphysical dynamics, permitting the study of systems that evolve over otherwise prohibitively large time scales. A well-known example is the cluster algorithm for lattice spin models introduced by Swendsen and Wang (SW) [3], which suppresses dynamic slowing down near a critical point. Since the conception of this method, its generalization to off-lattice fluids of interacting particles has been an elusive goal, the main bottleneck being the absence of particle-hole symmetry. Also away from the critical point the existence of several different time and length scales constitutes a major obstacle in the simulation of complex fluids. This situation commonly arises in multicomponent systems, such as binary mixtures, colloidal suspensions, and colloid-polymer mixtures, and has essentially precluded the computational study of many such systems. In this Letter, we present a novel, rejection-free cluster Monte Carlo method of considerable generality that alleviates this problem. It greatly facilitates the canonical simulation of large classes of continuum systems, such as complex fluids, by generating particle configurations according to the Boltzmann distribution, without suffering from severe slowing down in the presence of large size differences.

The SW lattice cluster algorithm and its improvement by Wolff [4] are based upon the Fortuin-Kasteleyn [5] mapping of the Potts model onto the random-cluster model, which decomposes a system of spins (or Potts variables) into independent clusters. This is manifestly different from collective update schemes in which more or less arbitrary groups of spins (particles) are flipped (moved). While such multiple-particle moves have yielded significant improvements in specific situations [6–9], their acceptance rate generally is an exponentially decreasing function of the number of particles involved. By contrast, the SW algorithm is rejection-free: every completed cluster is flipped without an additional evaluation of the resulting energy difference. Efficient *off-lattice* cluster algorithms are known only for the Widom-Rowlinson and Stillinger-Helfand models for fluid mixtures [10,11], in which identical particles do not interact at all. Furthermore, for hard-sphere fluids Dress and Krauth [12] have proposed a cluster algorithm based upon geometric operations that is capable of relaxing size-asymmetric mixtures [13] and model glass formers [14]. However, hitherto no general off-lattice equivalent of the SW approach has been developed. In this Letter, we demonstrate that the geometric method can be formulated as a Wolff single-cluster algorithm and subsequently be extended to arbitrary pair potentials between the constituents, while maintaining its rejection-free nature. The resulting *generalized* geometric cluster algorithm (GCA) handles interactions in the same manner as the SW algorithm and, in this respect, can be considered as its counterpart for continuum systems. Lattice cluster methods as well as the GCA exploit invariance of the Hamiltonian under global symmetry operations.

In the original GCA [12] a molecular configuration is rotated around an arbitrarily chosen pivot and overlaid with its original (nonrotated) version. Objects that overlap between the original and rotated configurations lead to "clusters" of particles. The particles belonging to these clusters are exchanged between the original and the rotated configuration. Since the pair potential is either zero or infinity, each configuration without particle overlaps has the same Boltzmann factor and hence the same probability. It has been suggested [12,15] to extend this approach to other pair potentials by introducing a Metropolis-type criterion for the acceptance of a cluster move. However, this approach faces serious drawbacks. (i) It cannot be applied to soft-core potentials, since the cluster-construction process fails to generate configurations containing interpenetrating potentials. (ii) The efficiency strongly deteriorates, since the algorithm is no longer rejection-free. Indeed, the stronger the interactions, the less relevant the (athermal) clusters become, and for many practical cases a conventional single-particle Metropolis algorithm will be more efficient [16]. It is noteworthy that for lattice spin models the

original GCA has successfully been generalized to include attractive short-range interactions [17]. However, this approach implicitly exploits particle-hole symmetry by relying on a mapping between sites in the original and the rotated lattice structure.

In order to formulate a geometric cluster algorithm for interacting fluids, we first rephrase the cluster construction for the original GCA as follows. After a random pivot has been chosen, the first particle is picked at random and moved via a point reflection with respect to the pivot (this reflection replaces the rotation). If this leads to one or more overlaps, the corresponding particles are also moved with respect to the same pivot. This procedure is reiterated recursively until no more overlaps are present. For the next cluster, a new pivot is chosen. In the presence of a general pair potential $V(r)$, we generalize this scheme as illustrated in Fig. 1. After the first particle i has been moved from position $\mathbf{r}_i$ to its new position $\mathbf{r}_i'$, two classes of particles are identified: (a) particles that interact with i in its original position; (b) particles that interact with i in its new position. Every particle that belongs to category (a) or (b) is subsequently considered for inclusion in the cluster, i.e., for reflection with respect to the pivot. Particles that fall into both categories are considered only once. While the first particle i is always moved, subsequent particles j are added to the cluster with a probability $p_{ij} = \max[1 - \exp(-\beta\Delta_{ij}), 0]$, where $\Delta_{ij} = V(|\mathbf{r}_i' - \mathbf{r}_j|) - V(|\mathbf{r}_i - \mathbf{r}_j|)$ and $\beta = 1/k_B T$. Thus, the cluster addition probability for particle j depends *solely* on the energy difference corresponding to a change in relative position of i and j. Other energy differences resulting from a move of particle j are not taken into account, which distinguishes this method from a standard Metropolis algorithm with multiple-particle moves and makes it the analog of the Wolff cluster algorithm. Instead, the procedure is carried out iteratively. If particle j is added to the cluster, then all its interacting neighbors [both in category (a) and in category (b)] that have not yet been added to the cluster are considered for inclusion as well. The cluster construction is completed once all interacting neighbors have been considered.

A particle j in category (a) that is added to the cluster can be viewed as "moving with" particle i; a particle j in category (b) is then interpreted as "moving from" particle i in its new position. However, in either case particles i and j maintain their original separation. The system evolves by virtue of the particles that are *not* included in the cluster. Again, this is analogous to a spin cluster algorithm, in which all spins within a given cluster maintain their relative orientation. In the limit of a pure hard-core repulsion, category (a) particles do not exist and the addition probability for category (b) particles is unity. Thus, the original GCA [12] indeed constitutes a special case of the generalized GCA.

The ergodicity of this algorithm follows from the fact that there is a nonvanishing probability that a cluster consists of only one particle, which can be moved over an arbitrarily small distance, since the location of the pivot is chosen at random. Despite the presence of a variable addition probability and the existence of two categories of particle moves, the proof of detailed balance proceeds in a similar way as for the Wolff algorithm [4]. In the transition from a given configuration X (energy E_X) to a new configuration Y (energy E_Y), an energy change is induced by every interacting particle that is *not* added to the cluster. The probability of such a "broken bond" k is given by $1 - p_k$, which is unity if the *pair energy* decreases. This is the analog of a pair of antiparallel spins in a lattice cluster algorithm. For an *increase* in pair energy Δ_k, the probability of breaking a bond is $\exp(-\beta\Delta_k)$. Accordingly, the creation of a certain cluster corresponds to breaking a number of bonds, which has a probability

$$T(X \to Y) = C\prod_k (1 - p_k) = C\exp\left[-\beta\sum_l \Delta_l\right], \quad (1)$$

where the product runs over the set $\{k\}$ of all broken bonds, which is comprised of the subset $\{l\}$ of broken bonds l that lead to an increase in pair energy and the

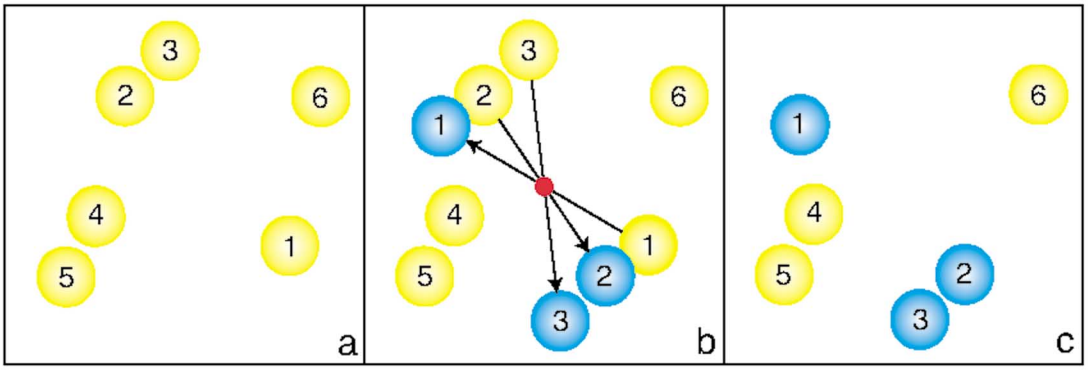

FIG. 1 (color online). Two-dimensional illustration of the interacting geometric cluster algorithm. Light and dark colors label the particles before and after the geometrical operation, respectively. The small disk denotes the pivot. (a) Initial configuration; (b) construction of a new cluster via point reflection of particles 1–3 with respect to the pivot; (c) final configuration.

subset $\{m\}$ of broken bonds that lead to a decrease in pair energy. The factor C accounts for the probability of creating a specific arrangement of bonds inside the cluster. The probability for the reverse move runs over the same set $\{k\}$, but all energy differences have changed sign (indicated by $\bar{p}$) and the sum over Δ_l is replaced by the negative sum over the complementary set $\{m\}$,

$$T(Y \to X) = C\prod_k (1 - \bar{p}_k) = C\exp\left[+\beta\sum_m \Delta_m\right]. \quad (2)$$

The probability of picking a specific particle as the starting point for this cluster is identical in the forward and the reverse move. Moreover, we require the geometric operation to be self-inverse. For clusters thus constructed, we then indeed have succeeded in fulfilling detailed balance while maintaining an acceptance ratio of unity:

$$\frac{T(X \to Y)}{T(Y \to X)} = \exp\left[-\beta\sum_k \Delta_k\right] = \frac{\exp(-\beta E_Y)}{\exp(-\beta E_X)}. \quad (3)$$

Figure 2 illustrates the agreement between the generalized GCA and a conventional NVT molecular dynamics simulation for a binary Lennard-Jones mixture containing 800 small and 400 large particles at a total packing fraction $\eta \approx 0.213$. The respective particle diameters are $\sigma_{11} = 1.0$ and $\sigma_{22} = 5.0$ and the interaction strengths equal $\varepsilon_{11} = 0.40$ and $\varepsilon_{22} = 0.225$, supplemented by the Lorentz-Berthelot mixing rules [2]. The particles are contained in a cubic cell with periodic boundary conditions. All interactions are cut off at $3\sigma_{22}$. Evidently, the GCA is capable of handling soft-core potentials.

The true advantage of the generalized GCA transpires upon consideration of its efficiency. As a simple model system with intrinsically slow dynamics, we again consider a binary fluid mixture of N_1 small and N_2 large spherical particles with size ratio $\alpha \equiv \sigma_{22}/\sigma_{11} \geq 1$. The particles are contained in a fixed volume, at equal packing fractions $\eta_1 = \eta_2 = 0.1$. N_2 is fixed at 150 and N_1 increases from 1200 to 506 250 as α is varied from 2 to 15. While pairs of small particles, as well as pairs involving a large and a small particle, act like hard spheres, the large particles have a Yukawa repulsion,

$$U_{22}(r) = \begin{cases} +\infty & r \leq \sigma_{22} \\ J\exp[-\kappa(r - \sigma_{22})]/(r/\sigma_{22}) & r > \sigma_{22}, \end{cases} \quad (4)$$

where $\beta J = 3.0$ and the screening length $\kappa^{-1} = \sigma_{11}$. The Hamiltonian describing the system is given by the sum over all pair interactions. As a measure of efficiency we consider the integrated autocorrelation time τ for the energy [18]. For conventional MC calculations, τ rapidly increases with increasing α, because large particles tend to get trapped by particles belonging to the smaller species (this situation will further deteriorate in the presence of an attraction between large and small particles). Indeed, for $\alpha > 7$ it was not even feasible to accurately estimate τ within a reasonable amount of CPU time. By contrast, the generalized GCA has an autocorrelation time that only weakly depends on the size ratio, as illustrated in Fig. 3. At $\alpha = 7$ the resulting efficiency gain already amounts to more than 3 orders of magnitude.

To explore the performance of our algorithm near a critical point, we have simulated the one-component Lennard-Jones fluid with a potential cutoff $r_c = 2.5\sigma$ at $T^* = k_B T/\varepsilon = 1.19$ and $\rho^* = \rho\sigma^3 = 0.3197$, very close to criticality [19]. The energy autocorrelation time τ exhibits a power-law dependence on the linear system size L for local moves as well as cluster moves; see Fig. 4. Since the density is a conserved quantity,

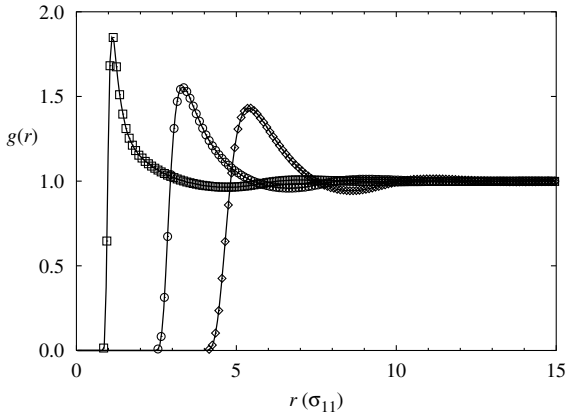

FIG. 2. Comparison between a conventional molecular dynamics calculation (solid lines) and the geometric cluster algorithm (symbols), for a size-asymmetric binary Lennard-Jones mixture. Shown are, from left to right, the correlation functions for small-small, large-small, and large-large pairs. The agreement is clearly excellent.

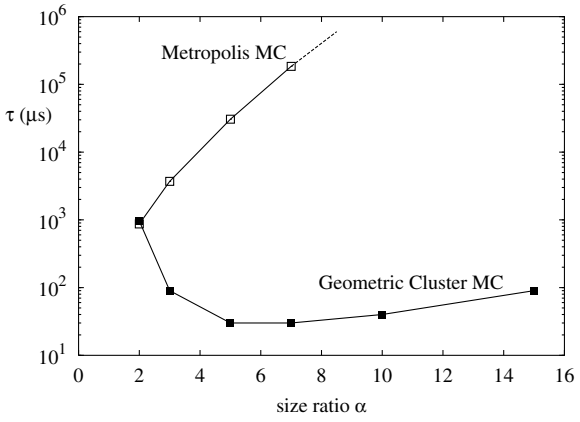

FIG. 3. Efficiency comparison between a conventional local update algorithm (open symbols) and the generalized geometric cluster algorithm (solid symbols), for a size-asymmetric binary mixture of Yukawa particles. As opposed to the local algorithm, the autocorrelation time per particle (expressed in microseconds of CPU time) for the GCA depends only weakly on size ratio α (variations correspond to changes in the volume ratio of large vs small particles in the cluster), resulting in an efficiency improvement of several orders of magnitude already for moderate α.

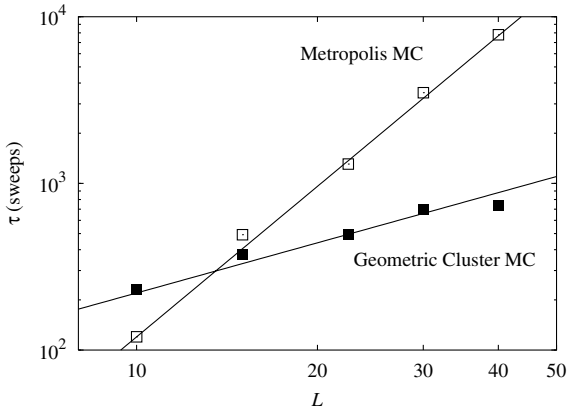

FIG. 4. Energy autocorrelation times τ vs linear system size for a critical Lennard-Jones fluid, in units of particle sweeps.

hydrodynamic slowing down must be anticipated [20]. Owing to field mixing [21], this will also manifest itself in the critical energy correlations. Thus, the acceleration $\sim L^{2.1}$ achieved by the GCA cannot unequivocally be ascribed to the (partial) suppression of critical slowing down. This is consistent with the observation that the average relative cluster size grows faster than $L^{\gamma/\nu}$. Given the number of factors that determine the cluster-growth process, care must be taken to generalize these observations to the performance of the GCA at the critical point of other fluids.

Suppression of critical slowing down is the primary benefit of cluster algorithms for lattice systems, making it a crucial requirement that the percolation threshold of the cluster-formation process coincides with the critical point. The generalized GCA, on the other hand, addresses a much larger class of problems by accelerating fluid simulations over a wide range of temperatures and packing fractions. Its essential limitation is that the clusters must occupy only part of the system. The average cluster size depends not only on the interaction strength, but also on the total packing fraction and size and shape of all constituents. Although no unique percolation threshold can be defined in a continuum system of interacting particles, we have observed that the average relative cluster size increases abruptly above a certain packing fraction, rapidly lowering the computational efficiency. This packing fraction depends on temperature and system properties, but $\eta \approx 0.23$–0.25 represents a typical threshold. For increasing size ratio or degree of polydispersity, we expect the window of accessible packing fractions to grow, in accordance with the increase of the percolation threshold as a function of polydispersity [22]. Indeed, for the binary mixtures of Fig. 3, the relative cluster size rapidly decreases with increasing α at fixed total packing fraction.

In summary, we have introduced the first general rejection-free cluster algorithm for off-lattice systems. Its premier significance lies in a performance increase of many orders of magnitude for complex fluids in which the constituents exhibit a large size asymmetry, thus enabling the simulation of mixtures that were hitherto accessible only via an effective one-component approach. Size ratios up to 100 have been reached in simulations involving several millions of particles. Our approach can be extended in several ways, including the treatment of nonspherical particles and electrostatic interactions.

This material is based upon work supported by the U.S. Department of Energy, Division of Materials Sciences under grant No. DEFG02-91ER45439, through the Frederick Seitz Materials Research Laboratory at the University of Illinois at Urbana-Champaign, and by the STC Program of the National Science Foundation under Agreement No. CTS-0120978.

*Corresponding author.
Email address: luijten@uiuc.edu

[1] *The Monte Carlo Method in Condensed Matter Physics*, edited by K. Binder, Topics in Applied Physics Vol. 71 (Springer, Berlin, 1992).
[2] M. P. Allen and D. J. Tildesley, *Computer Simulations of Liquids* (Clarendon, Oxford, 1987).
[3] R. H. Swendsen and J.-S. Wang, Phys. Rev. Lett. **58**, 86 (1987).
[4] U. Wolff, Phys. Rev. Lett. **62**, 361 (1989).
[5] C. M. Fortuin and P. W. Kasteleyn, Physica (Amsterdam) **57**, 536 (1972).
[6] D. Wu, D. Chandler, and B. Smit, J. Phys. Chem. **96**, 4077 (1992).
[7] A. Jaster, Physica (Amsterdam) **264A**, 134 (1999).
[8] L. Lue and L. V. Woodcock, Mol. Phys. **96**, 1435 (1999).
[9] V. Lobaskin and P. Linse, J. Chem. Phys. **111**, 4300 (1999).
[10] G. Johnson, H. Gould, J. Machta, and L. K. Chayes, Phys. Rev. Lett. **79**, 2612 (1997).
[11] R. Sun, H. Gould, J. Machta, and L. W. Chayes, Phys. Rev. E **62**, 2226 (2000).
[12] C. Dress and W. Krauth, J. Phys. A **28**, L597 (1995).
[13] A. Buhot and W. Krauth, Phys. Rev. Lett. **80**, 3787 (1998).
[14] L. Santen and W. Krauth, Nature (London) **405**, 550 (2000).
[15] J. G. Malherbe and S. Amokrane, Mol. Phys. **97**, 677 (1999).
[16] E. C. Mbamala and G. Pastore, Physica (Amsterdam) **313A**, 312 (2002).
[17] J. R. Heringa and H. W. J. Blöte, Phys. Rev. E **57**, 4976 (1998).
[18] K. Binder and E. Luijten, Phys. Rep. **344**, 179 (2001).
[19] N. B. Wilding, Phys. Rev. E **52**, 602 (1995).
[20] P. C. Hohenberg and B. I. Halperin, Rev. Mod. Phys. **49**, 435 (1977).
[21] A. D. Bruce and N. B. Wilding, Phys. Rev. Lett. **68**, 193 (1992).
[22] K. R. Mecke and A. Seyfried, Europhys. Lett. **58**, 28 (2002).