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A collective translational and rotational Monte Carlo cluster move for general pairwise interaction

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Virtual move Monte Carlo (VMMC) is a cluster algorithm which was originally developed for strongly attractive colloidal, molecular or atomistic systems in order to both approximate the collective dynamics and avoid sampling of unphysical kinetic traps. In this paper, we present the algorithm in the form, which selects the moving cluster through a wider class of virtual states, and which is applicable to general pairwise interactions, including hard-core repulsion. The newly proposed way of selecting the cluster increases the acceptance probability by up to several orders of magnitude especially for rotational moves. The results have their applications in simulations of systems interacting via anisotropic potentials both to enhance the sampling of the phase space and to approximate the dynamics.

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I. INTRODUCTION

Anisotropic particles are of increasing interest to colloidal or molecular self-assembly, because their shape is known to affect the long-range crystal structure [1]. Computer simulations using simple models of such particles are essential in understanding the microscopic origins of the forces that drive the formation of these structures. Single-particle Monte Carlo (SPMC) simulations with small displacements [2, 3] are usually used to sample the kinetically realistic parts of the phase diagram or to approximate the dynamical evolution of such systems. Alternatives are to use molecular dynamics methods, for which several suitable algorithms and packages exist [4–7], or hybrid methods of the Brownian Dynamics or Smart Monte Carlo type [8]. Monte Carlo methods, generally, provide more flexibility to introduce moves which accelerate the sampling in particular ways (for example, configuration-biased Monte Carlo of polymers [9]), or use more complicated potentials (such as hard-core repulsions combined with longer-ranged attractions). Nevertheless, single-particle displacements may not fully represent all degrees of freedom present in the system and collective motion may need to be considered. This may be the case in a system at high densities [10, 11], in conditions where strong clustering precedes the crystallization [12, 13], or in situations where stable clusters form the essential building blocks of the system [14–17]. Collective Monte Carlo moves have thus been developed both to preserve the realistic physical motion [18–20] and to alter the kinetics in order to efficiently sample the equilibrium properties [21–23]. This paper presents a way of designing local collective translational or rotational Monte Carlo moves by further developing the idea of virtual moves originally proposed by Whitlam and Geissler

[24, 25] and its symmetric version [26] systematically treated by us in Ref. 27. Such an approach may seem complicated, but its essence is merely a small modification of existing translational and rotational cluster algorithms [28, 29]. The advantage of virtual move Monte Carlo compared to other local Monte Carlo cluster algorithms [28–31] is that the particles are selected to the moving clusters according to the local forcefields. Its basis is to apply a fluctuation in the form of a Monte Carlo (MC) move map to a single (root) particle, and to statistically approximate the average region of all particles to which the fluctuation propagates. The region then represents the moving Monte Carlo cluster. Its main difference from previously proposed cluster algorithms [28, 29, 32–34] is that the move map is chosen before the particles are selected to the moving cluster and the selection is dependent on the properties of that map. The map determines the virtual states between particle pairs and defines the pairwise energy gradients, and thus the strength of the local forcefield. Here, we present a way of selecting the moving clusters throughout a wider class of virtual states which is applicable even to purely repulsive interactions. The inspiration for the generalization comes from the suggestion to extend the VMMC to hard spheres in the original paper of Whitlam and Geissler [24], from the description of the problem by enumerating the number of possible ‘avalanches’ [35], and from our formal description of VMMC published earlier in Ref. 27. For simplicity, the properties of the algorithm are tested on spherically symmetric potentials in this paper, although the main use of the algorithm remains in dynamically realistic simulations of anisotropically interacting particles in those cases for which satisfactory molecular dynamics algorithms are not available.

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II. DEFINITIONS

In what follows, the algorithm is illustrated and tested on a system \mathcal{S} of N interacting particles, with states being defined by the N position and orientation vectors of the particles. The interaction between particles is defined by a pairwise potential with a cutoff distance r_c . In common with other theories describing interacting systems, particle pairs are denoted (i, j) , where i and j denote two different particles in \mathcal{S} . We say that the pair (i, j) *interacts*, if particles i and j are separated by less than r_c . We shall assume that the aim is to sample the Boltzmann distribution of states, with probability $\propto \exp(-\beta E)$, where $\beta = 1/k_B T$, T being the temperature and k_B Boltzmann's constant. The pairwise energy interaction of (i, j) is denoted as ϵ_{ij} and depends on the pair separation.

Throughout the text, μ and ν denote two different states of \mathcal{S} , and E_μ and E_ν their respective energies. Since VMMC is a single-cluster algorithm [36], we shall assume that μ and ν differ by the positions of a single group of particles, to be specified later: we describe this motion using a *move map* M , taking the coordinates from μ to ν . We assume that the move map M , applied to a group of particles, consists of a rotation or translation. This guarantees that the pair interactions ϵ_{ij} between particles within the particle group are invariant under the map, and it also approximates the collective (semi-rigid) motion of a particle cluster that we aim to mimic. The inverse map to M is denoted M^{-1} .

It is convenient to use a special notation for different relative positions of particle pairs. This notation will also include the fact that the VMMC can be applied to anisotropic particles. Let us denote the position and orientation vector of particle i as $x = (r_i, h_i)$, and the image of x under the map M as $Mx = (Mr_i, Mh_i)$. Similarly, for particle $j \neq i$, we will use $y = (r_j, h_j)$, $My = (Mr_j, Mh_j)$. The pairwise energy of (x, y) in state μ is denoted as $\epsilon_{ij}^{(\mu)}$. We will consider four virtual states with relative positions of particle pairs denoted as follows. If (x, y) are the positions of particles in (i, j) in state μ , then (Mx, y) are the positions of (i, j) after applying M to i , with the corresponding pairwise energy $\epsilon_{i'j}^{(\mu)}$. Similarly, if (x, y) are the positions of (i, j) in μ and M is applied to j , then the positions of (i, j) are (x, My) with energy denoted as $\epsilon_{ij'}^{(\mu)}$. If (x, y) are the positions of (i, j) in ν and M^{-1} is applied to i , then the positions of (i, j) are $(M^{-1}x, y)$ with energy $\epsilon_{ij}^{(\nu)}$. Finally, if (x, y) are the positions of (i, j) in ν , and M^{-1} is applied to j , then the positions of (i, j) are $(x, M^{-1}y)$, and the energy is $\epsilon_{ij'}^{(\nu)}$.

Now, we describe in words the general process of selecting the set $\mathcal{C} \subset \mathcal{S}$ of moving particles called the *moving cluster* or simply *cluster*. In Ref. 27 we defined this process as the *free cluster selection*. The first particle of \mathcal{C} , called the root particle i_r , is chosen randomly from \mathcal{S} .

Other particles of \mathcal{C} are chosen in an iterative loop by attempting to link particles that are not yet in \mathcal{C} to the particles that are already in \mathcal{C} . The iterative loop is as follows. Take a random pair (i, j) , $i \in \mathcal{C}$, $j \notin \mathcal{C}$, to which a link has not yet been proposed. If no such pair exists, exit the iterative loop (the cluster selection is complete). If such a pair exists, link it with probability given by $p_{ij}^{(\mu)}$, which is defined below. If the link does not form, go back to the beginning of the iterative loop. If the link forms, include j into \mathcal{C} , and go back to the beginning of the iterative loop. Further details of the iterative selection procedure can be found in Ref. 27.

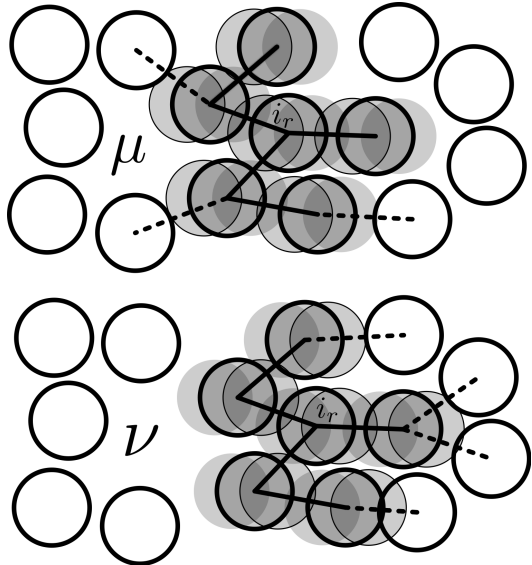


FIG. 1. Illustration of the translational virtual move Monte Carlo on a system \mathcal{S} composed of soft repulsive disks where the range of interaction r_c is determined by the radius of the disk. State ν (bottom) is created from μ (top) by applying a translational move map M to the particles in \mathcal{C} which are represented by shaded disks with thick margin. Particles in virtual states corresponding to M in μ (or M^{-1} in ν) are represented by shaded disks with no margin, and particles in virtual states corresponding to M^{-1} in μ (or M in ν) by shaded disks with thin margin. Full lines between particles represent formed links \mathcal{L} . Dashed lines are failed links defining the boundary of \mathcal{C} . There are no failed links internal to the cluster \mathcal{F} in this specific picture. As described in the main text, the cluster is selected by applying the map M to the root particle, and by iterative linking of particles to the root. From a physical perspective, this selection is a statistical approximation of the region to which the fluctuation M propagates from the root i_r .

The linking probabilities are defined as follows. Given a move map M , the probability that a link forms between (i, j) is given by

$$p_{ij}^{(\mu)} = 1 - \Phi \left(\Delta\epsilon_{ij}^{(\mu)}, \Delta\epsilon_{ij'}^{(\mu)} \right), \quad (1)$$

where $\Delta\epsilon_{ij}^{(\mu)} = \epsilon_{i'j}^{(\mu)} - \epsilon_{ij}^{(\mu)}$ is the energy gradient associated

with the virtual move of i in μ , and $\Delta\epsilon_{ij'}^{(\mu)} = \epsilon_{ij'}^{(\mu)} - \epsilon_{ij}^{(\mu)}$ is the same quantity for j . The function Φ is a suitably chosen real function satisfying

$$0 < \Phi(x, y) \leq 1, \quad (2a)$$

$$\Phi(x, y) = \Phi(y, x), \quad (2b)$$

$$\Phi(0, 0) = 1, \quad (2c)$$

for all real numbers x and y . The probability that a link fails to form is defined as $q_{ij}^{(\mu)} = 1 - p_{ij}^{(\mu)}$. Similarly for the reverse move, the probability of linking a pair (i, j) in state ν under M^{-1} is defined as

$$p_{ij}^{(\nu)} = 1 - \Phi\left(\Delta\epsilon_{ij'}^{(\nu)}, \Delta\epsilon_{ij'}^{(\mu)}\right), \quad (3)$$

where $\Delta\epsilon_{ij'}^{(\nu)} = \epsilon_{ij'}^{(\nu)} - \epsilon_{ij}^{(\nu)}$, and $\Delta\epsilon_{ij'}^{(\mu)} = \epsilon_{ij'}^{(\mu)} - \epsilon_{ij}^{(\mu)}$. The corresponding link-failure probability is $q_{ij}^{(\nu)} = 1 - p_{ij}^{(\nu)}$.

III. DERIVATION

The set of all pairs to which a link is proposed during the selection of \mathcal{C} can be uniquely decomposed as $\mathcal{L} \cup \mathcal{F} \cup \mathcal{B}$. Here \mathcal{L} denotes pairs which were linked, \mathcal{F} denotes pairs which were not linked with both particles being in

\mathcal{C} , and \mathcal{B} denotes non-linked pairs (i, j) such that the first particle belongs to \mathcal{C} and the second particle is outside \mathcal{C} . The triple of sets $(\mathcal{L}, \mathcal{F}, \mathcal{B})$ represents the *realization* of the cluster \mathcal{C} , and is denoted as $R_{\mathcal{C}}$.

To derive the cluster acceptance probability, let us consider the identities

$$\left. \begin{aligned} \epsilon_{ij}^{(\mu)} &= \epsilon_{ij}^{(\nu)} \\ \epsilon_{ij'}^{(\mu)} &= \epsilon_{ij'}^{(\nu)} \\ \epsilon_{i'j}^{(\nu)} &= \epsilon_{i'j}^{(\mu)} \end{aligned} \right\} \forall (i, j) \notin \mathcal{B}, \quad (4)$$

which yield

$$\left. \begin{aligned} \Delta\epsilon_{ij'}^{(\mu)} &= \Delta\epsilon_{ij'}^{(\nu)} \\ \Delta\epsilon_{i'j}^{(\nu)} &= \Delta\epsilon_{i'j}^{(\mu)} \end{aligned} \right\} \forall (i, j) \notin \mathcal{B}, \quad (5)$$

and hence the link-formation probability relations

$$\left. \begin{aligned} p_{ij}^{(\mu)} &= p_{ij}^{(\nu)} \\ q_{ij}^{(\mu)} &= q_{ij}^{(\nu)} \end{aligned} \right\} \forall (i, j) \notin \mathcal{B}. \quad (6)$$

Equations (2) and (6) imply that if $R_{\mathcal{C}}$ has a non-zero probability in state μ , it also has a non-zero probability in state ν . We can thus require the probability of selecting and accepting $R_{\mathcal{C}}$ to be the same in states μ and ν . This is given by the superdetailed balance condition [9, 37] of the form

$$\begin{aligned} \exp(-\beta E_{\mu}) p^{(\mu)}(\{b\}) \prod_{(i,j) \in \mathcal{L}} p_{ij}^{(\mu)} \prod_{(i,j) \in \mathcal{F}} q_{ij}^{(\mu)} \prod_{(i,j) \in \mathcal{B}} q_{ij}^{(\mu)} W_{\text{acc}}^{(\mu \rightarrow \nu | R)} \\ = \exp(-\beta E_{\nu}) p^{(\nu)}(\{b\}) \prod_{(i,j) \in \mathcal{L}} p_{ij}^{(\nu)} \prod_{(i,j) \in \mathcal{F}} q_{ij}^{(\nu)} \prod_{(i,j) \in \mathcal{B}} q_{ij}^{(\nu)} W_{\text{acc}}^{(\nu \rightarrow \mu | R)}. \end{aligned} \quad (7)$$

The leftmost terms on each side are the Boltzmann weights of states μ and ν . The term $p^{(\mu)}(\{b\})$ is the probability of generating auxiliary variables $\{b\}$ in state μ . It is a product of two (or more) components

$$p^{(\mu)}(\{b\}) = p^{(\mu)}(M) p^{(\mu)}(i_r), \quad (8)$$

specifically the probabilities of selecting the move map M and the root particle i_r . The term $p^{(\nu)}(\{b\})$ on the right of Eq. (7) represents a similar product in state ν . The explicit products over links on the left of Eq. (7) combine to give the probability of constructing the specific realization $R_{\mathcal{C}}$, which is conditional upon $\{b\}$. Analogous terms for state ν appear on the right. Finally, the terms $W_{\text{acc}}^{(\mu \rightarrow \nu | R)}$ and $W_{\text{acc}}^{(\nu \rightarrow \mu | R)}$ are the acceptance probabilities that we seek. By selecting the root particles and displacements M randomly, it is easy to ensure $p^{(\mu)}(\{b\}) = p^{(\nu)}(\{b\}) > 0$. The products over \mathcal{L} and \mathcal{F} cancel out because of Eq. (6), and the fact that

$\Phi(x, y) > 0$. The SDB condition (7) can thus be simplified and the acceptance probability of moving the cluster \mathcal{C} by M can be expressed in the Metropolis-Rosenbluth form as

$$W_{\text{acc}}^{(\mu \rightarrow \nu | R)} = \min \left\{ 1, e^{-\beta(E_{\nu} - E_{\mu})} \prod_{(i,j) \in \mathcal{B}} \frac{q_{ij}^{(\nu)}}{q_{ij}^{(\mu)}} \right\}. \quad (9)$$

Proposing the links to all pairs (i, j) , $i \in \mathcal{C}$, $j \notin \mathcal{C}$, is not very efficient, because links have non-zero chance to form only if they are proposed to pairs interacting in one of the states

$$(x, y), (Mx, y), (x, My). \quad (10)$$

The essence of the generalized scheme is thus to propose the links only to pairs (i, j) , $i \in \mathcal{C}$, $j \notin \mathcal{C}$ which interact in one of the states listed in Eq. (10). This cluster selection is termed *restricted* [27], because, as will be discussed

below, it is impossible to guarantee that if $R_{\mathcal{C}}^{(\mu)}$ is a realization in μ , then there is a realization $R_{\mathcal{C}}^{(\nu)}$ in state ν , such that $R_{\mathcal{C}}^{(\nu)} = R_{\mathcal{C}}^{(\mu)}$. Table I assumes the free cluster selection and helps to identify those pairs in the restricted selection to which a link is proposed both in states μ and ν , and to which a link is proposed in only one of the states μ or ν . The table shows that, in the restricted selection, if (i, j) is a particle pair from the cluster in state μ , then the link is also proposed to that pair in state ν . However, if (i, j) is a pair from the boundary of \mathcal{C} in one of the states μ or ν , it is generally not guaranteed that (i, j) is a boundary pair in the other state. Following the terminology of Ref. 27, we can say that the realization has a symmetric core and an asymmetric boundary. In what follows, we will show that, despite this asymmetry, the cluster acceptance probability (9) can still be used, provided we distinguish between the boundaries of \mathcal{C} in states μ and ν , which we denote as $\mathcal{B}^{(\mu)}$ and $\mathcal{B}^{(\nu)}$, respectively. Let us consider the following four different cases.

First, if (i, j) is a boundary pair in μ interacting in (x, y) or in (Mx, y) , then (i, j) is a boundary pair in ν interacting in (Mx, y) or in $(M^{-1}Mx, y)$, and a link is proposed to that pair in state ν . [Since $M^{-1}M = I$, the identity map, $(M^{-1}Mx, y)$ is the same as (x, y) .]

Second, let (i, j) be a boundary pair in μ not interacting both in (x, y) and in (Mx, y) , but interacting in (x, My) . Then (i, j) is a boundary pair in ν not interacting both in (Mx, y) and in $(M^{-1}Mx, y)$, but is not necessarily interacting in $(Mx, M^{-1}y)$. The link is thus

Original state:

(x, y)
 (Mx, y)
 (x, My)

Both i and j move under M : Only i moves under M :

(Mx, My) (Mx, y)
 $(M^{-1}Mx, My)$ $(M^{-1}Mx, y)$
 $(Mx, M^{-1}My)$ $(Mx, M^{-1}y)$

TABLE I. Given a pair of particles (i, j) in state μ to which a link is to be proposed, the table lists all relative positions of (i, j) , which are considered during the free selection of \mathcal{C} both in state μ under M and in state ν under M^{-1} . The top three positions correspond to the original and two virtual states of (i, j) in state μ . The bottom three positions on the left are the original and two virtual states of (i, j) in state ν under the inverse map M^{-1} and under the assumption that both particles i and j are part of the cluster in state μ under M . The bottom three positions on the right are the original and two virtual states of (i, j) in state ν under M^{-1} , and under the assumption that (i, j) is a boundary pair of \mathcal{C} in state μ . The table shows that each relative position of (i, j) is equivalent to the relative position of (i, j) in one of the top three states, with the exception of the position $(Mx, M^{-1}y)$. These equivalences can be seen if we realize that the translational and rotational Monte Carlo move map M is an isometric operation, and that $M^{-1}M = I$ is the identity map.

not necessarily proposed to that pair in state ν . We can discuss these two cases. If such a pair is interacting in $(Mx, M^{-1}y)$, then the link is proposed to that pair in ν by definition of the restricted selection. If such a pair is not interacting in $(Mx, M^{-1}y)$, then a corresponding link is guaranteed to fail by the definition of the linking function in Eq. (3), and we can proceed as if a link is proposed to that pair although it is not.

Third, if (i, j) is a boundary pair in μ not interacting in any of the states (x, y) , (Mx, y) , (x, My) but interacting in $(Mx, M^{-1}y)$, then the link is not proposed to such a pair in state μ , but is proposed to that pair in state ν . The condition in Eq. (2c) again implies that such a pair fails to form in state μ , and we can again proceed as if a link is proposed to that pairs in state μ , although it is not. This class of pairs needs to be detected and included in the bias of the acceptance probability.

Fourth, if (i, j) is a boundary pair in μ not interacting in any of the states (x, y) , (Mx, y) , (x, My) , and $(Mx, M^{-1}y)$, then the link has no chance to form both in states μ and ν , and we can again proceed as if the link is proposed to that pair although it is not.

In summary, the above considerations show that, if the pair selection is restricted only to pairs interacting in one of the states in Eq. (10), the set of pairs in the boundary of the cluster to which a link is proposed during the cluster selection is not the same in states μ and ν . It is shown that the asymmetry does not violate the SDB condition in Eq. (7), and the method can proceed as if free cluster selection had been used, even though the restricted selection is used in the algorithm.

IV. LINKING FUNCTIONS

We now consider two specific choices of the linking function Φ defined in Eq. (2). Firstly we consider the case

$$\Phi \left(\Delta\epsilon_{i'j}^{(\mu)}, \Delta\epsilon_{ij'}^{(\mu)} \right) = \min \left\{ 1, \exp \left(-\beta \min \left\{ \Delta\epsilon_{i'j}^{(\mu)}, \Delta\epsilon_{ij'}^{(\mu)} \right\} \right) \right\}, \quad (11)$$

which as shown later is equivalent to the linking in the original symmetrized scheme [26, 27]. The form (11) is such that if (i, j) is non-interacting in (x, y) and (Mx, y) , then $q_{ij}^{(\mu)} = q_{ij'}^{(\nu)} = 1$. Thus when selecting the particles to \mathcal{C} , it is enough to consider only pairs (i, j) interacting in (x, y) or in (Mx, y) , and omit pairs interacting in (x, My) or in $(Mx, M^{-1}y)$. This speeds up the simulation, because fewer nearest neighbors need to be taken into account when using cell lists for the nearest neighbour search. A drawback of the choice (11) is that no clusters are formed in systems with purely repulsive potentials.

The second possible choice of Φ discussed here is

$$\Phi \left(\Delta \epsilon_{i'j}^{(\mu)}, \Delta \epsilon_{ij'}^{(\mu)} \right) = \min \left\{ 1, \exp \left(-\beta \max \left\{ \Delta \epsilon_{i'j}^{(\mu)}, \Delta \epsilon_{ij'}^{(\mu)} \right\} \right) \right\}, \quad (12)$$

which as opposed to (11) forms clusters not only in systems with attractive but also in systems with purely repulsive potentials. In the particular case of hard spheres or disks, any pair (i, j) , which interacts in one of the states (Mx, y) or (x, My) is linked.

V. SUMMARY OF THE ALGORITHM

The selection of the moving cluster is analogous to the iterative selection in conventional single-cluster algorithms [24, 28, 29, 32], and was described in detail by us in Ref. 27. These algorithms select the particles to the moving cluster by considering only those particle pairs which interact in the original state (x, y) . The present algorithm considers not only pairs interacting in (x, y) , but also pairs interacting in one of the virtual states (Mx, y) or (x, My) . Another difference is that a more complex form of the probability linking the particles to the moving cluster is used. The cluster move of this paper can be summarized as follows:

1. Pick a random particle, and use it as the first (root) particle of the cluster \mathcal{C} . Choose the map M randomly.
2. Perform the iterative loop selecting all other particles to \mathcal{C} .
 - (a) Pick a random pair (i, j) , $i \in \mathcal{C}$, $j \notin \mathcal{C}$, which interacts in one of the states (x, y) , (Mx, y) , (x, My) , and to which a link has not yet been proposed. If no such pair exists, finish the cluster selection by exiting the iterative loop.
 - (b) Attempt to create a link between (i, j) with probability defined by Eq. (1).
 - (c) If the link forms, mark (i, j) as a formed link, include j into \mathcal{C} and go to (a).
 - (d) If the link does not form, mark (i, j) as a failed link (pair), go to (a).
3. Identify the boundary $\mathcal{B}^{(\mu)}$ as those pairs to which a link was proposed, but failed to form. By definition, they include pairs (i, j) , $i \in \mathcal{C}$, $j \notin \mathcal{C}$, which interact in at least one of the states (x, y) , (Mx, y) or in (x, My) .
4. Identify the boundary $\mathcal{B}^{(\nu)}$ as the set of all pairs (i, j) in state μ , such that $i \in \mathcal{C}$, $j \notin \mathcal{C}$, and such that they interact in (x, y) , (Mx, y) or in $(Mx, M^{-1}y)$.

5. Accept the cluster move with probability

$$W_{\text{acc}}^{(\mu \rightarrow \nu | R)} = \min \left\{ 1, e^{-\beta(E_\nu - E_\mu)} \frac{\prod_{(i,j) \in \mathcal{B}^{(\nu)}} q_{ij}^{(\nu)}}{\prod_{(i,j) \in \mathcal{B}^{(\mu)}} q_{ij}^{(\mu)}} \right\}. \quad (13)$$

VI. EARLY REJECTION SCHEME

Let us show that the choice of Φ in (11) is equivalent to the early rejection scheme proposed by Whitelam and Geissler [25] and summarized by us in Ref. 27. The links form as follows. Let (i, j) be a pair to which a link is to be proposed. We define the pre-link formation probabilities in state μ as

$$p_{i'j}^{(\mu)} = \max \left\{ 0, 1 - \exp \left(-\beta \Delta \epsilon_{i'j}^{(\mu)} \right) \right\}, \quad (14)$$

$$p_{ij'}^{(\mu)} = \max \left\{ 0, 1 - \exp \left(-\beta \Delta \epsilon_{ij'}^{(\mu)} \right) \right\}. \quad (15)$$

The link then forms in two random tests. The first test represents the link formation under the forward move and its success is merely given by $p_{i'j}^{(\mu)}$. The second test aims to ensure balance of the link formation and is successful with probability $\min\{1, p_{i'j}^{(\mu)}/p_{ij'}^{(\mu)}\}$. The link between (i, j) then forms only if both tests are successful, i.e.

$$p_{ij}^{(\mu)} = \text{Prob} \left\{ X_1 < p_{i'j}^{(\mu)}; X_2 < \min(1, p_{i'j}^{(\mu)}/p_{ij'}^{(\mu)}) \right\}, \quad (16)$$

where X_1, X_2 are two random numbers drawn from the uniform distribution $\mathcal{U}(0, 1)$. If the first test fails (i, j) is marked as *outright* failed independently of the outcome of the second test. If the first test succeeds and the second test fails (i, j) is marked as *frustrated*. The cluster is selected in an iterative loop analogous to that described above. We have shown [27] that the cluster is accepted whenever the boundary of the cluster only contains outright failed links and is rejected otherwise.

Let us now show that the linking probability defined in Eq. (11) is equal to that defined in Eq. (16) for the early rejection scheme. We express the linking probability in Eq. (16) as

$$p_{ij}^{(\mu)} = p_{i'j}^{(\mu)} \min \left\{ 1, \frac{p_{i'j}^{(\mu)}}{p_{ij'}^{(\mu)}} \right\} = \min \left\{ p_{i'j}^{(\mu)}, p_{ij'}^{(\mu)} \right\}. \quad (17)$$

By using definitions (14), (15) and the relation

$$\begin{aligned} & \min \left\{ \max [0, 1 - e^x], \max [0, 1 - e^y] \right\} \\ &= \min \left\{ 1 - e^{\min[0, x]}, 1 - e^{\min[0, y]} \right\} \\ &= 1 - \max \left\{ e^{\min[0, x]}, e^{\min[0, y]} \right\} \\ &= 1 - e^{\max\{\min[0, x], \min[0, y]\}} = 1 - e^{\min\{0, \max[x, y]\}} \\ &= 1 - \min \left\{ 1, e^{\max[x, y]} \right\} = 1 - \min \left\{ 1, e^{-\min[-x, -y]} \right\}, \end{aligned} \quad (18)$$

valid for all real numbers x, y , this leads to

$$p_{ij}^{(\mu)} = 1 - \min \left\{ 1, \exp \left(-\beta \min \left\{ \Delta\epsilon_{ij}^{(\mu)}, \Delta\epsilon_{ij'}^{(\mu)} \right\} \right) \right\}, \quad (19)$$

which is identical to $p_{ij}^{(\mu)}$ defined by (1) and (11).

The early rejection scheme can also be formulated for hard particles. In such an algorithm, the links are proposed to all pairs interacting in one of the states (x, y) , (Mx, y) , (x, My) , or $(Mx, M^{-1}y)$. With the aid of Eq. (12), the rule for linking can be formulated as follows. Form a link if (i, j) overlaps (is interacting) in one of the states (Mx, y) or (x, My) . If (i, j) does not overlap in (Mx, y) , (x, My) and in $(Mx, M^{-1}y)$, label it as outright failed. If (i, j) does not overlap in (Mx, y) , (x, My) but overlaps in $(Mx, M^{-1}y)$, label it as frustrated. Accept the cluster, if boundary \mathcal{B} is only composed of outright failed links. Reject the cluster, if there is a frustrated link in \mathcal{B} . We tested the validity of this algorithm by comparing the radial distribution functions obtained from VMMC and SPMC simulations in a 3D hard sphere fluid in the NpT -ensemble with pressure $p = 10$ and number of particles $N = 1152$. These results are unpublished.

VII. RESULTS

To test the algorithm summarized in Sec. V and in the Appendix, we use a system of spherical particles interacting via the potential

$$V(r) = A \frac{e^{-r/\xi}}{r/\xi} + 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{2\alpha} - \left(\frac{\sigma}{r} \right)^\alpha \right] - V_c, \quad (20)$$

where the first term in the sum is the long-range Yukawa repulsion, and the second term is the short-range generalized Lennard-Jones attraction [38]. The potential is truncated and shifted at a cut-off distance r_c , with the constant V_c chosen such that $V(r_c) = 0$. We use the canonical ensemble with fixed number of particles N , volume V , and temperature T . We take $N = 2000$ and $\sigma = 1.0$. The screening length is chosen as $\xi = 2.0$ and the range of the attraction as $\alpha = 18$. Other parameters are specifically chosen for the simulations of the fluid and for the simulations of the transient or stabilized clusters.

A. Simulations of a fluid

To simulate the fluid, we use the potential in Eq. (20), but we set $A = 0$, which leaves us with only the attractive part of the potential. We use $T = 0.6$, $\epsilon = 1.0$, packing fraction $\phi = \pi/6 \cdot N/V = 0.225$, and cutoff $r_c = 1.8\sigma$. These conditions are known to correspond to the fluid phase [38]. We use either SPMC or VMMC simulations. The length of the simulations is 10^6 MC sweeps. An SPMC sweep consists of N translations with maximum translational displacement $\delta = 0.02\sigma$ applied to each particle in \mathcal{S} . A VMMC sweep consists of N virtual moves

with the same maximum displacement size, applied to random particles. The VMMC simulations are such that they only contain translations or rotations. We also perform the VMMC simulations which only form the moving clusters via either of the linking schemes defined in Eqs. (11) or (12). For each such choice of the parameters we perform ten independent simulations, which start from different well equilibrated states.

Figure 2(a) shows the radial distribution functions from the SPMC simulations and from the VMMC simulations, which only contain translational displacements and linking defined in Eq. (12). The functions are within the error range of each other, which is a necessary (not sufficient [27]) requirement for the validity of the VMMC. Figure 2(b) shows the time evolution of the single-particle mean square displacement (MSD). Although the time measured in the number of MC sweeps is non-physical, the gradient of the MSD displacement is interpreted as the diffusion constant. The diffusion under the VMMC using the original form of linking in Eq. (11) is comparable to the diffusion under the SPMC. This is a consequence of link formation via attractive interactions, and of our temperature choice, which results in a relatively weak strength of attraction. Interestingly, diffusion in the VMMC is slightly lower than in the SPMC, despite the fact that more particles are attempted to be moved in the VMMC cycle.

The MSD grows twice as fast for the linking in Eq. (12) than for the linking in Eq. (11). Higher diffusion for linking in Eq. (12) is a consequence of stronger linking via the repulsive interactions given by another form of the linking function.

Similarly to what we have reported previously in Ref. 27, particles under the rotational VMMC diffuse much slower than particles under the translational VMMC. Again, diffusion is larger when linking via Eq. (12) is used.

B. Simulations of transient clusters

It is known that the system of particles with short-range attraction and long-range repulsion forms phases of stable, meta-stable, or transient clusters [14–17, 39, 40]. To test the VMMC we use the potentials in Eq. (20), with parameters $A = 0.60$, $T = 0.25$, $\epsilon = 2.0$, $\phi = 0.01$, and $r_c = 3.0$. The inset of Fig. 3 shows that the equilibrium state of such system is characterized by small isolated drops. We perform SPMC and VMMC simulations with length 10^7 sweeps, maximum displacement $\delta = 0.20\sigma$, and with various initial equilibrated states. The VMMC simulations contain 50% translational and 50% rotational moves with rotational parameters identical to those of Ref. 27. For each cluster, the cluster size is also restricted by an upper limit N_C , taken as $1/x$, where x is a random number from the uniform distribution $\mathcal{U}(0, 1)$. This modification of VMMC is described in more detail in the Appendix and in Ref. 27.

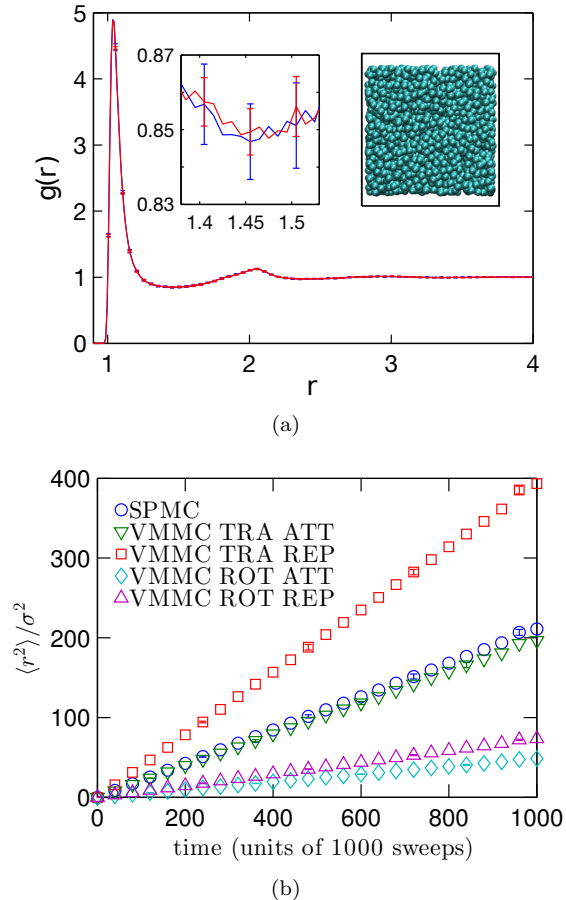


FIG. 2. (Color online) Tests of the algorithm. (a) Radial distribution functions from the single-particle MC (blue) and the collective VMMC (red). The VMMC moves use the repulsive linking of Eq. (12). Insets: Magnification of the first minimum in $g(r)$, and a snapshot of equilibrium configuration. (b) Mean square displacement versus time measured in 1000 MC sweeps. The VMMC either contains only rotations (ROT) or only translations (TRA), and the linking is either only attractive (ATT) or only repulsive (REP) following Eqs. (11) and (12), respectively.

We observe that the small drops shown in Fig. 3 are meta-stable (transient), i.e. they exchange particles, and constantly rearrange, dissolve, and nucleate on the timescale of our simulations. Such properties are suitable to compare VMMC with SPMC. The results are shown in Fig. 3. The exact match between the radial distribution functions is a necessary requirement for the validity of the VMMC algorithms, providing numerical evidence which is much stronger than that of Fig. 2 or in Ref. 27. This is because the movement of clusters of size about ten particles is comparable to single-particle motion in the VMMC simulations in either type of linking given by Eqs. (11) and (12).

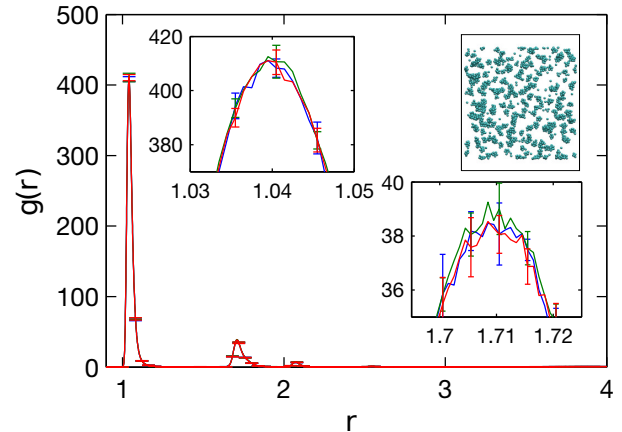


FIG. 3. (Color online) More rigorous tests of VMMC are performed on an equilibrium fluid with transient clusters. They compare the radial distribution functions from SPMC (blue) and VMMC with linking functions in Eqs. (11) and (12) (green and red). Insets: Magnification of the first and second maximum in $g(r)$ and a snapshot of equilibrium configuration. The error bars are over ten independent simulations.

C. Simulations of stabilized clusters

In what follows, we use a non-equilibrium system to show that the simulation of repulsive interactions via linking in Eq. (12) plays a key role in the generation of rotational VMMC moves. We use the same potentials and simulation parameters as in the previous section, except that the repulsion and attractions are weaker ($A = 0.08$, $\epsilon = 1.0$), allowing to form larger aggregates. We rapidly quench the system from a fluid phase to the temperature $T = 0.25$. We let the system evolve until it phase separates into several isolated aggregates. These aggregates keep growing very slowly during the course of the simulation and equilibrium size is not reached, suggesting that gas-crystal coexistence may be the thermodynamically stable state of the system.

Figure 4 shows the time evolution of the MSD, which is measured immediately from the start of the simulation, with no averaging over time origins. Similarly to what we discussed for this system in Ref. 27, the difference between SPMC and VMMC with attractive linking (11) is not large, due to weak attractive bonds leading to the VMMC dynamics being dominated by single-particle motion. The difference from the SPMC becomes larger when links are formed by Eq. (12) simulating collective motion resulting from repulsive interactions.

We also analyze the time evolution of the fraction of cluster moves which are generated and accepted depending on the cluster size. Let $N_g(n_c)$ be the average number of all generated clusters of size n_c . Similarly, $N_a(n_c)$ is the average number of all accepted clusters of size n_c . The average is taken over several (typically ten) independent simulations and a specified time. We study the

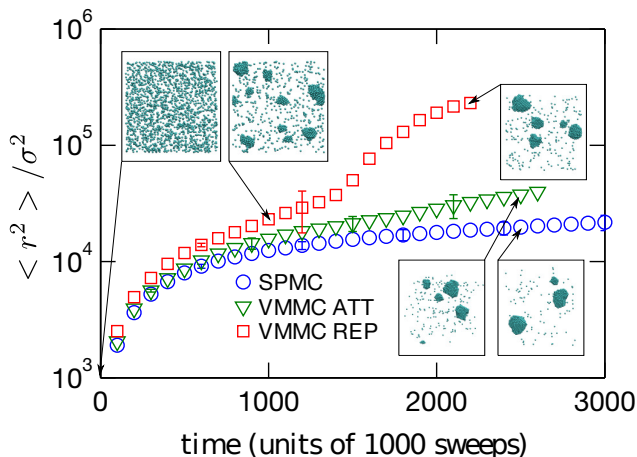


FIG. 4. (Color online) Mean square displacement versus time for short-range attractive and long-range repulsive fluid measured from the quench to $T = 0.25$. All error bars are estimated from 10 independent simulations. Insets show example snapshots of the system at different stages of the simulation including the initial state.

probability density of generating a cluster of size n_c defined as $f_g(n_c) = N_g(n_c) / \sum_{n_c=1}^N N_g(n_c)$, and the ratio of accepted versus proposed clusters $N_a(n_c) / N_g(n_c)$. Both linking options in Eqs. (11) and (12) are taken into account, with maximum displacement $\delta = 0.20\sigma$ in both cases. Figure 5 shows that linking the particles through the function in Eq. (12) increases the proportion of accepted moves both for rotations and translations, and that the fraction of accepted rotational moves is about two orders of magnitude higher for large clusters. Such an enhancement of acceptance probability is an example, where linking defined in Eq. (12) performs much better than the original VMMC algorithm. We note that the increase of acceptance probability is dependent on the system parameters, and that only a small increase was observed for the transient clusters studied in the previous section (not shown).

VIII. DISCUSSION

The original aim of the VMMC simulation was to approximate the dynamics in short-range attractive systems with overdamped dynamics. Particles were selected to the moving cluster according to the local energy gradients; however, the links created with Eq. (11) have a chance to form only for the specific energetic situation, such that $\Delta\epsilon_{i'j}^{(\mu)} > 0$ and $\Delta\epsilon_{ij'}^{(\mu)} > 0$. In other situations, such as $\Delta\epsilon_{i'j}^{(\mu)} > 0$ and $\Delta\epsilon_{ij'}^{(\mu)} = 0$, the links do not form, although they should form. The new way of linking the particles defined in this paper by Eq. (12) solves this problem, but can also include to the cluster

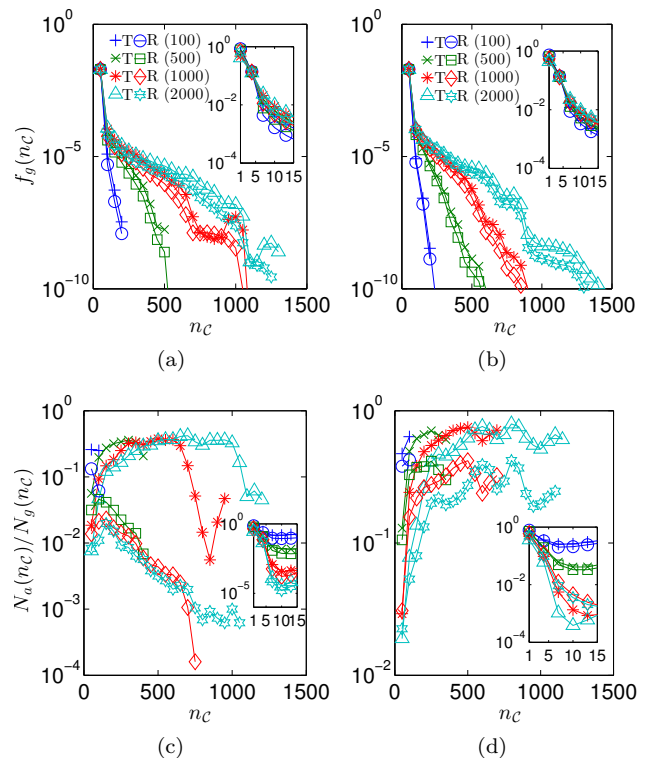


FIG. 5. (Color online) Probabilities of generating and accepting a moving cluster of size n_c at different time windows of the simulation showing that the acceptance probability of rotations is up to three orders of magnitude higher when the alternative linking is used to select the cluster. (a) generating density $f_g(n_c)$ for the attractive linking given by Eq. (11). (b) generating density $f_g(n_c)$ for the repulsive linking given by Eq. (12). (c) and (d) show acceptance ratio $N_a(n_c)/N_g(n_c)$ corresponding to (a) and (b), respectively. Symbols corresponding to translations (T) and rotations (R), together with the upper limit of the time window (in MC sweeps) are given in the legend. The same color refers to the same time window. The symbols represent arithmetic averages over a cluster size window with radius equal to the distance between the symbols. Error bars can reach several orders of magnitude, and are not displayed. Insets are magnifications for small moving clusters.

those particles of the system which would have not been linked in the classical mechanical picture. An example of such mechanically unrealistic linking is a particle pair with $\Delta\epsilon_{i'j}^{(\mu)} = 0$ and $\Delta\epsilon_{ij'}^{(\mu)} > 0$. The linking defined in Eq. (12) thus generates a different collection of moving clusters, which are kinetically realistic, but may be generated according to unphysical local energy gradients, or gradients which are unlikely. In contrast, the clusters selected by the original linking in Eq. (11) are closer to the realistic gradients, but capture only a certain class of possible physical collective motions. It can be expected that other functions Φ , satisfying conditions (2), lead to different classes of kinetically realistic moving clusters, which may or may not be selected according to realistic local energetics. It is possible to have a set of functions

satisfying conditions (2), and use them randomly according to a certain distribution in order to select and accept moving clusters with a rich range of topologies. A simple example of such a multifunctional VMMC, is to take the function in Eq. (11) with probability 1/2, and the function in Eq. (12) with probability 1/2. Such a simulation clearly still samples from the Boltzmann distribution. The combination of a wider class of linking functions is expected to provide a richer spectrum of moving cluster topologies, thus enhancing the relaxation.

Considering different functions Φ satisfying conditions (2) may not be the only way of achieving a realistic dynamics. In fact, condition (2b) significantly reduces the generation of realistic dynamical clusters, and even makes it impossible, because a link formed under the gradient $\Delta\epsilon_{ij}^{(\mu)} < 0$ should normally form with a different probability than a link under the gradient $\Delta\epsilon_{ij'}^{(\mu)} > 0$, or *vice versa*. Although the condition (2b) greatly simplifies the acceptance probability, because it guarantees the equality between the link formation probabilities in Eq. (6), it seems better to return to the original formulation of the VMMC [24], for which $p_{ij}^{(\mu)}$ is not necessarily equal to $p_{ij'}^{(\nu)}$ for pairs in the cluster. In such a scheme, the linking probabilities would have to be chosen carefully according to a real physical picture, the links would be proposed not only to pairs interacting in state μ as was done originally [24], but to any pairs interacting in one of the states in (10) as is discussed in this paper. This way of linking may result in a fully generalized VMMC, and is outside the scope of this paper.

One may argue that proposing links to pairs interacting in (x, My) may not be needed in systems such as purely repulsive particles. However, there are still physical reasons to consider these interactions. If the system is suspended in a liquid, this interaction may result from hydrodynamic forces. In an ideal hard sphere system, the force may be thought of as an entropic force. Clearly, a particle pair interacting in (x, My) should not be linked with probability one, but with a lower probability, which is why the omission of condition (2b) is necessary. Related to this, it worth noticing that proposing links to pairs interacting in (x, My) offers a workaround to the problem with enumerating the number of possible ‘avalanches’, which are simply possible ways of selecting the cluster via a movement of a single-particle by map M [35]. The number of these avalanches is generally not the same under the forward and under the reverse move, which is why proposing links to pairs interacting in (Mx, y) and ignoring those in (x, My) is not sufficient, and violates detailed balance as also discussed for hard disks by Krauth [35].

The implementation of VMMC may seem complicated, but its essence is only a small modification of the static cluster algorithm [29, 30]. The main technical difference is in the nearest neighbors search, i.e. search of particles which are considered for linking to the moving cluster. Contrary to the static algorithm, where particle pairs

interacting only in (x, y) are considered to the moving cluster, the VMMC requires to verify whether pairs interact in (Mx, y) or in (x, My) . [Or equivalently, verify whether $(x, M^{-1}y)$ or (x, My) interact.] If a cell list is used, this can be done if all particles in the cell, which are not yet part of the cluster, are moved by M and M^{-1} with respect to their original state with new position and orientation vectors being stored. These vectors then also determine the boundary, i.e. all pairs $i \in \mathcal{C}$, $j \notin \mathcal{C}$ interacting in $(Mx, M^{-1}y)$. The cells must be larger. In cubic cells the size of the cell is $r_c + 2\delta$ in the VMMC compared to r_c in SPMC or in the static cluster algorithm. Recall that r_c denotes the cutoff distance or the maximum dimension of the particle. If rotational moves are part of the simulation, and r_c is the maximum rotational displacement [27], the size of the cell is $3r_c$. We also emphasize that one should not expect difficulties for anisotropically interacting potentials. If an SPMC for anisotropic and a VMMC for spherically symmetric particles are available, extension of the VMMC is straightforward, because the routine determining the pairwise energy between particles with a given orientation and position is already present in the SPMC.

Now, we briefly comment on general and other technical aspects of the VMMC. First, the superdetailed balance condition should allow one to distinguish between straight and reflected moves [19] even when selecting clusters in the VMMC. If reflection is used during the linking, the displacement M does not remain constant during the iterative selection of the cluster, and changes according to the symmetry axis of pair collisions. The VMMC move might then become even more versatile and realistic. Second, rotations and translations are isometric operations, and the isometric property is essential for simplifying the acceptance probability. Since the reflection operation is also an isometry, we may expect to use the ideas of those paper to derive algorithms which incorporate the reflection operation for anisotropic particles [22, 23]. Third, collective moves of hard particles may sometimes lead to overlaps caused by the numerical precision. These overlaps need to be accounted for and corrected. Fourth, a disadvantage of the single-cluster MC algorithms is that parallelization is not straightforward, because the size of the moving cluster is not known at the outset, and may span the entire system. A possible way of parallelizing the VMMC may follow the approach by Kaupužs *et al.* [41], designed for the Wolff cluster algorithm for lattice spin systems. Their parallelization does not separate the lattice into domains, but different threads are assigned to different pairs to which a link is to be proposed.

Finally, we point out that the original form of VMMC [26, 27] or the linking function in Eq. (11) can also be used to construct the moving clusters in systems interacting via repulsive interactions without any attractions, provided the attraction is artificially added to the repulsion [3]. These artificial potentials, termed fictitious potentials, are only employed during the cluster selection, and to bias the cluster acceptance probability. The clus-

ter itself is accepted with a probability governed by the real potentials. The moving clusters created in this way, are still not created according to the repulsive forces, but capture a different topology of moving clusters compared to the generalized linking described earlier in this paper. The way these two approaches complement each other is outside the scope of this work.

IX. CONCLUSION

This paper discussed the way in which clusters are defined in virtual move Monte Carlo methods for simulating condensed phase systems. Specifically, we presented and analyzed a complete set of virtual states which need to be considered to select the cluster via a general function linking not only attractive but also repulsive potentials. This opens up a simple way to study the role of collective degrees of freedom in self-assembling systems interacting via complex purely repulsive interactions [1]. Moreover, the simulation of repulsion generally increases the acceptance probability, which is a result desirable not only in the efficient sampling of phase space, but also in the approximation of dynamical motion by MC schemes [42]. The approximation of the dynamics by VMMC is generally expected to be efficient (compared to the Molecular Dynamics methods) in low-density systems where cluster motion is an important degree of freedom [24], in conditions where hydrodynamic effects are not negligible [3], and in situations where pairwise interaction is too complex for a dynamical simulation. Dynamical Monte Carlo

methods are also suitable for non-equilibrium simulations such as transition path sampling techniques [9] or exact determination of fluctuation-dissipation ratios [43].

The present paper shows that the simulation of repulsion may increase the acceptance probability of rotational moves by up to several orders of magnitude. Another possible application thus results from the work of Hedges and Whitelam [44], which suggests that access to the rotational degrees of freedom affects the formation of amorphous drops prior to crystallization and decides whether the crystallization path is classical or non-classical. Precise control over the collective rotations may, indeed, play an important role in the simulation of hierarchical self-assembly in short-range attractive and long-range repulsive systems [17] forming modulated phases such as Wigner glasses, cluster crystals [14], or even in mesocrystals [45], where rotations of nanocrystals are expected to be responsible for the oriented attachment.

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Appendix A: Summary of the move which controls the cluster size

Here we summarize the cluster move of the main text, which controls the cluster size in a similar way as we previously described in Ref. 27. As discussed in Ref. 27, this modification of the VMMC can also be used to control the collective rotations. Its validity can be seen again, if

we assume the free cluster selection first, and we consider the consequences of selecting the cluster in the restricted selection. The summary of the move is as follows:

1. Pick a random particle, and use it as the first (root) particle of the cluster \mathcal{C} . Choose the map M randomly.
2. Take a random number x from the uniform distribution $\mathcal{U}(0, 1)$. Define the maximum cluster size as $N_{\mathcal{C}} = \text{NINT}(1/x)$, where NINT is the nearest integer function.
3. Perform the iterative loop selecting all other particles to \mathcal{C} .
 - (a) Pick a random pair (i, j) , $i \in \mathcal{C}$, $j \notin \mathcal{C}$, which interacts in one of the states (10), and to which a link has not yet been proposed. If no such pair exists, finish the cluster selection by exiting the iterative loop.
 - (b) If the current number of particles in \mathcal{C} is equal to $N_{\mathcal{C}}$, mark (i, j) as a forced failed link (pair), go to (a).
 - (c) If the current number of particles in \mathcal{C} is lower than $N_{\mathcal{C}}$, attempt to create a link between (i, j) with probability defined by Eq. (1).
 - i. If the link forms, mark (i, j) as a formed link, include j into \mathcal{C} and go to (a).
 - ii. If the link does not form, mark (i, j) as a failed link (pair), go to (a).
4. Identify the boundary \mathcal{B}^* as those pairs $i \in \mathcal{C}$, $j \notin \mathcal{C}$, which interact in at least one of the states (x, y) , (Mx, y) , (x, My) or $(Mx, M^{-1}y)$, and which were not forced to fail by the condition in point 3(b).
5. Accept the cluster move with probability

$$W_{\text{acc}}^{(\mu \rightarrow \nu | R)} = \min \left\{ 1, e^{-\beta(E_{\nu} - E_{\mu})} \prod_{(i,j) \in \mathcal{B}^*} \frac{q_{ij}^{(\nu)}}{q_{ij}^{(\mu)}} \right\}.$$