Collective translational and rotational Monte Carlo moves for attractive particles

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Virtual move Monte Carlo is a Monte Carlo (MC) cluster algorithm forming clusters via local energy gradients and approximating the collective kinetic or dynamic motion of attractive colloidal particles. We carefully describe, analyze, and test the algorithm. To formally validate the algorithm through highlighting its symmetries, we present alternative and compact ways of selecting and accepting clusters which illustrate the formal use of abstract concepts in the design of biased MC techniques: the superdetailed balance and the early rejection scheme. A brief and comprehensive summary of the algorithms is presented, which makes them accessible without needing to understand the details of the derivation.

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I. INTRODUCTION

Virtual move Monte Carlo (VMMC) is a sequel to other cluster algorithms [1–6] for the computer simulation of atomic systems. Its basis is to apply a Monte Carlo (MC) move map to all particles in a cluster. The links between particles, defining the cluster, are created *a priori* by considering the application of the same map to individual particles in the relevant particle pairs. The moving cluster in this algorithm can then be physically interpreted as a region of particles to which a fluctuation propagates from an initially disturbed particle. VMMC was designed by Whitelam and Geissler [7], later corrected [8], and a two-step link formation was proposed by the same authors [9]. One of its advantages is the ability to approximate, in a coarse-grained fashion, the kinetic evolution of the system, and hence the ability to capture physical (and avoid nonphysical) kinetic traps. This can make it resemble Brownian or Stokesian dynamics, if the parameters within the method are chosen with regard to physical quantities, such as size-dependent diffusion coefficients. Although VMMC has begun to be used in the simulation of various aggregation or self-assembly processes [10–17], we believe that there is a need to present the algorithm in a completely clear form, especially in its symmetrized version. For clarity, and for reasons described below, the Brownian or Stokesian dynamical aspects are not considered here. VMMC can, indeed, be used just to investigate the thermodynamic properties [14].

Selection of a MC cluster generally proceeds via a recursive linking of particles that are not yet part of the cluster to the particles that are already in the cluster. As opposed to previously designed MC cluster schemes linking particle pairs with probability depending only on pairwise energy, VMMC creates links with probability depending on pairwise energy gradients corresponding to the direction of the move. This linking approach allows us to approximate a dynamically realistic cluster, but formulation of the microscopic reversibility condition is associated with a problem, because the pairwise energy change in the forward direction between particles in the moving cluster is not the same as the pairwise energy change in the reverse direction. The *unsymmetrized* version of VMMC [7] solves this issue by recording the forward and reverse linking probabilities between all pairs to which a link is proposed during the cluster selection, and uses them to calculate a complex factor [8] which biases the probability with which the cluster is accepted. A two-step symmetric linking procedure was later proposed in a so-called *symmetrized* VMMC [9], which reduced the set of pairs in the biasing factor to only a subset of pairs in the boundary of the cluster. Both the unsymmetrized and symmetrized versions of the VMMC algorithm were validated through imposing the microscopic reversibility condition on link patterns, called the *realizations* of the cluster. In this paper, we use the main ideas of the original proofs, but treat them with slightly modified algebra and definitions. We define the realization of the cluster through the set of all pairs to which a link is proposed, and we discuss whether the same pattern can be selected under the reverse move. Our definitions, basic algebraic relations between pairwise and virtual energies together with the discussion of the order in which the links are proposed, provide an alternative insight into the validation of this abstract algorithm, and can simplify its implementation.

We present three equivalent ways of selecting the cluster. The first, general way, called the free cluster selection (Sec. IV), attempts to include in the moving cluster all particles of the system that are not yet part of the cluster. This selection procedure is not efficient, and is presented only for theoretical purposes because its cluster acceptance probability is simple, and can be easily derived. The second way of cluster selection (Secs. V and VI) is newly presented in this paper. As opposed to that of Sec. IV, it only considers certain particles of the system, and is efficient in simulations, especially if proposed clusters are likely to be accepted. The form of the acceptance probability is again simple, and allows us to efficiently control the properties and distribution of proposed clusters. Finally, Sec. VIII addresses the original way of selecting the moving cluster [9] from an even smaller number of particles. This version of the algorithm is still equivalent to other versions presented here, and is particularly efficient if the acceptance probability of proposed clusters is low.

A reader seeking to rapidly implement the VMMC may skip the lengthy derivations of acceptance probabilities, and focus on the definitions of pairwise and virtual energies in Sec. II, linking probabilities in Sec. III, and use one of the algorithm summaries presented in Secs. V, VI, or VIII. If the acceptance probability is expected to be low, the original symmetrized

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VMMC [9] described in Sec. VIII should be fastest. If the acceptance probability is expected to be high, the version described in Sec. V should be simpler to implement with a negligible difference in efficiency compared to the version of Sec. VIII. If properties of proposed clusters are controlled by some auxiliary variables, and if unsuitable clusters are expected to have some chance to be accepted, the version presented in Sec. VI may increase the overall acceptance probability, and become more efficient than that presented in Sec. VIII. Finally, Sec. IX distinguishes between two orders of selecting the cluster. Random ordering is conventional and should work well in most simulations. Isotropic ordering is newly presented here, and may better approximate dynamical clusters, or increase the cluster move acceptance probability, thereby improving the efficiency.

Before implementing the VMMC, one should consider whether the aim is to approximate a physical dynamics, or to enhance sampling of an equilibrium distribution, also whether collective translational moves are sufficient, and more complicated collective rotational moves can be omitted. It should also be considered whether, and at which stage of self-assembly or aggregation, the collective motion becomes important. In fluids, for example, single particle MC is expected to be sufficient both for approximation of the dynamics and for sampling the equilibrium distribution. In simulation of gelation in quenched attractive systems, collective motion becomes dominant only in a narrow simulation window [9,18]. If one has a working VMMC code, some time should be allowed for optimizing the parameters of the VMMC for a specific system. In particular, the optimum choice of the maximum translational or rotational displacement drastically affects the efficiency of the algorithm [18]. If the dynamics is of interest, properties of proposed clusters need to be controlled, and approximation of the time step associated with a MC cycle composed of collective moves (Appendix of Ref. [11]) also needs to be taken into account.

Ideas and summaries presented in this paper can help with the implementation of VMMC. We do not provide any major efficiency enhancements compared to the previous schemes. The aim is to formally describe the algorithm, and provide a unification of underlying concepts which is helpful in the generalization of this algorithm [18] to any form of pairwise interaction.

II. DEFINITIONS AND BASIC RELATIONS

In what follows, $\mathcal{S}$ will denote a system of N interacting particles with states being defined by N position (and orientation) vectors of the particles. The interaction between particles is defined by an attractive pairwise potential $-\infty < V(r) \leqslant +\infty$ with a cutoff distance R_c. The typical interaction is a repulsive core and short-ranged attraction. The inverse temperature of the system is denoted by $\beta = 1/k_B T$, where k_B is the Boltzmann constant. In analogy with other cluster methods, VMMC works with particle pairs (or links between them), denoted by (i,j), where i and j denote two different particles in $\mathcal{S}$. The set of all pairs in $\mathcal{S}$ will be denoted as $\mathcal{A}$. For the purposes of this paper, it is enough to assume that the set $\mathcal{A}$ does not distinguish between (i,j) and (j,i). We say that (i,j) is an *interacting pair*, if particles i and j are separated by a distance less than R_c. Throughout the text, μ and ν denote two different states of $\mathcal{S}$, with energies E_μ and E_ν, respectively. Since VMMC is a single-cluster algorithm [6], we shall assume that μ and ν differ in the position of a single group of particles called the *moving cluster* or simply *cluster* and denoted by $\mathcal{C}$. To approximate realistic kinetics, we will further assume that the difference in the position of $\mathcal{C}$ is given by the application of a small translational or rotational map applied to all the particles in the cluster, representing a rigid motion of the cluster. The map will be denoted as M and its inverse as M^{-1}. We note that the moving cluster or cluster was referred to as a pseudocluster in the unsymmetrized formulation of the scheme [7], which used the term physical cluster or simply cluster not for the moving cluster but for what is conventionally referred to as the partition. In this paper, there is no need to distinguish between the partition and the moving cluster, and the term pseudocluster is thus not used.

The selection of particles from the system $\mathcal{S}$ to the cluster $\mathcal{C}$ proceeds recursively. The first particle of $\mathcal{C}$ is selected randomly from $\mathcal{S}$. Successive particles of $\mathcal{C}$ are selected by recursive linking of those particles in $\mathcal{S}$ that are not yet part of $\mathcal{C}$, i.e., we check the existence of a pair (i,j) in state μ such that

$$i \in \mathcal{C},\ j \notin \mathcal{C}, \tag{1a}$$

$$\text{a link has not yet been proposed to } (i,j), \tag{1b}$$

$$\text{an optional condition imposed on } (i,j) \text{ is satisfied.} \tag{1c}$$

If there is no pair (i,j) with properties (1), the cluster selection is complete. If a pair with properties (1) exists, a link is proposed to that pair. The link forms with a probability which will be denoted as $p_{ij}^{(\mu)}$ and defined later. If the link forms, j becomes a new member of $\mathcal{C}$. The existence of pairs with properties (1) is checked recursively until there are no such pairs (the cluster is selected). If the selection of the cluster only follows conditions (1a) and (1b), we say that the selection is *free*. If there is an extra condition (1c) on top of the conditions (1a) and (1b), we term it *restricted* selection. After the cluster selection, the set of all pairs in $\mathcal{S}$ can then be uniquely decomposed as

$$\mathcal{A} = \mathcal{L}^{(\mu)} \cup \mathcal{F}^{(\mu)} \cup \mathcal{B}^{(\mu)} \cup \mathcal{X}^{(\mu)}, \tag{2}$$

where $\mathcal{L}^{(\mu)}$ is the set of pairs to which a link was proposed and formed, $\mathcal{F}^{(\mu)}$ is the set of pairs (i,j), $i \in \mathcal{C}$, $j \in \mathcal{C}$, to which a link was proposed and failed to form, $\mathcal{B}^{(\mu)}$ is the set of pairs (i,j), $i \in \mathcal{C}$, $j \notin \mathcal{C}$, to which a link was proposed and failed to form, and $\mathcal{X}^{(\mu)}$ are all other pairs in $\mathcal{A}$. Set $\mathcal{X}^{(\mu)}$ clearly includes pairs (i,j), $i \in \mathcal{C}$, $j \in \mathcal{C}$, and depending on the condition (1c), pairs (i,j), $i \notin \mathcal{C}$, $j \notin \mathcal{C}$, or other pairs (i,j), $i \in \mathcal{C}$, $j \notin \mathcal{C}$, to which a link was not proposed. The triple of sets $(\mathcal{L}^{(\mu)},\mathcal{F}^{(\mu)},\mathcal{B}^{(\mu)})$ is called the *realization* of the cluster $\mathcal{C}$ in state μ under the map M, and is denoted as $R_{\mathcal{C}}^{(\mu)}$. The set $\mathcal{B}^{(\mu)}$ will be called the boundary (of the cluster $\mathcal{C}$). An example situation for restricted cluster selections is illustrated in Fig. 1.

Let us now show for the case of free cluster selection that if $R_{\mathcal{C}}^{(\mu)}$ has a nonzero probability in state μ under M, then there exists a realization of $\mathcal{C}$ in state ν under M^{-1}, denoted as $R_{\mathcal{C}}^{(\nu)}$, such that $R_{\mathcal{C}}^{(\nu)} = R_{\mathcal{C}}^{(\mu)}$. This will allow us to impose the microscopic reversibility condition on generating

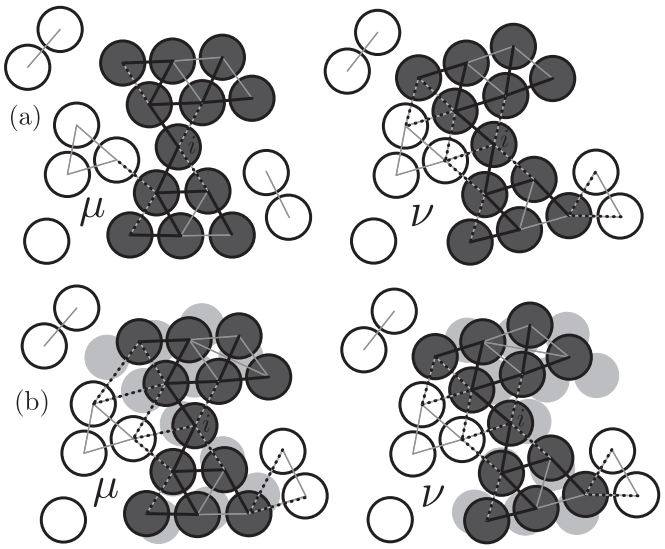


FIG. 1. The difference between the original and alternative formulations of the symmetrized VMMC is illustrated on a 2D system $\mathcal{S}$, consisting of circular particles (disks) in a plane, in two states μ and ν, interacting via a short-range attraction. State ν is created from μ by applying a rotational move map M to the particles in $\mathcal{C}$ (dark disks). Black full lines represent formed links $\mathcal{L}$. Black dotted lines are failed links internal to the cluster $\mathcal{F}$, and failed links defining the boundary of $\mathcal{C}$. (a) Asymmetric boundary. Links are proposed only to pairs interacting in state μ under the forward move M, and to pairs interacting in ν under the reverse move M^{-1}. Gray lines connect the pairs interacting in μ and ν in the respective states μ and ν. (b) Symmetric boundary. Links are proposed to pairs interacting in state μ or in virtual state μ_i under the forward move M, and to pairs interacting in ν or in ν_i under the reverse move M^{-1}. Gray lines connect the pairs interacting in μ or in μ_i and ν or in ν_i, in the respective states μ and ν. Gray disks in the background are particles in their virtual position μ_i in state μ, and ν_i in state ν. From a physical perspective, the root particle is randomly displaced, and the cluster represents a possible region to which this fluctuation propagates.

the realization in states μ and ν. We will need to show not only that each pair in $R_{\mathcal{C}}^{(\mu)}$ can form or fail in state ν, but will also need to show that the recursive selection is such that a link is proposed to that pair under M^{-1} in state ν. Recall that $p_{ij}^{(\mu)}$ denotes the probability of forming a link between pair (i,j) in state μ under M. We will require that $p_{ij}^{(\mu)}$ is defined such that

$$0 \leqslant p_{ij}^{(\mu)} < 1 \quad \forall\,(i,j)\, i,j \in \mathcal{S}, \tag{3a}$$

$$p_{ij}^{(\mu)} = p_{ij}^{(\nu)} \quad \forall\,(i,j)\, i,j \in \mathcal{C}, \tag{3b}$$

where $p_{ij}^{(\nu)}$ denotes the link formation probability in state ν under M^{-1}. Clearly, if $(i,j) \in \mathcal{L}^{(\mu)}$, then $i,j \in \mathcal{C}$, $p_{ij}^{(\mu)} > 0$, and property (3b) implies that the link between (i,j) can also form in state ν, and hence $\mathcal{L}^{(\nu)}$ such that $\mathcal{L}^{(\nu)} = \mathcal{L}^{(\mu)}$ can be generated in state ν with nonzero probability. Property (3a) then guarantees that each link which fails to form in μ under M can also fail in ν under M^{-1}, and hence $\mathcal{F}^{(\nu)}$ such that $\mathcal{F}^{(\nu)} = \mathcal{F}^{(\mu)}$ can be generated with nonzero probability in state ν under M^{-1}. The fact that links are proposed to the same set of pairs in state μ under M, and in state ν under M^{-1} follows from the recursive rules (1a), (1b), and the fact that $\mathcal{L}^{(\nu)}$ has nonzero probability in state ν. It is clear that recursive rules (1a), (1b) imply that $\mathcal{B}^{(\nu)} = \mathcal{B}^{(\mu)}$. We have thus shown that the recursive rules (1a), (1b), and linking properties (3) imply that if $R_{\mathcal{C}}^{(\mu)}$ in the free cluster selection has nonzero probability in μ, then $R_{\mathcal{C}}^{(\nu)}$ such that $R_{\mathcal{C}}^{(\nu)} = R_{\mathcal{C}}^{(\mu)}$ has nonzero probability in ν.

Conditions (1a) and (1b) are general rules for the recursive cluster selection, and will be used for the validation of the algorithm. From the practical point of view, considering all pairs satisfying (1a) and (1b) is not very efficient. To speed up the cluster selection, the pairs to which a link is proposed to select the cluster are further restricted by the optional condition (1c). A consequence of this restriction will be that the set of pairs to which a link is proposed is not generally the same in states μ and ν. More explicitly, there might be pairs in state ν to which a link is proposed under M^{-1}, but can not be proposed in state μ under M; and *vice versa*, there might be pairs to which a link is proposed in state μ under M, but not in state ν under M^{-1}. In Sec. V, the recursive selection of the cluster considers pairs with properties (1a), (1b), restricted by (1c) such that (i,j) is interacting in μ or in state μ modified by applying M to particle i. It is shown in Appendix A that the difference between pairs to which a link is proposed does not affect the probability of selecting or accepting the cluster, which will serve as an argument that the acceptance probability of Sec. IV derived for the free cluster selection can also be used in Sec. V for the cluster selected more efficiently via the restriction (1c). Section VIII considers an even stronger condition (1c) restricting the pairs to which a link is proposed to just pairs that interact in state μ. The difference between the pairs considered in the cluster selection in μ and ν can no longer be ignored: it must be detected after the cluster selection and included in the bias of the acceptance probability to preserve the exact sampling.

The link formation probability $p_{ij}^{(\mu)}$ will depend on various pairwise energy changes due to the movement by M. It is thus useful to have a compact notation for the energies of pairs of particles before and after one or the other has been moved by M. The energy of (i,j) in state μ is denoted by $\epsilon_{ij}^{(\mu)}$. Clearly, if (i,j) is not an interacting pair in μ, then $\epsilon_{ij}^{(\mu)} = 0$. Given a pair (i,j), the move map M is said to be virtual if it is applied to a particle only in order to determine the pairwise energy change associated with that move or to determine the set of nearest neighbors of the moved particle. If the system $\mathcal{S}$ is in state μ, and M is applied to particle i, $\mathcal{S}$ is then said to be in the *virtual state* μ_i. Virtual state μ_j will denote a state μ after applying M to particle j; ν_i will be $\mathcal{S}$ in ν after applying M^{-1} to i; and ν_j will be $\mathcal{S}$ in ν after applying M^{-1} to j. $\epsilon_{i'j}^{(\mu)}$ will denote the energy of (i,j) in μ_i; $\epsilon_{ij'}^{(\mu)}$ will be the energy of (i,j) in μ_j; $\epsilon_{i'j}^{(\nu)}$ will be the energy of (i,j) in ν_i; and $\epsilon_{ij'}^{(\nu)}$ will be the energy of (i,j) in ν_j. We note that the Boltzmann distribution of states implies that the pairwise energy $\epsilon_{ij}^{(\mu)}$ is strictly different from $+\infty$, and with the above defined properties of the pairwise potential $V(r)$, we can write $-\infty < \epsilon_{ij}^{(\mu)} < +\infty$. The virtual energy, on the other hand, can be assumed $+\infty$. For example, the virtual state μ_i generally has $-\infty < \epsilon_{i'j}^{(\mu)} \leqslant +\infty$. These inequalities will be used later. We also emphasize that the

pairwise energy change is the energy change only between particles i and j, not the energy change of the system. In practice, the energy $\epsilon_{i'j}^{(\mu)}$ is obtained in three steps. Given a pair (i,j) in state μ, first, move particle i by M; second, measure pairwise energy of (i,j), denote it as $\epsilon_{i'j}^{(\mu)}$; third, move particle i back (restore its original position). Energies $\epsilon_{ij'}^{(\mu)}$, $\epsilon_{i'j}^{(\nu)}$, $\epsilon_{ij'}^{(\nu)}$ can be obtained analogously.

Let us define the *complete boundary* as

$$\mathcal{B} = \mathcal{B}^{(\mu)} \cup \mathcal{B}^{(\nu)}. \tag{4}$$

Clearly, for the free cluster selection case

$$\mathcal{B} = \mathcal{B}^{(\mu)} = \mathcal{B}^{(\nu)}. \tag{5}$$

The following energy identities apply to the classes of pairs identified above. For any pair outside the complete boundary of $\mathcal{C}$ in state μ and ν, it holds that

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

For boundary pairs,

$$\left.\begin{aligned} \epsilon_{i'j}^{(\mu)} &= \epsilon_{ij}^{(\nu)} \\ \epsilon_{i'j}^{(\nu)} &= \epsilon_{ij}^{(\mu)} \end{aligned}\right\} \quad \forall\, (i,j) \in \mathcal{B}. \tag{7}$$

It is useful to denote

$$\begin{aligned} \Delta\epsilon_{i'j}^{(\mu)} &= \epsilon_{i'j}^{(\mu)} - \epsilon_{ij}^{(\mu)}, \quad \Delta\epsilon_{i'j}^{(\nu)} = \epsilon_{i'j}^{(\nu)} - \epsilon_{ij}^{(\nu)}, \\ \Delta\epsilon_{ij'}^{(\mu)} &= \epsilon_{ij'}^{(\mu)} - \epsilon_{ij}^{(\mu)}, \quad \Delta\epsilon_{ij'}^{(\nu)} = \epsilon_{ij'}^{(\nu)} - \epsilon_{ij}^{(\nu)}, \end{aligned} \tag{8}$$

which by using Eqs. (7) and (6) leads to the identity

$$\Delta\epsilon_{i'j}^{(\mu)} = -\Delta\epsilon_{i'j}^{(\nu)} \quad \forall\, (i,j) \in \mathcal{B}\,, \tag{9}$$

and identities

$$\left.\begin{aligned} \Delta\epsilon_{i'j}^{(\mu)} &= \Delta\epsilon_{ij'}^{(\nu)} \\ \Delta\epsilon_{i'j}^{(\nu)} &= \Delta\epsilon_{ij'}^{(\mu)} \end{aligned}\right\} \quad \forall\, (i,j) \notin \mathcal{B}. \tag{10}$$

We will now use the above notation in order to express a trivial fact, that by moving a cluster of particles, the energy change of the system is given by the energy change of the boundary of the cluster. Relation (2) implies that the total energy of the system in state μ can then be expressed as

$$\begin{aligned} E_\mu = &\sum_{(i,j)\in\mathcal{L}^{(\mu)}} \epsilon_{ij}^{(\mu)} + \sum_{(i,j)\in\mathcal{F}^{(\mu)}} \epsilon_{ij}^{(\mu)} + \sum_{(i,j)\in\mathcal{B}^{(\mu)}} \epsilon_{ij}^{(\mu)} \\ &+ \sum_{(i,j)\in\mathcal{X}^{(\mu)}} \epsilon_{ij}^{(\mu)}. \end{aligned} \tag{11}$$

Similarly, the total energy of $\mathcal{S}$ in state ν is

$$E_\nu = \sum_{(i,j)\in\mathcal{L}^{(\nu)}} \epsilon_{ij}^{(\nu)} + \sum_{(i,j)\in\mathcal{F}^{(\nu)}} \epsilon_{ij}^{(\nu)} + \sum_{(i,j)\in\mathcal{B}^{(\nu)}} \epsilon_{ij}^{(\nu)} + \sum_{(i,j)\in\mathcal{X}^{(\nu)}} \epsilon_{ij}^{(\nu)}. \tag{12}$$

Since $R_{\mathcal{C}}^{(\mu)} = R_{\mathcal{C}}^{(\nu)}$, and $\epsilon_{ij}^{(\mu)} = \epsilon_{ij}^{(\nu)}$, provided (i,j) is in any of the sets $\mathcal{L}^{(\mu)} = \mathcal{L}^{(\nu)}$, $\mathcal{F}^{(\mu)} = \mathcal{F}^{(\nu)}$, or $\mathcal{X}^{(\mu)} = \mathcal{X}^{(\nu)}$, by using Eqs. (8) and (5) we can express

$$E_\nu - E_\mu = \sum_{(i,j)\in\mathcal{B}} \Delta\epsilon_{i'j}^{(\mu)}. \tag{13}$$

III. LINK FORMATION PROBABILITIES

We have briefly explained the way in which particles, or rather pairs, are selected for consideration in the construction of the cluster, but we have not given any expressions for the acceptance or rejection of the link proposals, and this is the topic of the current section. After the cluster is constructed, we anticipate accepting or rejecting the Monte Carlo cluster move with a certain probability. The expression for this can be significantly simplified, if the link formation probability is the same for the forward and reverse moves, for pairs outside the boundary of the cluster. Let us thus express condition (3b) imposed on the link formation probability in terms of the complete boundary as

$$p_{ij}^{(\mu)} = p_{ij}^{(\nu)} \quad \forall\, (i,j) \notin \mathcal{B}. \tag{14}$$

Clearly, if (14) is satisfied, then (3b) is satisfied. The requirement (14) can be easily achieved in conventional (static) cluster algorithms because $p_{ij}^{(\mu)}$ only depends on the energy of (i,j) in state μ, and $p_{ij}^{(\nu)}$ only depends on the energy of (i,j) in state ν, and these energies are clearly the same for pairs outside the boundary [see the first identity in Eq. (6) which applies for $(i,j) \notin \mathcal{B}$]. In contrast, $p_{ij}^{(\mu)}$ in (dynamic) VMMC also depends on the energy of (i,j) in state ν. To satisfy relation (14) in the dynamical linking process is not so straightforward because it is not known whether (i,j) belongs to the boundary of $\mathcal{C}$, during the construction of $\mathcal{C}$. Hence, it is assumed that during the cluster selection (i,j) does not belong to the boundary, and this assumption is corrected by a bias in the cluster move acceptance probability for pairs which end up in the boundary. Moreover, in order to apply the early rejection scheme [19], which simplifies and accelerates the algorithm, the link is formed in two link formation tests as follows.

Given a pair (i,j) in state μ, we consider the following two probabilities defined as

$$p_{i'j}^{(\mu)} = \max\left\{0, 1 - \exp\left(-\beta\Delta\epsilon_{i'j}^{(\mu)}\right)\right\}, \tag{15a}$$

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

The former represents the prelink formation probability between (i,j) in state μ under the map M. The latter represents the prelink formation probability in ν under M^{-1}; note, we assume that particles are linked in the forward move, and this interpretation formally uses the equality (10). The link between (i,j) then forms in two random tests. The success probability of the first test is merely given by $p_{i'j}^{(\mu)}$, and that of the second is given by $\min\{1, p_{ij'}^{(\mu)}/p_{i'j}^{(\mu)}\}$. The link between (i,j) forms only if both tests are successful. Hence, the link formation

probability can be defined as the joint probability

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

where (X_1, X_2) are two independent random numbers drawn from a uniform distribution $\mathcal{U}(0,1)$. If the first test fails, then (i,j) is marked as an *outright failed* link (or pair) independently of the outcome of the second test. If the first test succeeds and the second test fails, then (i,j) is marked as a *frustrated* link (or pair). Note that, if $p_{i'j}^{(\mu)} = 0$, we do not need to consider the ill-defined fraction $p_{ij'}^{(\mu)}/p_{i'j}^{(\mu)}$, as (i,j) is always outright failed.

The link failure probability is defined as

$$q_{ij}^{(\mu)} = 1 - p_{ij}^{(\mu)}. \quad (17)$$

It is useful to define the prelink failure probability as

$$q_{i'j}^{(\mu)} = 1 - p_{i'j}^{(\mu)}, \quad (18)$$

and express it as

$$q_{i'j}^{(\mu)} = \exp\left(-\beta \max\left\{0, \Delta\epsilon_{i'j}^{(\mu)}\right\}\right). \quad (19)$$

We point out that, in the wider context of recursive cluster selection, the link formation probability defined in this way is conditional upon μ, and upon a set of auxiliary variables $\{b\}$ comprising M, and (optionally) a limit specifying the maximum size of the cluster. We will later discuss the case where $p_{i'j}^{(\mu)}$ explicitly depends upon the current number of particles in the cluster. Note also that definitions (15a), (15b), and (18) use a notation which is slightly different (but more accurate) than that used in the original papers [9]. It shows that the prelink probability is not only conditional upon M (through the appearance of i' and j' in the above expressions) but, more importantly, it also shows that the probability is conditional upon the state μ itself.

Finally, let us show that the link formation probability defined in Eq. (16) does satisfy the desired equality (14). First, the equalities (10) imply that

$$\left.\begin{aligned} p_{i'j}^{(\mu)} &= p_{ij'}^{(\nu)} \\ p_{ij'}^{(\mu)} &= p_{i'j}^{(\nu)} \end{aligned}\right\} \quad \forall\ (i,j) \notin \mathcal{B}. \quad (20)$$

Hence, if both $p_{i'j}^{(\mu)} > 0$ and $p_{ij'}^{(\mu)} > 0$, then both $p_{i'j}^{(\nu)} > 0$ and $p_{ij'}^{(\nu)} > 0$, and the link formation probability (16) can be expressed as

$$\begin{aligned} p_{ij}^{(\mu)} &= p_{i'j}^{(\mu)} \min\left\{1, \frac{p_{ij'}^{(\mu)}}{p_{i'j}^{(\mu)}}\right\} = \min\left\{p_{ij'}^{(\mu)}, p_{i'j}^{(\mu)}\right\} \\ &= \min\left\{p_{i'j}^{(\nu)}, p_{ij'}^{(\nu)}\right\} = p_{i'j}^{(\nu)} \min\left\{1, \frac{p_{ij'}^{(\nu)}}{p_{i'j}^{(\nu)}}\right\} = p_{ij}^{(\nu)} \end{aligned} \quad (21)$$

for $\forall\ (i,j) \notin \mathcal{B}$, where equality (20) was used again. Similarly, if $p_{i'j}^{(\mu)} = 0$ or $p_{ij'}^{(\mu)} = 0$, then $p_{i'j}^{(\nu)} = 0$ or $p_{ij'}^{(\nu)} = 0$, and $p_{ij}^{(\mu)} = p_{ij}^{(\nu)} = 0$. This completes the proof that the definition (16) of $p_{ij}^{(\mu)}$ satisfies Eq. (14) or (3b).

For the sake of clarity, let us express the probability that a link between (i,j) does not form. This probability is given by the probability that (i,j) is outright failed or that (i,j) is frustrated which reads as

$$\begin{aligned} &q_{i'j}^{(\mu)} + p_{i'j}^{(\mu)}\left(1 - \min\left\{1, p_{ij'}^{(\mu)}/p_{i'j}^{(\mu)}\right\}\right) \\ &\quad = q_{i'j}^{(\mu)} + p_{i'j}^{(\mu)} - \min\left\{p_{i'j}^{(\mu)}, p_{ij'}^{(\mu)}\right\} \\ &\quad = 1 - \min\left\{p_{i'j}^{(\mu)}, p_{ij'}^{(\mu)}\right\} = 1 - p_{ij}^{(\mu)} = q_{ij}^{(\mu)}. \end{aligned}$$

IV. FREE CLUSTER SELECTION

In this section, we derive a cluster move acceptance probability for the algorithm, which proceeds through the free cluster selection. Selecting the cluster in this general way is inefficient, but the corresponding acceptance probability can be easily derived because the set of pairs to which a link is proposed during the cluster selection does not differ in the old and in the new state. We will thus refer to the realization of the cluster to have both a *symmetric core* ($\mathcal{L}^{(\mu)} = \mathcal{L}^{(\nu)}$, $\mathcal{F}^{(\mu)} = \mathcal{F}^{(\nu)}$) and a *symmetric boundary* ($\mathcal{B}^{(\mu)} = \mathcal{B}^{(\nu)}$). The other significantly more efficient ways of selecting the cluster through asymmetric realizations are presented later in the paper. In what follows, we will assume that the cluster is selected freely, i.e., by considering all pairs (i,j) satisfying Eqs. (1a) and (1b). We will use the two-step link formation probability defined in the previous section to link particles to the cluster, which allows us to define an early rejection scheme simplifying the cluster move acceptance probability.

Let us only consider those $R_{\mathcal{C}}^{(\mu)}$ such that $\mathcal{B}^{(\mu)}$ consists entirely of outright failed links. We anticipate imposing the condition that all realizations of $\mathcal{C}$ with at least one frustrated link in the boundary are rejected, and it is shown in Appendix C 1 that the scheme samples from the Boltzmann distribution, subject to this condition.

Since the linking probability $p_{ij}^{(\mu)}$ defined in the previous section satisfies conditions (3), for each $\mathcal{L}^{(\mu)}$ and $\mathcal{F}^{(\mu)}$, there is a nonzero chance to recursively obtain $\mathcal{L}^{(\nu)}$ and $\mathcal{F}^{(\nu)}$, with $\mathcal{L}^{(\mu)} = \mathcal{L}^{(\nu)}$ and $\mathcal{F}^{(\mu)} = \mathcal{F}^{(\nu)}$. Let us now show that if $\mathcal{B}^{(\mu)}$ is a corresponding boundary with outright failed links in state μ under M, then $\mathcal{B}^{(\nu)}$ can also be a boundary with outright failed pairs in state ν under M^{-1}. Indeed, $-\infty < \epsilon_{ij}^{(\mu)} = \epsilon_{i'j}^{(\nu)} < +\infty$, and the fact that $p_{i'j}^{(\mu)} < 1$ implies that $p_{i'j}^{(\nu)} < 1$, and an outright failed pair in μ under M can become an outright failed boundary pair in ν under M^{-1}. We can thus expect that if $R_{\mathcal{C}}^{(\mu)}$ is such that $\mathcal{B}^{(\mu)}$ only has outright failed pairs, a realization $R_{\mathcal{C}}^{(\nu)}$ with $\mathcal{B}^{(\nu)}$ having outright failed pairs can be constructed with nonzero probability in ν under M^{-1}. In total, we have that for each $R_{\mathcal{C}}^{(\mu)}$ with outright failed boundary pairs, there is a nonzero chance to construct an $R_{\mathcal{C}}^{(\nu)}$ with outright failed boundary pairs such that $R_{\mathcal{C}}^{(\mu)} = R_{\mathcal{C}}^{(\nu)}$. This will be used to simplify the following.

Let us impose the microscopic reversibility condition on generating the realizations $R_{\mathcal{C}}^{(\mu)}$ and $R_{\mathcal{C}}^{(\nu)}$ with outright failed boundary pairs. This condition can also be seen as the superdetailed balance (SDB) condition [19,20] imposed on the realization of the cluster in states μ and ν. The condition

reads as

$$\exp(-\beta E_\mu)\, p^{(\mu)}(\{b\}) \prod_{(i,j)\in\mathcal{L}^{(\mu)}} p_{ij}^{(\mu)} \prod_{(i,j)\in\mathcal{F}^{(\mu)}} q_{ij}^{(\mu)} \prod_{(i,j)\in\mathcal{B}^{(\mu)}} q_{i'j}^{(\mu)}\, W_{\rm acc}^{(\mu\to\nu|R)}$$
$$= \exp(-\beta E_\nu)\, p^{(\nu)}(\{b\}) \prod_{(i,j)\in\mathcal{L}^{(\nu)}} p_{ij}^{(\nu)} \prod_{(i,j)\in\mathcal{F}^{(\nu)}} q_{ij}^{(\nu)} \prod_{(i,j)\in\mathcal{B}^{(\nu)}} q_{i'j}^{(\nu)}\, W_{\rm acc}^{(\nu\to\mu|R)}. \quad (22)$$

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, and it is a product of three components

$$p^{(\mu)}(\{b\}) = p^{(\mu)}(M)p^{(\mu)}(i)p^{(\mu)}(N_{\mathcal{C}}), \quad (23)$$

specifically the probability of selecting the move map M, the root particle i, and the maximum cluster size $N_{\mathcal{C}}$ in state μ. The term $p^{(\nu)}(\{b\})$ on the right represents a similar product in state ν. The explicit products over links on the left of Eq. (22) combine to give the probability of constructing the specific realization $R_{\mathcal{C}}^{(\mu)}$, which is conditional upon $\{b\}$. Analogous terms for state ν appear on the right. Finally, the terms $W_{\rm acc}^{(\mu\to\nu|R)}$ and $W_{\rm acc}^{(\nu\to\mu|R)}$ are the cluster move acceptance probabilities that we seek.

We note that the set of all pairs satisfying conditions (1a) and (1b) generally changes during the cluster selection, and that even if we proceed through the free cluster selection, the SDB condition in Eq. (22) may be seen not to express exactly what the algorithm is doing. In Sec. X, we will take the change of set with (1a) and (1b) into account, and we will distinguish between the probability with which a pair (i,j) is selected, and the probability with which a link between (i,j) is formed. This will allow us to formulate the SDB condition in a slightly more explicit way than in Eq. (22).

Let us simplify the SDB condition (22). We suppose being able to ensure that $p^{(\mu)}(\{b\}) = p^{(\nu)}(\{b\}) > 0$, so that these terms cancel out. The products over linked pairs $\mathcal{L}^{(\mu)}$, $\mathcal{L}^{(\nu)}$, and unlinked pairs $\mathcal{F}^{(\mu)}$, $\mathcal{F}^{(\nu)}$ also cancel because of Eq. (14), the fact that these sets are the same in states μ and ν, and the fact that the probability of generating $R_{\mathcal{C}}^{(\nu)}$ such that $R_{\mathcal{C}}^{(\nu)} = R_{\mathcal{C}}^{(\mu)}$ is strictly positive. Hence, Eq. (22) thus involves only products over boundary pairs $\prod_{\mathcal{B}^{(\mu)}}$ and $\prod_{\mathcal{B}^{(\nu)}}$ on each side. The reduced form of the SDB condition then reads as

$$\exp(-\beta E_\mu) \prod_{(i,j)\in\mathcal{B}^{(\mu)}} q_{i'j}^{(\mu)}\, W_{\rm acc}^{(\mu\to\nu|R)}$$
$$= \exp(-\beta E_\nu) \prod_{(i,j)\in\mathcal{B}^{(\nu)}} q_{i'j}^{(\nu)}\, W_{\rm acc}^{(\nu\to\mu|R)}, \quad (24)$$

with a Metropolis (Rosenbluth factor) type of solution

$$W_{\rm acc}^{(\mu\to\nu|R)} = \min\left\{1, \exp[-\beta(E_\nu - E_\mu)] \frac{\prod_{(i,j)\in\mathcal{B}^{(\nu)}} q_{i'j}^{(\nu)}}{\prod_{(i,j)\in\mathcal{B}^{(\mu)}} q_{i'j}^{(\mu)}}\right\}. \quad (25)$$

This expression can be simplified as follows. Let us separate the products over pairs into those for which $\Delta\epsilon_{i'j}^{(\mu)} > 0$, denoted by a superscript $+$, and those for which $\Delta\epsilon_{i'j}^{(\mu)} \leqslant 0$, denoted by $-$. Using expression (19), and relations (5), (9), and (13), the ratio of products in Eq. (25) can be expressed as

$$\frac{\prod_{(i,j)\in\mathcal{B}^{(\nu)}} q_{i'j}^{(\nu)}}{\prod_{(i,j)\in\mathcal{B}^{(\mu)}} q_{i'j}^{(\mu)}} = \frac{\prod_{(i,j)\in\mathcal{B}}^{+} \exp\left(-\beta\Delta\epsilon_{i'j}^{(\nu)}\right)}{\prod_{(i,j)\in\mathcal{B}}^{+} \exp\left(-\beta\Delta\epsilon_{i'j}^{(\mu)}\right)}$$
$$= \prod_{(i,j)\in\mathcal{B}}^{-} \exp\left(\beta\Delta\epsilon_{i'j}^{(\mu)}\right) \prod_{(i,j)\in\mathcal{B}}^{+} \exp\left(\beta\Delta\epsilon_{i'j}^{(\mu)}\right)$$
$$= \prod_{(i,j)\in\mathcal{B}} \exp\left(\beta\Delta\epsilon_{i'j}^{(\mu)}\right) = \exp[\beta(E_\nu - E_\mu)], \quad (26)$$

and the cluster move acceptance probability (25) can be simplified to

$$W_{\rm acc}^{(\mu\to\nu|R)} = 1, \quad (27a)$$

provided all pairs in the boundary $\mathcal{B}$ are outright failed, and as

$$W_{\rm acc}^{(\mu\to\nu|R)} = 0, \quad (27b)$$

if there is a frustrated pair in $\mathcal{B}$. This means that the cluster is accepted whenever the boundary only contains outright failed links and is rejected otherwise. This form of the acceptance probability is similar to the original rejection-free cluster algorithms [3,5], and represents an example where the early rejection scheme is useful when applied to many-particle moves [19].

V. SELECTION OF THE CLUSTER UNDER HIGH ACCEPTANCE PROBABILITY

This section formulates the version of symmetrized VMMC, which has a very simple form of the cluster acceptance probability, and which is efficient, in particular, if we expect the cluster acceptance probability to be high. Section VI will show that this simpler formulation forms a basis for a further alteration of the algorithm which allows us to control properties of proposed clusters, without rejecting them *in situ*. Compared to the free cluster selection presented in Sec. IV, the speed is gained by restricting the pairs to which a link is proposed, from the set of pairs satisfying conditions (1a) and (1b) to the set of pairs satisfying conditions (1a), (1b), and (1c), where (1c) requires that (i,j) is interacting in μ or in μ_i. This is a natural restriction because if (i,j) is not interacting in μ and in μ_i, then $\epsilon_{ij}^{(\nu)} = \epsilon_{i'j}^{(\mu)} = 0$, and the definition of linking probability (15a) implies that a link proposed to (i,j) is outright failed in states μ under M. If (i,j) ends up outside the boundary, Eqs. (20) and (21) imply that (i,j) fails to form in state ν under M^{-1}. If (i,j) ends up in the boundary, Eqs. (7) imply that $p_{i'j}^{(\nu)} = 0$, and that (i,j) is outright failed in state ν. There is thus no reason to propose a link to that pair in the free cluster selection.

As discussed earlier for the SDB condition, the set of pairs to which a link is proposed in states μ and ν must be guaranteed to be the same to ensure the existence of $R_{\mathcal{C}}^{(\nu)}$ such that $R_{\mathcal{C}}^{(\nu)} = R_{\mathcal{C}}^{(\mu)}$. It is shown in Appendix A that although these sets are not the same under the restriction (1c) of this section, nothing changes in the algorithm if we assume that the sets are identical, and we can thus use the simple form of the acceptance cluster probability (27) for the free cluster selection. Since generally $\mathcal{F}^{(\mu)} \neq \mathcal{F}^{(\nu)}$ and $\mathcal{B}^{(\mu)} = \mathcal{B}^{(\nu)}$, we say that the realization of the cluster has *asymmetric core* and *symmetric boundary*.

The cluster move derived in Sec. IV and accelerated by condition (1c) defined in this section can be summarized as follows:

(1) Pick a random particle, and use it as the first (root) particle of the cluster $\mathcal{C}$.

(2) Perform the recursive loop selecting all other particles to $\mathcal{C}$.

(a) Pick randomly a pair (i,j), $i \in \mathcal{C}$, $j \notin \mathcal{C}$, which interacts in state μ or in virtual state μ_i, and to which a link has not yet been proposed. If no such pair exists, finish the cluster selection by exiting the recursive loop.

(b) Attempt to create a link between (i,j) as follows.

(i) Form a prelink with probability

$$p_{i'j}^{(\mu)} = \max\left\{0, 1 - \exp\left[-\beta\left(\epsilon_{i'j}^{(\mu)} - \epsilon_{ij}^{(\mu)}\right)\right]\right\}.$$

(ii) If the prelink does not form, label (i,j) as outright failed, go to (a).

(iii) If the prelink forms, calculate the reverse link formation probability

$$p_{ij'}^{(\mu)} = \max\left\{0, 1 - \exp\left[-\beta\left(\epsilon_{ij'}^{(\mu)} - \epsilon_{ij}^{(\mu)}\right)\right]\right\},$$

where $\epsilon_{ij'}^{(\mu)}$ denotes the energy of (i,j) in μ after applying the move map M only to j, and form the link with probability

$$\min\left\{1, p_{ij'}^{(\mu)} / p_{i'j}^{(\mu)}\right\}.$$

(c) If the link does not form, label (i,j) as frustrated, go to (a).

(d) If the link forms, include j into $\mathcal{C}$, go to (a).

(3) Identify the boundary $\mathcal{B}$ of cluster $\mathcal{C}$ as those pairs (i,j), $i \in \mathcal{C}$, $j \notin \mathcal{C}$, to which a link was proposed but failed to form, i.e., is either outright failed or frustrated.

(4) Accept the cluster move, provided the boundary $\mathcal{B}$ only contains outright failed links. If $\mathcal{B}$ contains a frustrated link, the move of $\mathcal{C}$ is rejected.

VI. CONTROLLING THE CLUSTER SIZE

Cluster size control can be useful when generating small rotational Monte Carlo cluster moves, intended to preserve kinetic evolution of the system, or to represent the dynamics of Stokesian or Brownian particle motion [21], or in conditions of high particle density, where the moving cluster might otherwise span the entire system [6]. The original symmetrized or unsymmetrized VMMC schemes control the size distribution of the moving clusters simply by rejecting any move reaching a certain limit (number of particles in the cluster is an example of such a limit). In the symmetrized version of VMMC, this leads to a combination of two early rejection schemes: one by frustrated links in the boundary, the other by a maximum cluster size. Here, we present a way of accepting the clusters which would otherwise have been rejected by the latter scheme. This makes this approach potentially more efficient than the original symmetrized VMMC [9] summarized in Sec. VIII.

Let us assume that the auxiliary conditions $\{b\}$, chosen at the beginning of the cluster construction, include a number $N_{\mathcal{C}}$ determining the maximum number of particles in the chosen cluster. We now redefine the prelink formation probabilities in state μ as

$$\left.\begin{aligned} p_{i'j}^{(\mu)} &= \max\left[0, 1 - \exp\left(-\beta\Delta\epsilon_{i'j}^{(\mu)}\right)\right] \\ p_{ij'}^{(\mu)} &= \max\left[0, 1 - \exp\left(-\beta\Delta\epsilon_{ij'}^{(\mu)}\right)\right] \end{aligned}\right\} \quad \text{if } n_{\mathcal{C}} < N_{\mathcal{C}}, \tag{28a}$$

where $n_{\mathcal{C}}$ denotes the number of particles in $\mathcal{C}$, and

$$p_{i'j}^{(\mu)} = 0 \quad \text{if } n_{\mathcal{C}} = N_{\mathcal{C}}. \tag{28b}$$

The link again forms as a result of two random tests, and the realization $R_{\mathcal{C}}^{(\mu)}$ is constructed recursively from the root as described above. Hence, when the $N_{\mathcal{C}}$th particle is linked to the cluster, the selection is finished, and all pairs (i,j), $i \in \mathcal{C}$, $j \notin \mathcal{C}$, interacting in one of the states μ or μ_i, and to which a link has not yet been proposed, will become boundary pairs with probability $q_{ij}^{(\mu)} = 1$.

To derive the acceptance probability, let $N_{\mathcal{C}}$ be a random integer $1 \leqslant N_{\mathcal{C}} \leqslant N$, and let $R_{\mathcal{C}}^{(\mu)} = (\mathcal{L}^{(\mu)}, \mathcal{F}^{(\mu)}, \mathcal{B}^{(\mu)})$ be a realization after selecting $\mathcal{C}$ via the free cluster selection following the recursive rules (1a) and (1b), and using the probability defined in Eq. (28). The boundary can be uniquely decomposed as

$$\mathcal{B}^{(\mu)} = \mathcal{B}^{*(\mu)} \cup \mathcal{B}^{\dagger(\mu)}, \tag{29}$$

where $\mathcal{B}^{*(\mu)}$ denotes pairs in $\mathcal{B}^{(\mu)}$ which failed by definition (28a), i.e., failed probabilistically, and $\mathcal{B}^{\dagger(\mu)}$ denotes pairs which failed by definition (28b), i.e., were forced to fail because the cluster reached its maximum size. Since $p_{ij}^{(\mu)}$ defined in Eqs. (28) satisfies conditions (3a) and (3b), one can construct $R_{\mathcal{C}}^{(\nu)}$ such that $R_{\mathcal{C}}^{(\nu)} = R_{\mathcal{C}}^{(\mu)}$. Moreover, if the notation (29) is used in state ν, it is clear $R_{\mathcal{C}}^{(\nu)}$ can be such that

$$\mathcal{B}^{*} = \mathcal{B}^{*(\mu)} = \mathcal{B}^{*(\nu)}, \tag{30a}$$

$$\mathcal{B}^{\dagger} = \mathcal{B}^{\dagger(\mu)} = \mathcal{B}^{\dagger(\nu)}, \tag{30b}$$

where sets $\mathcal{B}^{*}$ and $\mathcal{B}^{\dagger}$ have been defined.

We again use the SDB condition (22) to express the acceptance probability as in Eq. (27). Equation (27) can then be further simplified by considering relations (13) and (29) which imply

$$E_\nu - E_\mu = \sum_{(i,j)\in\mathcal{B}} \Delta\epsilon_{i'j}^{(\mu)} = \sum_{(i,j)\in\mathcal{B}^{*}} \Delta\epsilon_{i'j}^{(\mu)} + \sum_{(i,j)\in\mathcal{B}^{\dagger}} \Delta\epsilon_{i'j}^{(\mu)}. \tag{31}$$

In a similar way to Sec. IV, we further decompose the sums and products over pairs in the boundary $\mathcal{B}^{*}$ into those for which $\Delta\epsilon_{i'j}^{(\mu)} > 0$ (denoted by $+$) and those for which $\Delta\epsilon_{i'j}^{(\mu)} \leqslant 0$

(denoted by $-$). The Boltzmann factor of the energy difference in Eq. (25) can be expressed as

$$\exp[-\beta(E_\nu - E_\mu)] = \frac{\prod^{+}_{(i,j)\in\mathcal{B}^*}\exp\left(\beta\Delta\epsilon^{(\nu)}_{i'j}\right)}{\prod^{+}_{(i,j)\in\mathcal{B}^*}\exp\left(\beta\Delta\epsilon^{(\mu)}_{i'j}\right)}\prod_{(i,j)\in\mathcal{B}^\dagger}\exp\left(-\beta\Delta\epsilon^{(\mu)}_{i'j}\right). \quad (32)$$

Using definitions (29), (28), and relation (9), the product in Eq. (25) can then be expressed as

$$\prod_{(i,j)\in\mathcal{B}}\frac{q^{(\nu)}_{i'j}}{q^{(\mu)}_{i'j}} = \prod_{(i,j)\in\mathcal{B}^*}\frac{q^{(\nu)}_{i'j}}{q^{(\mu)}_{i'j}} = \frac{\prod^{+}_{(i,j)\in\mathcal{B}^*}\exp\left(-\beta\Delta\epsilon^{(\nu)}_{i'j}\right)}{\prod^{+}_{(i,j)\in\mathcal{B}^*}\exp\left(-\beta\Delta\epsilon^{(\mu)}_{i'j}\right)}. \quad (33)$$

Combining Eqs. (33) and (32) gives the cluster move acceptance probability

$$W^{(\mu\to\nu|R)}_{\rm acc} = \min\left\{1, \prod_{(i,j)\in\mathcal{B}^\dagger}\exp\left(-\beta\Delta\epsilon^{(\mu)}_{i'j}\right)\right\}, \quad (34a)$$

provided $\mathcal{B}^*$ only contains outright failed links, and

$$W^{(\mu\to\nu|R)}_{\rm acc} = 0 \quad (34b)$$

if $\mathcal{B}^*$ contains a frustrated link. Note that, if the cluster is not restricted by $N_{\mathcal{C}}$ or other conditions, then $\mathcal{B}^* = \mathcal{B}$, $\mathcal{B}^\dagger = \emptyset$, and the acceptance probability reduces to Eqs. (27). Also, in the derivation of the acceptance probability, we assumed that $\mathcal{C}$ was selected by free cluster selection, proposing links to all pairs satisfying (1a) and (1b). By using the results of Sec. V, it is easily seen that, in practice, it is enough to propose links to pairs satisfying (1a) and (1b), and interacting in one of the states μ or μ_i while still using Eqs. (34) to accept the cluster. The early rejection scheme is validated in Appendix C 2.

VII. COLLECTIVE ROTATIONAL MONTE CARLO MOVE

The move map for a rotation operation is specified by the position of the center of rotation, the direction of the axis about which the rotation is performed, and the angle (magnitude) of the rotation. Although it is generally not problematic to choose these variables such that their probabilities are the same in the original and in the final state, collective rotation operations may involve several hidden issues. First, rotating the cluster in periodic boundaries makes sense only if the cluster is smaller than half the minimum dimension L of the simulation box. A possible way of restricting the cluster size, to avoid this problem, is to extend the auxiliary conditions $\{b\}$ such that if (i,j), $i\in\mathcal{C}$, $j\notin\mathcal{C}$, is a pair to which a link is to be proposed, with the distance of j from the root particle larger than $L/4$, then the link is forced to fail, i.e., included in $\mathcal{B}^\dagger$. Second, since the size of the particle displacement increases with its distance from the center of rotation, any physically reasonable dynamics is approximated only if the displacement is restricted by a maximum distance specified again in $\{b\}$. Pairs (i,j), $i\in\mathcal{C}$, $j\notin\mathcal{C}$, interacting in μ or in μ_i, which have a single-particle displacement j larger than some maximum (typically σ), are then again included in $\mathcal{B}^\dagger$. (Instead of using $\mathcal{B}^\dagger$, one can also reject the cluster without any chance of being accepted as was originally proposed by Whitelam and Geissler [8].) Third, we observed that collective rotational moves require double floating point precision, especially in systems with discontinuous potentials. Although single floating point precision is usually sufficient for MC simulation, random collective rotation operations with single floating point precision can systematically decrease or increase interparticle distances, and bring pairs of particles in $\mathcal{C}$ from nonoverlapping to overlapping positions. In fact, overlaps can occasionally occur even when using double floating point precision, and translational moves. For hard-core systems or generally for systems with discontinuous potentials, we thus advise to check for the overlaps between particles of the moved cluster.

Let us now summarize the rotational move while applying the bias via forced failed links described in the previous section. The rotational move can be implemented as follows.

(1) Pick a random particle, and use it as the first (root) particle of the cluster $\mathcal{C}$. Let $\vec{r}_o$ denote the position vector (the center of mass) of the root particle.

(2) Pick the center of rotation as a point with position vector $\vec{r}_c$ defined as $\vec{r}_c = \vec{r}_o + a\vec{u}$, where $\vec{u}$ is a random unit vector, $a\in\mathcal{U}(0,a_{\max})$ is a random number selected from a uniform distribution, and $a_{\max}$ is a constant (typically $a_{\max}\approx\sigma$).

(3) Pick another random unit vector $\vec{u}_o$ defining the orientation of rotation, and a random angle with size $\theta\in\mathcal{U}(0,\theta_{\max})$, where $\theta_{\max}$ is a suitable constant. (Typically, $\theta_{\max}\approx\delta/\sigma$, with δ being the maximum size of the translational displacement.) Define the rotation matrix A corresponding to $\vec{u}_o$ and θ. Let $\vec{r}_i$ denote the position vector of particle i. The position vector of particle i after applying the Monte Carlo move is expressed as $M\vec{r}_i = A(\vec{r}_i - \vec{r}_c) + \vec{r}_c$.

(4) Perform the recursive loop selecting all other particles to $\mathcal{C}$.

(a) Pick randomly a pair (i,j), $i\in\mathcal{C}$, $j\notin\mathcal{C}$, which interacts in state μ or in virtual state μ_i, and to which a link has not yet been proposed. If no such pair exists, finish the cluster selection by exiting the recursive loop.

(b) Test the maximum displacement size: If the size of $M\vec{r}_j - \vec{r}_j$ is larger than σ, label (i,j) as forced failed, and go to (a). Carry on, otherwise. (For small θ, this is equivalent to the test that $\vec{r}_j - \vec{r}_c$ is larger than σ/θ.)

(c) Test periodic boundaries: If the size of $\vec{r}_j - \vec{r}_c$ is larger than $L/4$, label (i,j) as forced failed, and go to (a). Carry on, otherwise.

(d) Attempt to create a link between (i,j) as follows.

(i) Form a prelink with probability

$$p^{(\mu)}_{i'j} = \max\left\{0, 1-\exp\left[-\beta\left(\epsilon^{(\mu)}_{i'j} - \epsilon^{(\mu)}_{ij}\right)\right]\right\}.$$

(ii) If the prelink does not form, label (i,j) as outright failed, go to (a).

(iii) If the prelink forms, calculate the reverse link formation probability

$$p^{(\mu)}_{ij'} = \max\left\{0, 1-\exp\left[-\beta\left(\epsilon^{(\mu)}_{ij'} - \epsilon^{(\mu)}_{ij}\right)\right]\right\},$$

where $\epsilon^{(\mu)}_{ij'}$ denotes the energy of (i,j) in μ after applying the move map M only to j, and form the link with

probability

$$\min\left\{1, p_{ij'}^{(\mu)}/p_{i'j}^{(\mu)}\right\}.$$

(e) If the link does not form, label (i,j) as frustrated, go to (a).

(f) If the link forms, include j into $\mathcal{C}$, go to (a).

(5) Identify the boundary $\mathcal{B}$ of cluster $\mathcal{C}$ as those pairs (i,j), $i \in \mathcal{C}$, $j \notin \mathcal{C}$, to which a link was proposed but failed to form, i.e., is outright failed, forced failed, or frustrated.

(6) Divide $\mathcal{B}$ into forced failed pairs $\mathcal{B}^{\dagger}$, and all other pairs $\mathcal{B}^{*}$.

(7) Accept the cluster move with probability

$$W_{\mathrm{acc}}^{(\mu\to\nu|R)} = \min\left\{1, \prod_{(i,j)\in\mathcal{B}^{\dagger}} \exp\left(-\beta\Delta\epsilon_{i'j}^{(\mu)}\right)\right\}, \qquad (35)$$

provided $\mathcal{B}^{*}$ only contains outright failed links. If $\mathcal{B}^{*}$ contains a frustrated link, the move of $\mathcal{C}$ is rejected.

VIII. SELECTION OF THE CLUSTER UNDER LOW ACCEPTANCE PROBABILITY

In this section, we present a version of the symmetrized VMMC algorithm, which is suitable for situations where the cluster acceptance probability is expected to be low. Low acceptance can be caused naturally by, for example, high density and large moves, or artificially by accepting only clusters with some specific properties. This version of the algorithm has been described before [9,21], but the following description is more detailed. Compared to Secs. IV and V, the algorithm works with a cluster selection, which is further speeded up by proposing links only to pairs satisfying (1a), (1b), and (1c), where (1c) requires that (i,j) is interacting in state μ. This restriction again leads to an asymmetry of realizations of $\mathcal{C}$ because the boundary of the clusters in state μ and ν can not be required to be the same. In contrast to Sec. V, the difference between the realizations can not be ignored, and needs to be corrected with a bias in the acceptance probability (36). The bias is derived in Appendix B and the corresponding early rejection scheme validated in Appendix C 3. Since $\mathcal{L}^{(\mu)} = \mathcal{L}^{(\nu)}$, $\mathcal{F}^{(\mu)} = \mathcal{F}^{(\nu)}$, but generally $\mathcal{B}^{(\mu)} \neq \mathcal{B}^{(\nu)}$, the realizations of clusters are said to have *symmetric core* and *asymmetric boundary*.

The algorithm can be summarized as follows.

(1) Pick a random particle, and use it as the first (root) particle of the cluster $\mathcal{C}$.

(2) Perform the recursive loop selecting all other particles to $\mathcal{C}$.

(a) Pick a pair (i,j), $i \in \mathcal{C}$, $j \notin \mathcal{C}$, which interacts in state μ, and to which a link has not yet been proposed. If no such pair exists, finish the cluster selection by exiting the recursive loop.

(b) Attempt to create a link between (i,j) as follows:

(i) Form a prelink with probability

$$p_{i'j}^{(\mu)} = \max\left\{0, 1-\exp\left[-\beta\left(\epsilon_{i'j}^{(\mu)} - \epsilon_{ij}^{(\mu)}\right)\right]\right\}.$$

(ii) If the prelink does not form, label (i,j) as outright failed, go to (a).

(iii) If the prelink forms, calculate the reverse link formation probability

$$p_{ij'}^{(\mu)} = \max\left\{0, 1-\exp\left[-\beta\left(\epsilon_{ij'}^{(\mu)} - \epsilon_{ij}^{(\mu)}\right)\right]\right\},$$

and form the link with probability $\min\{1, p_{ij'}^{(\mu)}/p_{i'j}^{(\mu)}\}$.

(c) If the link does not form, label (i,j) as frustrated, go to (a).

(d) If the link forms, include j into $\mathcal{C}$, go to (a).

(3) Identify the boundary $\mathcal{B}^{(\mu)}$ of cluster $\mathcal{C}$ as those pairs (i,j), $i \in \mathcal{C}$, $j \notin \mathcal{C}$, to which a link was proposed, but not formed, i.e., is either outright failed or frustrated.

(4) If $\mathcal{B}^{(\mu)}$ contains a frustrated link, reject the move of $\mathcal{C}$.

(5) If $\mathcal{B}^{(\mu)}$ only contains outright failed links, proceed as follows:

(a) Identify those pairs in $\mathcal{B}^{(\mu)}$ that are interacting in the original state μ but not interacting in the final state ν. Denote these pairs $\mathcal{B}^{(\mu\overline{\nu})}$.

(b) Identify pairs (i,j), $i \in \mathcal{C}$, $j \notin \mathcal{C}$, that are outside the interaction region in the original state μ, but end up in the interaction region in the final state ν. Denote these pairs $\mathcal{B}^{(\overline{\mu}\nu)}$.

(c) Accept the cluster move with probability

$$\min\left\{1, \frac{\prod_{(i,j)\in\mathcal{B}^{(\overline{\mu}\nu)}}^{+} \exp\left(-\beta\epsilon_{ij}^{(\nu)}\right)}{\prod_{(i,j)\in\mathcal{B}^{(\mu\overline{\nu})}}^{+} \exp\left(-\beta\epsilon_{ij}^{(\mu)}\right)}\right\}, \qquad (36)$$

where the plus sign above the product in the numerator says that the product runs only over those pairs in $\mathcal{B}^{(\overline{\mu}\nu)}$ such that $\epsilon_{ij}^{(\nu)} > 0$. Similarly, the product in the denominator runs over pairs in $\mathcal{B}^{(\mu\overline{\nu})}$ such that $\epsilon_{ij}^{(\mu)} > 0$.

IX. RECURSIVE SELECTION OF THE CLUSTER

Cluster algorithms generally select the cluster under the implicit assumption that pairs to which a link is proposed are taken randomly from all pairs satisfying conditions (1). Since we use the SDB condition to validate the algorithm, we discuss the rules of the cluster selection more carefully, and we distinguish between a random and an isotropic way of selecting the cluster. This will be used in the next section to formulate the SDB condition such that it takes the pair selection probabilities into account.

The general selection of the cluster (a random tree in graph theory) starts with a random choice of auxiliary variables, usually denoted by $\{b\}$, specifying the properties of $\mathcal{C}$, and the selection rules. We will consider a case where the definition of auxiliary variables $\{b\}$ consists of

(1) random selection of the first (root) particle of $\mathcal{C}$;

(2) random selection of the maximum number of particles in the cluster, denoted by $N_{\mathcal{C}}$; and

(3) random selection of the move map M.

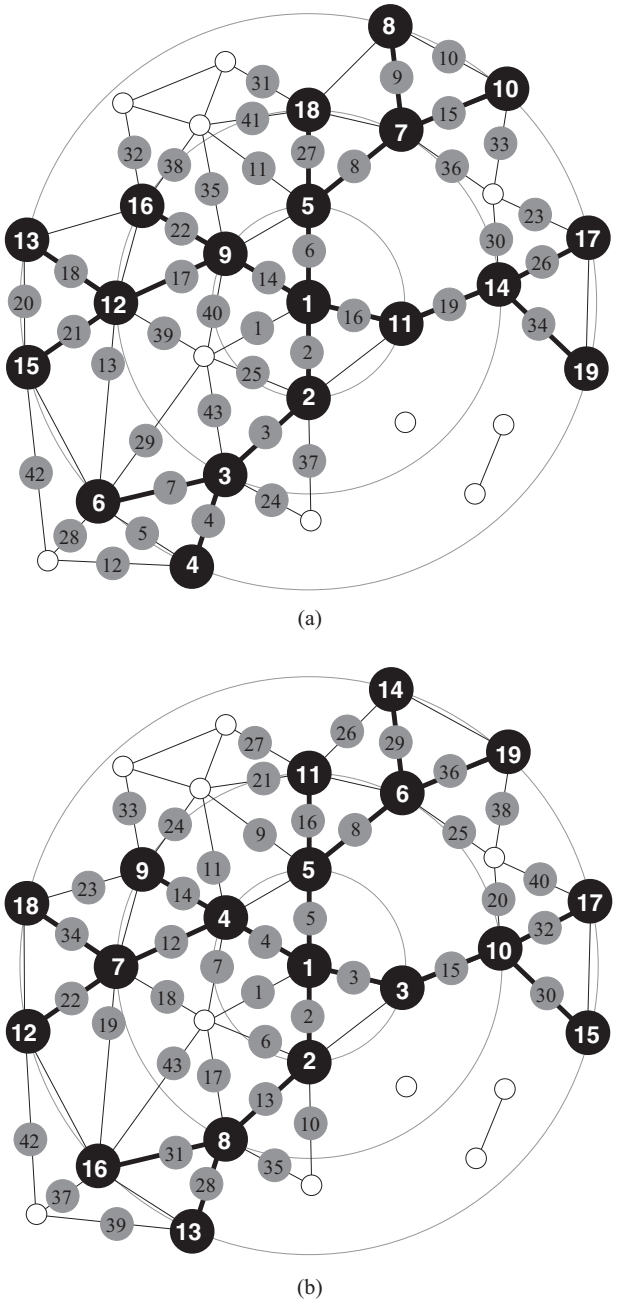
The cluster $\mathcal{C} \subset \mathcal{S}$ will again be selected in a recursive loop by linking particles of $\mathcal{S}$ to $\mathcal{C}$. Let us define the queue as the set of pairs satisfying conditions (1). A link is proposed to a randomly chosen pair in the queue. If the link between (i,j) forms, j becomes a new member of $\mathcal{C}$, all pairs (k,l) such that $l = j$ are erased from the queue, and all pairs (j,l) satisfying (1) that are not yet part of the queue are added to the queue. If the link does not form, the pair is erased from the queue.

Selecting pairs from the queue randomly like this is simple, intuitive, and common to most papers treating the single-cluster Monte Carlo algorithms [3–5,22]. We call this rule *random ordering*; the resulting sequence of proposed links is called *random link order*; and the outcome is a *randomly ordered* cluster. An example of a randomly ordered cluster, and the corresponding random link order of $\mathcal{C}$, are illustrated in Fig. 2(a).

Random ordering may not be the best choice, depending on the objectives of the simulation. There may be physical reasons, which make it desirable to produce a cluster which is, for example, spatially distributed in a more isotropic fashion about the root than a typical randomly ordered cluster. This could mimic a physical fluctuation, propagating isotropically in all directions from the root, out to some typical distance, which resulted in the coherent motion of a group of particles. Also, in the Brownian/Stokesian interpretation, it might be more justifiable to relate diffusion coefficients to cluster size, if the clusters are generated in this way. Alternatively, more isotropic or more compact clusters might be found (empirically) to generate more efficient simulations, in some circumstances.

Let us now illustrate how such a different rule for cluster selection might be formulated. We rely on the unique definition of *distance* between any two particles (vertices) in a tree, as the number of links (edges) joining them. Each particle in the growing cluster $\mathcal{C}$ has a unique distance from the root, determined (once and for all) when it is added to the cluster. It is convenient to define a *generation* of particles in $\mathcal{C}$ as the set of particles at the same distance from the root, measured in this way; the terminology is intentionally reminiscent of a family tree. A *living generation* is one such that there exists at least one pair (k,l) in the queue with k belonging to that generation, in other words, one which still has a chance to connect further particles l to the cluster. The *oldest* living generation is then the living generation with the shortest distance from the root (as defined above). The cluster selection then proceeds as above, but the links are proposed only to randomly selected pairs in the oldest living generation. A consequence of this selection rule is that there can be no more than two living generations at any stage. By analogy with the random case, we use the terminology *isotropic ordering*, *isotropic link order*, and *isotropically ordered* cluster (although this does not imply that the above rule is the only way of achieving similar results). An example is illustrated in Fig. 2(b). It might be possible to derive another kind of deterministic selection sequence by considering spiral ordering [23].

It is easy to see that every isotropic link order is also a possible random link order, but not *vice versa*. This implies that the number of random link orders is higher than the number of isotropic link orders for a given $\mathcal{C}$, and hence that the probability of selecting an isotropic link order or isotropically ordered cluster is lower in random ordering than in isotropic ordering. If the cluster size is then restricted by an upper limit, say five particles in the cluster of Fig. 2, then the cluster has a higher chance of isotropic topology if isotropic ordering is used than if random ordering is used. Isotropic ordering is thus an example of a cluster selection rule which affects the distribution of the moving cluster topologies.



(a)

(b)

FIG. 2. Diagrams showing two different orders in which the particles become members of the cluster, along with the order in which the links are proposed in a restricted cluster selection. Black numbered disks are particles in the cluster; small white disks are particles outside the cluster; thick black lines are formed links; thin black lines connect pairs interacting in μ (or in μ_i depending on the choice of the algorithm); numbered gray circles determine the link order. (In the next section, the link order is denoted as $S_R^{(\mu)}$ for the free cluster selection.) Large concentric circles identify particles within the same generation. (a) Random ordering. (b) Isotropic ordering.

X. EXPLICIT FORMULATION OF THE SUPERDETAILED BALANCE CONDITION

The SDB condition presented in Sec. IV is implicit in that it does not take into account that the link formation probability

$p_{ij}^{(\mu)}$ is conditional upon the probability of selecting a pair to which the link is proposed. In what follows, we will take the pair selection probabilities into account, and we will formulate the SDB condition explicitly.

We will again consider the free cluster selection, and we will denote the sequence of pairs to which a link was proposed during the recursive selection of $R_{\mathcal{C}}^{(\mu)}$ as

$$S_R^{(\mu)} = \{(i,j|r^{(\mu)})\}, \tag{37}$$

where $(i,j|r^{(\mu)})$ denotes the $r^{(\mu)}$th pair to which a link was proposed. This sequence can be uniquely decomposed into subsequences

$$\{(i,j|r_l^{(\mu)})\}; \quad \{(i,j|r_f^{(\mu)})\}; \quad \{(i,j|r_b^{(\mu)})\}, \tag{38}$$

running over linked pairs $\mathcal{L}^{(\mu)}$, pairs in $\mathcal{F}^{(\nu)}$, and boundary pairs $\mathcal{B}^{(\mu)}$, respectively. Clearly, there is, in general, more than one recursive sequence $S_R^{(\mu)}$ leading to the realization $R_{\mathcal{C}}^{(\mu)}$. We shall denote the set of all possible sequences leading to $R_{\mathcal{C}}^{(\mu)}$ as $\{S_R^{(\mu)}\}$. Also, there is generally more than one realization $R_{\mathcal{C}}^{(\mu)}$ selecting particles to $\mathcal{C}$. The set of all possible realizations of $\mathcal{C}$ in state μ will be denoted as $\{R_{\mathcal{C}}^{(\mu)}\}$.

Let $L(r^{(\mu)})$ denote the number of pairs in the queue before the $r^{(\mu)}$th iterative step is applied. In random ordering, the probability of selecting a specific pair in the rth iterative step is thus given by $1/L(r^{(\mu)})$.

For the free cluster selection, it is easily seen that

$$\{S_R^{(\mu)}\} = \{S_R^{(\nu)}\} \text{ and } \{R_{\mathcal{C}}^{(\mu)}\} = \{R_{\mathcal{C}}^{(\nu)}\}, \tag{39}$$

and also that for each $S_R^{(\mu)}$ and $S_R^{(\nu)}$ such that $S_R^{(\mu)} = S_R^{(\nu)}$, it holds that

$$\begin{aligned} L(r_l^{(\mu)}) &= L(r_l^{(\nu)}), \\ L(r_f^{(\mu)}) &= L(r_f^{(\nu)}), \\ L(r_b^{(\mu)}) &= L(r_b^{(\nu)}), \end{aligned} \tag{40}$$

which means that pair selection probabilities $1/L(r^{(\mu)})$ are the same in the old and in the new states at each step of the recursive cluster selection. We shall also denote

$$\begin{aligned} p(i,j|r^{(\mu)}) &= p_{ij}^{(\mu)}, \\ q(i,j|r^{(\mu)}) &= q_{ij}^{(\mu)}, \\ q(i,'j|r^{(\mu)}) &= q_{i'j}^{(\mu)} \end{aligned}$$

for a pair (i,j), which is the rth member of sequence $S_R^{(\mu)}$. The probability of selecting $S_R^{(\mu)}$ can then be expressed as

$$\begin{aligned} W_{\text{sel}}(S_R^{(\mu)}) = &\prod_{\{(i,j|r_l^{(\mu)})\}} \frac{1}{L(r_l^{(\mu)})} p(i,j|r_l^{(\mu)}) \\ &\times \prod_{\{(i,j|r_f^{(\mu)})\}} \frac{1}{L(r_f^{(\mu)})} q(i,j|r_f^{(\mu)}) \\ &\times \prod_{\{(i,j|r_b^{(\mu)})\}} \frac{1}{L(r_b^{(\mu)})} q(i',j|r_b^{(\mu)}), \end{aligned} \tag{41}$$

and the SDB condition imposed on $\{S_R^{(\mu)}\}$ and $\{S_R^{(\nu)}\}$ such that $\{S_R^{(\nu)}\} = \{S_R^{(\mu)}\}$ can be written as

$$\begin{aligned} &\exp(-\beta E_\mu)\, p^{(\mu)}(\{b\}) W_{\text{sel}}^{(\mu)}(S_R^{(\mu)})\; W_{\text{acc}}^{(\mu\to\nu|S)} \\ &\quad = \exp(-\beta E_\nu)\, p^{(\nu)}(\{b\}) W_{\text{sel}}^{(\nu)}(S_R^{(\nu)})\; W_{\text{acc}}^{(\nu\to\mu|S)} \end{aligned} \tag{42}$$

with terms having a similar meaning in Eq. (22). By using a reasoning analogous to that in Sec. IV, and by using relations (39) and (40), the explicit SDB condition (42) can be simplified into the form (25), and further into the form (27). We note that auxiliary conditions in the SDB condition were originally defined such that $\{b\}$ should also include the probability of generating $S_R^{(\mu)}$. Since $1/L(r^{(\mu)})$ is conditional upon the set of already formed links, we do not adhere to this definition, and express $1/L(r^{(\mu)})$ separately from $p^{(\mu)}(\{b\})$.

One can also proceed slightly differently, and express the probability of selecting a realization as

$$W_{\text{sel}}(R_{\mathcal{C}}^{(\mu)}) = \sum_{\{S_R^{(\mu)}\}} W_{\text{sel}}(S_R^{(\mu)}). \tag{43}$$

The SDB condition imposed on $R_{\mathcal{C}}^{(\mu)}$ and $R_{\mathcal{C}}^{(\nu)}$ such that $R_{\mathcal{C}}^{(\mu)} = R_{\mathcal{C}}^{(\nu)}$ then reads as

$$\begin{aligned} &\exp(-\beta E_\mu) p^{(\mu)}(\{b\}) W_{\text{sel}}^{(\mu)}(R_{\mathcal{C}}^{(\mu)})\; W_{\text{acc}}^{(\mu\to\nu|R)} \\ &\quad = \exp(-\beta E_\nu)\, p^{(\nu)}(\{b\}) W_{\text{sel}}^{(\nu)}(R_{\mathcal{C}}^{(\nu)})\; W_{\text{acc}}^{(\nu\to\mu|R)}, \end{aligned} \tag{44}$$

and can again be simplified into Eq. (25) or (27). Equation (44) is, in fact, equivalent to the implicit formulation of the SDB condition in Eq. (22) or to the previous formulations of the detailed balance conditions [2,4,22] validating the cluster algorithms, where the realization of the cluster is understood as a "static pattern" of pairs rather than a "dynamic sequence" of pairs. The SDB condition applied to sequences of pairs offers an alternative insight into the validity of the algorithms described above, both for random and isotropic ordering. Note that there are alternative ways [24] to see that the selection of a specific pattern of pairs in the old and in the new state has the same probability.

XI. RESULTS

We first test the VMMC method on a system of $N = 2000$ particles interacting via a short-ranged attractive generalized Lennard-Jones [25] potential given by

$$V(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{2\alpha} - \left(\frac{\sigma}{r}\right)^{\alpha}\right] - V_c, \tag{45}$$

with $\alpha = 18, \sigma = 1.0, \epsilon = 1.0$, in reduced units. The potential was truncated and shifted [19] at a cutoff distance $r_c = 1.8$, with the constant V_c chosen such that $V(r_c) = 0$. The simulations were carried out in the constant NVT ensemble. We took the critical packing fraction $\phi = \pi/6 \cdot N/V = 0.225$, and temperature $T = 0.6$ corresponding to the fluid phase [25]. We use the version of VMMC described in Sec. V, and the isotropic ordering. A Monte Carlo cycle consists of N virtual translational or rotational moves. The rotational moves were performed in the same way as described in Sec. VII. The decision about performing a translation or a rotation is random, with on average 50% translations and 50% rotations. The size

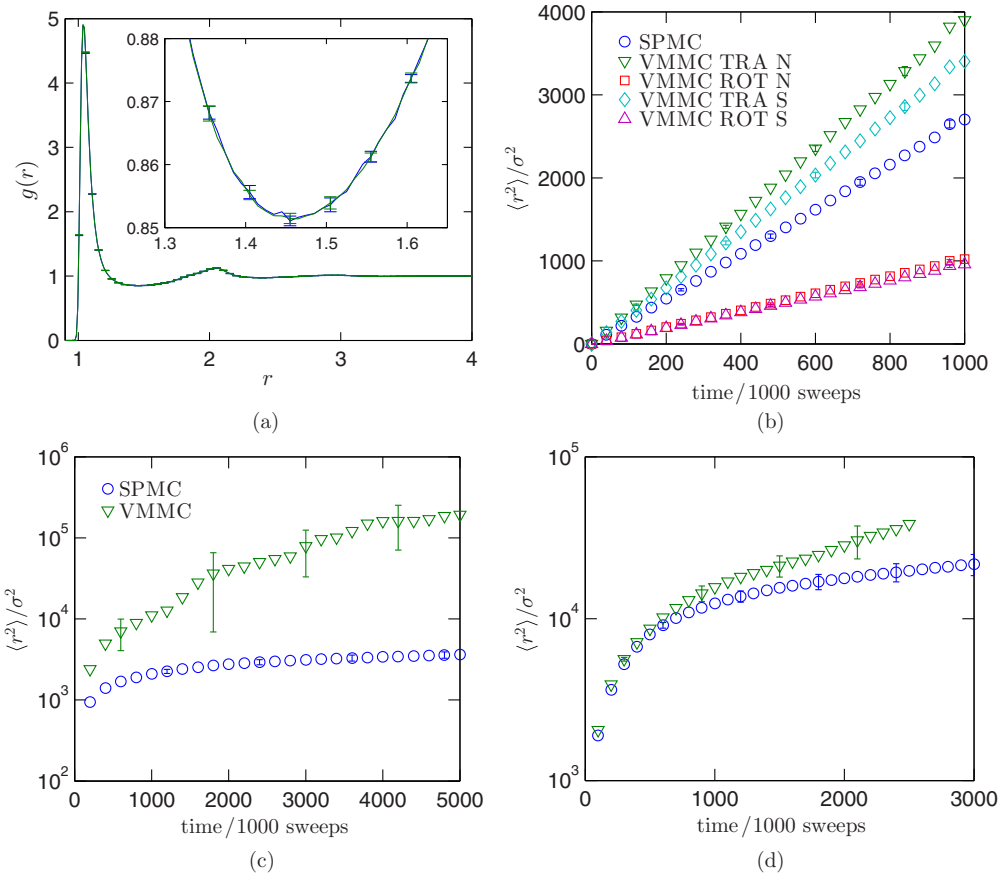


FIG. 3. (Color online) Simulations comparing single-particle MC (blue) and collective VMMC moves (green). Radial distribution functions in a fluid state of the system at $T = 0.6$ and $\phi = 0.225$. Inset: Magnification of the first minimum in $g(r)$. Mean square displacement versus time measured in 1000 MC sweeps for the fluid at $T = 0.6$ and $\phi = 0.225$. VMMC either contains only rotations (ROT) or only translations (TRA), and simulations are either not scaled (N) or scaled (S) by $N_C = 1/x$. MSD for the fluid at $\phi = 0.01$ measured from the quench to $T = 0.25$. MSD for short-range attractive and long-range repulsive fluid at $\phi = 0.01$ measured from the same quench. All error bars are estimated from 10 independent simulations.

of the translational displacement was chosen randomly from the interval $(-\delta,\delta)$. The maximum sizes of translational and rotational displacements were taken as $\delta/\sigma = \theta_{\max} = 0.10$, $a_{\max} = \sigma$. The size of δ can drastically affect the efficiency of the algorithm, and our optimum choice will be discussed elsewhere. We compare the radial distribution functions $g(r)$ generated both with single-particle Monte Carlo (SPMC) and VMMC only. For each case, the $g(r)$ is averaged over 10 independent simulations. The results are depicted in Fig. 3(a) and show that $g(r)$ are within the error range of each other. Similar tests were performed for fluid phases of similar short-ranged attractive systems at different temperatures, densities, and also in the constant NpT ensemble. The VMMC method described in Sec. VIII was tested elsewhere [24].

Figure 3(b) compares the mean square displacement (MSD) of SPMC with the MSD of VMMC. The SPMC has the same maximum displacement as the VMMC, equal to 0.1σ. The VMMC is tested with four different setups. A MC sweep either includes 100% of rotational or 100% of translational moves, and the cluster selection is or is not scaled by condition (28). By scaled or not scaled dynamics we understand that the limit on the maximum cluster size in Eq. (28) is, or is not, applied. We use $N_C = 1/x$, with x being a random number from the uniform distribution $\mathcal{U}(0,1)$. The scaling of the cluster selection can be used to approximate the Brownian dynamics by collective MC moves [9,26]. Although the time is nonphysical, the gradient of the MSD is constant, defining a diffusion coefficient for each simulation in Fig. 3(b). Diffusion by the nonscaled and scaled translational VMMC is higher than in SPMC by 44% and 26%, respectively. This corresponds to the fact that more particles are moved in an average VMMC cycle. Indeed, the number of displaced particles in the respective VMMC simulations was higher, by 28% and 16%, than in SPMC. Diffusion by rotations is lower than by translations, despite the fact that the total number of displaced particles in the rotational VMMC is higher, by 22%, than in the translational VMMC. The rotational geometry of the displacements and the potentials is a plausible reason for this result.

Figure 3(c) shows the evolution of the MSD in the Lennard-Jones system of Eq. (45), with a low packing fraction $\phi = 0.01$, quenched to the temperature $T = 0.25$, corresponding to the fluid-solid metastable region where clustering occurs [27]. The VMMC is scaled by $N_C = 1/x$, and contains 50% of rotations and 50% of translations. The maximum displacements were chosen as $\delta/\sigma = \theta_{\max} = 0.30$. The initial configuration is a

high temperature fluid conformation. The MSD is measured immediately from the start of the simulation, with no averaging over time origins. It can be seen that in the SPMC simulation of this system, particles get trapped by their neighbors in isolated aggregates, which do not move, meaning that the growth of the mean square displacement is extremely slow at later times. VMMC, on the other hand moves, both single particles and particles with their neighbors, thus producing a gel-like structure spanning most particles in the system, which itself moves as a single large cluster. The MSD in VMMC is thus several orders of magnitude larger than in SPMC, and the situation displayed in Fig. 3(b) is an example where VMMC is significantly more efficient than SPMC (at least on a certain time scale).

Figure 3(d) shows the results from quenches with parameters identical to those presented in Fig. 3(c), except that $\delta/\sigma = \theta_{\max} = 0.20$ and the potential (45) has an additional long-range repulsive term of the Yukawa form $A\exp(r/\xi)/(r/\xi)$, where $A = 0.08$ and $\xi = 2.0$. The potential is cut off and shifted at $r_c = 3.0$. The long-range repulsion can stabilize droplets [28], and the system phase separates after the quench into 2–3 large and long-living aggregates. Figure 3(d) shows that the MSD in VMMC evolves at about the same pace as in the purely attractive system, whereas the MSD in SPMC grows about an order of magnitude faster. This is likely to be caused by a single-particle exchange between the isolated aggregates. From the MSD point of view, the VMMC would thus not significantly outperform the SPMC. However, contrary to SPMC, the VMMC moves these isolated structures, preserving their integrity, and can confirm their temporal stability against aggregation into a single domain. A detailed account of the interplay between the single-particle and collective motion will be published elsewhere [18].

XII. DISCUSSION

We have derived an alternative formulation of the symmetrized VMMC. Let us now discuss its efficiency. Proposing links to pairs interacting not only in μ but also in μ_i may seem to impact the speed, compared to the VMMC selecting clusters via realizations with symmetric core and asymmetric boundary, where links are proposed only to pairs interacting in state μ. However, one must take into account that determining the boundary of the cluster in the new state, in the latter version of VMMC, requires detection of the interacting neighbors of every particle in $\mathcal{C}$, in the new state. A similar reasoning applies to the static cluster algorithm [22]. Without testing, we anticipate that the speeds of both versions of VMMC are comparable in the limit of high acceptance probability. If the cluster acceptance probability is low, selecting clusters via realizations with symmetric core and asymmetric boundary should be faster because nearest neighbors in the new state do not need to be detected, provided the boundary contains a frustrated failed link. An advantage of the alternative version of the algorithm is that it may be simpler to implement, and allows us to simply accept clusters, which would have otherwise been rejected, through the scheme derived in Sec. VI. The efficiency generally depends on system properties and simulation parameters. For example, if the maximum size of displacement in M is smaller than the attractive range, and (i,j) is not interacting in μ but does so in μ_i, then also $p^{(\mu)}_{i'j} = 0$ and the proposed link is outright failed. This means that links can only be proposed to the pairs interacting in μ, while still using the simplified acceptance probability (27). (Under the assumption of small displacements, proposing links to pairs interacting in μ_i does not affect the validity of the algorithm, but would slow it down.) Another example is a one-dimensional (1D) system with short-range attractions, where the boundary of the cluster is given by at most two pairs (corresponding to two border particles of $\mathcal{C}$). The set $\mathcal{B}^{(\overline{\mu}\nu)}$ thus only includes neighbors of these two particles; neighbors of other particles in $\mathcal{C}$ can be omitted, and we can therefore expect the original version being faster than the reformulated version.

An alternative version and the original version of the symmetrized VMMC algorithm were again proved via the use of the SDB condition, but with realization of the cluster defined as the set of all pairs to which a link is proposed during the cluster selection. It was shown that translational and rotational cluster moves, with clusters selected by the recursive stochastic linking proposed to nearest neighbor pairs, can not generally possess a unique realization because the set of pairs to which a link is proposed under the forward move is not the same as the set of pairs to which a link is proposed under the reverse move. This problem, which can be related to the unsolved task of enumerating the number of independent graphs in Monte Carlo cluster algorithms [29], was described here in terms of the asymmetric core or boundary of the cluster (Sec. I) and can be briefly summarized as follows. If links are proposed only to pairs interacting in the original state, the set of proposed links internal to the cluster is the same in the old and in the new state, but the sets of pairs to which a link is proposed and which end up in the boundary are generally different. The realization has a symmetric core but an asymmetric boundary in this case. If links are proposed to pairs interacting in the original or in the virtual state, the set of pairs in the boundary of the cluster is the same, however, the sets of pairs internal to the cluster are generally different. The realization then has a symmetric boundary but an asymmetric core. These iterative selection rules thus do not generally yield realizations which would have symmetric core and boundary at the same time. The SDB condition, imposed on the realization of the cluster, was thus formulated differently in terms of the free cluster selection, where links were proposed to all pairs satisfying conditions (1a) and (1b). Realizations are then guaranteed to have both symmetric boundary and symmetric core, and the SDB condition can be formulated exactly. It is then shown that under certain assumptions, not proposing pairs to all (1a) and (1b), but only to certain pairs, does not affect the validity of the algorithm.

Let us relate the notion of symmetric boundary and symmetric core to other cluster algorithms [3,4,22]. In the Wolff cluster algorithm, the realization of the cluster has both symmetric core and symmetric boundary. The SDB condition can thus be imposed on the realization of $\mathcal{C}$ without any ambiguity. The symmetry of the core and boundary in the Wolff cluster algorithm follows from the fact that spins are flipped and stay at one lattice position, rather than being moved from one lattice position to another. The symmetry of the realization is also preserved in the translational cluster algorithm for charged lattice spin systems [4]. This is because the spins are linked with probability one, if they are close enough, and fail to form otherwise. A consequence of this

deterministic linking is that there are no such spins (particles) j outside the cluster to which a link would be proposed in one state and not in another state, and the requirement about equal chances of selecting the pairs at each step of the recursive selection is naturally satisfied by the definition of this linking probability. We note that the same authors proposed a possible extension of their theory to stochastic linking, without further specifying the exact rules of the cluster selection. If the selection of the cluster was recursive following random or isotropic ordering, the stochastic linking would lead to realizations of clusters having asymmetric boundaries, and considerations similar to those presented in this paper would be needed to validate the algorithm. In the algorithm of Troisi and Bhattacharyay [22,30], the links are not proposed in a recursive way, but to all pairs of the system. For each state μ this leads to the definition of a square matrix with elements given by $p_{ij}^{(\mu)}$, $i,j = 1,\ldots,N$. The cluster is then detected as those particles which are at least singly joined by links. This selection leads to a cluster acceptance probability which is, indeed, biased exactly by the energy change on the boundary of the cluster. In practice, the authors do not consider the entire matrix $p_{ij}^{(\mu)}$, but only a part of it by a recursive process described above in this paper. In fact, restriction of the whole matrix to only a part of it, used to validate their algorithm, is very similar to the restriction of pair selection by condition (1c) used to derive the acceptance probability in the VMMC.

We will now point out a weak point in our tests performed to numerically validate the VMMC. Figure 3(a) shows that the radial distribution function of a generalized Lennard-Jones fluid is within the error range of the radial distribution function obtained by a single-particle MC. We have thus verified that the VMMC samples the fluid phase within the accuracy of the single-particle MC. Although we performed these tests for square-well and 36-18 LJ fluids at different conditions, we emphasize that the probability of generating or accepting a cluster decreases exponentially with cluster size, and that the dominant moving cluster size is one or two particles. The contribution of larger clusters to the total number of accepted clusters is thus negligible, and large cluster moves are likely to have only a very little effect on generating an equilibrium MC chain. It would thus be appropriate to perform tests on an equilibrium (ergodic) system where the dominant moving cluster size is significantly higher than one particle. The simplest example of such systems might be particles with short-range attractions and long-range repulsions at a suitable $\epsilon/k_{\mathrm{B}}T$. Those systems were proved to form stable cluster phases [28,31], and we have observed that a suitably chosen displacement can indeed lead to a dominant moving cluster size larger than 1 (and smaller than N). We have not compared the radial distribution function with a radial distribution function of a single-particle MC because we know that the latter equilibrates those systems too slowly. Another nonlocal algorithm such as aggregation volume bias MC [32] would be needed in order to sample the configurational space of an equilibrium cluster phase. At sufficiently low densities such that structural arrest does not take place [31], this might then be used in a very long simulation, to verify that the cluster algorithm samples from the Boltzmann distribution even when the dominant clusters are large. These tests were not performed here. In addition to the 3D tests, we did 1D continuum model tests similar to the 1D lattice model tests of Ref. [22]. Our continuum model tests matched the analytical result [33] exactly. We emphasize that one-dimensional tests are necessary but not sufficient to validate the SDB condition because there is only one realization or one sequence of proposed links selecting the one-dimensional moving cluster. We thus conclude that although our tests confirm the validity of VMMC in the limit of small clusters, they do not provide strong numerical evidence that the algorithm is valid for large moving clusters, and in that limit we can only rely on analytical considerations deriving the VMMC. We stress that other unpublished tests [24] have been performed [14] comparing VMMC with molecular dynamics simulations in systems where collective motion is important.

We will now address a more general aspect of the algorithm. The form of the linking probability in Eq. (16) implies that no links and hence no clusters are formed as a result of a repulsive interaction ($\epsilon_{ij}^{(\mu)} = 0, \epsilon_{i'j}^{(\mu)} > 0$). In our future publication [18], we will show a general way of linking the particles and accepting the relevant collective translational and rotational MC moves, which is applicable to any form of pairwise interaction, including hard-core repulsion. Although this can also be done by fictitious potentials [21], the general linking is different in that it proposes links to pairs interacting in the virtual state corresponding to $\epsilon_{ij'}^{(\mu)}$, and defines general properties of the linking function. We also mention that new event-based rejection-free MC algorithms have recently been formulated for general potentials. First, event-chain Monte Carlo [34,35] displaces chains of particles in an efficient way. Second, event-driven Monte Carlo [36] displaces single particles, but selects and accepts them in a way which is dynamic. It would be interesting to see how these algorithms complement the VMMC methods in capturing the kinetic and thermodynamic crossover in glassy systems [26,37].

This paper aimed to clarify the way of creating collective translational and rotational Monte Carlo moves, based on local pairwise energy changes, and to shed more light on the technical details, as well as to provide a clear validation of the algorithm. Apart from the tests of the MSD in Fig. 3, Stokesian or Brownian scaling was not considered here because it requires us to approximate a MC sweep composed of collective rotations and translations with a time step. Presentation and tests of these approximations are outside the scope of this paper. Nevertheless, it is worth mentioning that one of the main reasons for the asymmetric boundary in the original version of the symmetrized VMMC was to speed up the generation of proposed clusters because a large fraction of them are rejected immediately without any chance of being accepted. This is done for clusters exceeding a certain size in order to approximate the real dynamics. Section VI provides a scheme controlling the cluster size, the advantage of which is that its acceptance rate is potentially higher than in the case of purely rejecting the clusters. Approximation of the dynamics by this scheme is an example situation where the alternative formulation of the VMMC algorithm (Secs. V and VI) might naturally outperform the original scheme (Sec. VIII and Ref. [9]) because more generated clusters can be accepted. Higher acceptance rate is, indeed,

desirable in MC schemes approximating Brownian or other dynamics [38]. Moreover, the size distribution of proposed clusters is strongly correlated with the maximum size of the Monte Carlo map M. We can speculate that to generate a realistic distribution of moving accepted clusters might be additionally tweaked, for example, by drawing the size of the Monte Carlo map M not from a uniform but from an optimized (possibly Gaussian) distribution such that the distribution of proposed and accepted cluster sizes ends up being closer to the distribution in a real dynamics.

XIII. CONCLUSION

We have formally described and analyzed the symmetric version of the VMMC algorithm and made additional numerical tests. The early-rejection scheme is explicitly used to show that the algorithm samples from the Boltzmann distribution, while treating the superdetailed balance condition in another way. To clarify the theory behind the algorithm, we have presented an alternative formulation of the VMMC algorithm which has a simple acceptance form. The main advantage of this reformulated scheme is that it provides an easy way of accepting clusters which would otherwise be rejected. This may find its use in controlling the cluster size distribution, but also in the implementation of kinetically realistic rotational moves. We anticipate that the original formulation of the symmetrized VMMC is still the fastest, but system- and simulation-dependent exceptions might exist.

We close by briefly mentioning an application of interest, which constitutes work in progress. Similarly to what was originally reported [9], our preliminary results show that the VMMC algorithm is particularly useful in predicting the gelation boundary of low- and intermediate-density short-ranged attractive systems below the critical point [27], where the density fluctuations [39], phase separation [40], or spinodal decomposition [41] lead to the formation of metastable droplets, fractal aggregates, or even stable clusters [28,31]. The cluster moves enhance the mobility of those structures which can kinetically slow down (arrest) and form glasses or gels. Our preliminary results, which will be published elsewhere, or results of Ref. [9] which report the effect of collective motion on gelation, are restricted to a narrow range of system parameters $(\rho,\epsilon/k_{\mathrm{B}}T,\alpha)$, determining the onset of gelation. Other simulation parameters, including the optimum displacement size, the simulation ensemble, particle shape, or the quench or compression (crunch) rate [42], may also affect the structure of the gel. One can thus imagine a whole class of possible studies examining the affect of collective motion on gel formation, or crystallization, in attractive colloidal or molecular systems, making use of cluster algorithms of this kind.

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APPENDIX A: INCONSEQUENTIAL NATURE OF THE ASYMMETRIC CORE IN SEC. V

In this appendix, we show why the asymmetric core of the realization of the cluster, in the algorithm of Sec. V, does not matter. Let us now assume that $R_{\mathcal{C}}^{(\mu)}$, with $\mathcal{L}^{(\mu)}$, $\mathcal{F}^{(\mu)}$, $\mathcal{B}^{(\mu)}$, is the realization of $\mathcal{C}$, generated by the restricted recursive selection of Sec. V.

Let (i,j) be a pair from $\mathcal{L}^{(\mu)}$. Any such pair is interacting in μ or in μ_i, and it must hold that $i \in \mathcal{C}$, $j \in \mathcal{C}$, $p_{ij}^{(\mu)} > 0$. We start with the trivial case: if (i,j) is interacting in μ, then (i,j) is interacting in ν, and a link is, indeed, proposed to that pair in ν. If (i,j) is not interacting in μ, but interacting in μ_i, then, with the aid of Eq. (21), we can write

$$p_{ij}^{(\mu)} = \min\left\{p_{i'j}^{(\mu)}, p_{ij'}^{(\mu)}\right\} = p_{ij}^{(\nu)} > 0. \tag{A1}$$

Equations (6), (15a), and (15b) then imply that $\epsilon_{i'j}^{(\nu)} > 0$ [(i,j) is interacting in ν_i], and hence that a link can also be proposed to (i,j) in state ν. Hence, given $\mathcal{L}^{(\mu)}$ in $R_{\mathcal{C}}^{(\mu)}$, we can assume the existence of $\mathcal{L}^{(\nu)}$ such that $\mathcal{L}^{(\nu)} = \mathcal{L}^{(\mu)}$.

Let (i,j) be a pair from $\mathcal{F}^{(\mu)}$. We distinguish between two cases, and decompose $\mathcal{F}^{(\mu)}$ as

$$\mathcal{F}^{(\mu)} = \mathcal{F}^{*(\mu)} \cup \mathcal{F}^{\dagger(\mu)}, \tag{A2}$$

where $\mathcal{F}^{\dagger(\mu)}$ denotes pairs (i,j) not interacting in μ but interacting in μ_i such that $p_{ij}^{(\mu)} = 0$. The set $\mathcal{F}^{*(\mu)}$ then denotes all other pairs in $\mathcal{F}^{(\mu)}$, and is thus composed either from pairs which interact in μ, or from pairs which do not interact in μ, but interact in μ_i such that $p_{ij}^{(\mu)} > 0$. Considerations, similar to those done for $\mathcal{L}^{(\mu)}$, imply that there exists $\mathcal{F}^{*(\nu)}$ such that $\mathcal{F}^{*(\nu)} = \mathcal{F}^{*(\mu)}$. However, it is generally not guaranteed that if (i,j) is from $\mathcal{F}^{\dagger(\mu)}$, then (i,j) $(i,j \in \mathcal{C})$ is also interacting in ν_i.

The fact that for each $\mathcal{B}^{(\mu)}$ there exists $\mathcal{B}^{(\nu)}$ such that $\mathcal{B}^{(\nu)} = \mathcal{B}^{(\mu)}$ follows from the properties of the cluster selection conditions (1), from the existence of $\mathcal{L}^{(\nu)} = \mathcal{L}^{(\mu)}$, and from the fact that if a boundary pair is interacting in μ or in μ_i, it is also interacting in ν or in ν_i. We have thus shown that it is only due to $\mathcal{F}^{\dagger(\mu)}$ that pairs to which a link is proposed in states μ can not be guaranteed to be the same in ν, and we can not ensure the existence of $R_{\mathcal{C}}^{(\nu)}$ such that $R_{\mathcal{C}}^{(\nu)} = R_{\mathcal{C}}^{(\mu)}$. Nevertheless, identity (14) implies that any pair proposed to $\mathcal{F}^{\dagger(\mu)}$ has no chance to form in state ν, and we can assume that a link was proposed to that pair although it was actually not. Hence, the set of pairs to which a link is proposed in the recursive selection of the cluster can in practice be assumed to be the same. The restricted cluster selection can be seen to be equivalent to the free cluster selection, in other words, the cluster can be accepted with probability given by Eq. (27), even if the links are only proposed to pairs interacting in μ or in μ_i, and not to all pairs satisfying (1a) and (1b).

APPENDIX B: DERIVATION OF THE ACCEPTANCE PROBABILITY OF THE ALGORITHM OF SEC. VIII

To derive the bias in the cluster acceptance probability needed to correct the asymmetry of the realization of a cluster selected by the procedure described in Sec. VIII, we define the

linking probabilities as

$$P_{i'j}^{(\mu)} = I_{ij}^{(\mu)} p_{i'j}^{(\mu)}, \quad Q_{i'j}^{(\mu)} = 1 - P_{i'j}^{(\mu)}, \tag{B1}$$

where $I_{ij}^{(\mu)} = 1$, if (i,j) is interacting in μ, and $I_{ij}^{(\mu)} = 0$, if (i,j) is not interacting in μ.

For simplicity, we assume again that $R_{\mathcal{C}}^{(\mu)}$ is a realization resulting from the free recursive selection of $\mathcal{C}$, but using the linking probabilities (B1). Since the probabilities (B1) satisfy relations (3a) and (3b), one can assume the existence of $R_{\mathcal{C}}^{(\nu)}$ such that $R_{\mathcal{C}}^{(\nu)} = R_{\mathcal{C}}^{(\mu)}$, allowing us to require the SDB between $R_{\mathcal{C}}^{(\mu)}$ and $R_{\mathcal{C}}^{(\nu)}$, and then simplify the acceptance probability, in a similar way as in Sec. IV, into the form

$$W_{\mathrm{acc}}^{(\mu\to\nu|R)} = \min\left\{1, \exp[-\beta(E_\nu - E_\mu)] \frac{\prod_{(i,j)\in\mathcal{B}^{(\nu)}} Q_{i'j}^{(\nu)}}{\prod_{(i,j)\in\mathcal{B}^{(\mu)}} Q_{i'j}^{(\mu)}}\right\}. \tag{B2}$$

The Rosenbluth factor in Eq. (B2) can be simplified as follows. Let us decompose the boundary of $\mathcal{C}$ into

$$\mathcal{B}^{(\mu)} = \mathcal{B}^{(\mu\nu)} \cup \mathcal{B}^{(\overline{\mu}\nu)} \cup \mathcal{B}^{(\mu\overline{\nu})} \cup \mathcal{B}^{(\overline{\mu}\overline{\nu})}, \tag{B3}$$

where $\mathcal{B}^{(\mu\nu)}$ are pairs from $\mathcal{B}$ which interact both in states μ and ν, $\mathcal{B}^{(\overline{\mu}\nu)}$ are boundary pairs which do not interact in μ but interact in ν, $\mathcal{B}^{(\mu\overline{\nu})}$ are boundary pairs which interact in μ but not in ν, and $\mathcal{B}^{(\overline{\mu}\overline{\nu})}$ are boundary pairs which do not interact both in μ and in ν. Boundary $\mathcal{B}^{(\nu)}$ in state ν can be decomposed similarly. Equation (7) and definition (8) then imply that

$$\Delta\epsilon_{i'j}^{(\mu)} = -\Delta\epsilon_{i'j}^{(\nu)} \quad \forall\,(i,j) \in \mathcal{B}^{(\mu\nu)}, \tag{B4a}$$

$$\Delta\epsilon_{i'j}^{(\nu)} = -\epsilon_{ij}^{(\nu)} \quad \forall\,(i,j) \in \mathcal{B}^{(\overline{\mu}\nu)}, \tag{B4b}$$

$$\Delta\epsilon_{i'j}^{(\mu)} = -\epsilon_{ij}^{(\mu)} \quad \forall\,(i,j) \in \mathcal{B}^{(\mu\overline{\nu})}. \tag{B4c}$$

Using Eq. (2), the total energy of the system in state μ can then be expressed as

$$E_\mu = \sum_{(i,j)\in\mathcal{L}^{(\mu)}} \epsilon_{ij}^{(\mu)} + \sum_{(i,j)\in\mathcal{F}^{(\mu)}} \epsilon_{ij}^{(\mu)} + \sum_{(i,j)\in\mathcal{B}^{(\mu\nu)}} \epsilon_{ij}^{(\mu)} + \sum_{(i,j)\in\mathcal{B}^{(\overline{\mu}\nu)}} \epsilon_{ij}^{(\mu)} + \sum_{(i,j)\in\mathcal{B}^{(\mu\overline{\nu})}} \epsilon_{ij}^{(\mu)} + \sum_{(i,j)\in\mathcal{B}^{(\overline{\mu}\overline{\nu})}} \epsilon_{ij}^{(\mu)} + \sum_{(i,j)\in\mathcal{X}^{(\mu)}} \epsilon_{ij}^{(\mu)}. \tag{B5}$$

Similarly, the total energy of $\mathcal{S}$ in state ν is

$$E_\nu = \sum_{(i,j)\in\mathcal{L}^{(\nu)}} \epsilon_{ij}^{(\nu)} + \sum_{(i,j)\in\mathcal{F}^{(\nu)}} \epsilon_{ij}^{(\nu)} + \sum_{(i,j)\in\mathcal{B}^{(\mu\nu)}} \epsilon_{ij}^{(\nu)} + \sum_{(i,j)\in\mathcal{B}^{(\overline{\mu}\nu)}} \epsilon_{ij}^{(\nu)} + \sum_{(i,j)\in\mathcal{B}^{(\mu\overline{\nu})}} \epsilon_{ij}^{(\nu)} + \sum_{(i,j)\in\mathcal{B}^{(\overline{\mu}\overline{\nu})}} \epsilon_{ij}^{(\nu)} + \sum_{(i,j)\in\mathcal{X}^{(\nu)}} \epsilon_{ij}^{(\nu)}. \tag{B6}$$

Since $\mathcal{L}^{(\mu)} = \mathcal{L}^{(\nu)}$, $\mathcal{F}^{(\mu)} = \mathcal{F}^{(\nu)}$, $\mathcal{X}^{(\mu)} = \mathcal{X}^{(\nu)}$, and $\epsilon_{ij}^{(\mu)} = \epsilon_{ij}^{(\nu)}$, for pairs (i,j) from these sets, we can express the energy difference as

$$E_\nu - E_\mu = \sum_{(i,j)\in\mathcal{B}^{(\mu\nu)}} \epsilon_{ij}^{(\nu)} - \sum_{(i,j)\in\mathcal{B}^{(\mu\nu)}} \epsilon_{ij}^{(\mu)} + \sum_{(i,j)\in\mathcal{B}^{(\overline{\mu}\nu)}} \epsilon_{ij}^{(\nu)} - \sum_{(i,j)\in\mathcal{B}^{(\mu\overline{\nu})}} \epsilon_{ij}^{(\mu)}, \tag{B7}$$

where we have also used the fact that

$$\sum_{(i,j)\in\mathcal{B}^{(\overline{\mu}\nu)}} \epsilon_{ij}^{(\mu)} = \sum_{(i,j)\in\mathcal{B}^{(\overline{\mu}\overline{\nu})}} \epsilon_{ij}^{(\mu)} = \sum_{(i,j)\in\mathcal{B}^{(\mu\overline{\nu})}} \epsilon_{ij}^{(\nu)} = \sum_{(i,j)\in\mathcal{B}^{(\overline{\mu}\overline{\nu})}} \epsilon_{ij}^{(\nu)} = 0.$$

Let us separate the terms in Eq. (B7) for which $\epsilon_{ij} > 0$ from those for which $\epsilon_{ij} \leqslant 0$, and identify the corresponding partial sums with $+$ and $-$, respectively, so that

$$E_\nu - E_\mu = \sum_{(i,j)\in\mathcal{B}^{(\mu\nu)}} \epsilon_{ij}^{(\nu)} - \sum_{(i,j)\in\mathcal{B}^{(\mu\nu)}} \epsilon_{ij}^{(\mu)} + \sum_{(i,j)\in\mathcal{B}^{(\overline{\mu}\nu)}}^{+} \epsilon_{ij}^{(\nu)} + \sum_{(i,j)\in\mathcal{B}^{(\overline{\mu}\nu)}}^{-} \epsilon_{ij}^{(\nu)} - \sum_{(i,j)\in\mathcal{B}^{(\mu\overline{\nu})}}^{+} \epsilon_{ij}^{(\mu)} - \sum_{(i,j)\in\mathcal{B}^{(\mu\overline{\nu})}}^{-} \epsilon_{ij}^{(\mu)}. \tag{B8}$$

Hence,

$$\exp[-\beta(E_\nu - E_\mu)] = \frac{\prod_{(i,j)\in\mathcal{B}^{(\mu\nu)}} \exp\left(-\beta\epsilon_{ij}^{(\nu)}\right)}{\prod_{(i,j)\in\mathcal{B}^{(\mu\nu)}} \exp\left(-\beta\epsilon_{ij}^{(\mu)}\right)} \frac{\prod_{(i,j)\in\mathcal{B}^{(\overline{\mu}\nu)}}^{+} \exp\left(-\beta\epsilon_{ij}^{(\nu)}\right)}{\prod_{(i,j)\in\mathcal{B}^{(\mu\overline{\nu})}}^{+} \exp\left(-\beta\epsilon_{ij}^{(\mu)}\right)} \frac{\prod_{(i,j)\in\mathcal{B}^{(\overline{\mu}\nu)}}^{-} \exp\left(-\beta\epsilon_{ij}^{(\nu)}\right)}{\prod_{(i,j)\in\mathcal{B}^{(\mu\overline{\nu})}}^{-} \exp\left(-\beta\epsilon_{ij}^{(\mu)}\right)}, \tag{B9}$$

where the $+$ and $-$ symbols have a meaning analogous to that in Eq. (B8). The next step is to decompose the products of link failure probabilities in (B2), in a similar way. Using Eq. (19), the ratio of products can be expressed as

$$\frac{\prod_{(i,j)\in\mathcal{B}^{(\nu)}} Q_{i'j}^{(\nu)}}{\prod_{(i,j)\in\mathcal{B}^{(\mu)}} Q_{i'j}^{(\mu)}} = \frac{\prod_{(i,j)\in\mathcal{B}^{(\nu)}}^{+} \exp\left(-\beta\Delta\epsilon_{i'j}^{(\nu)}\right)}{\prod_{(i,j)\in\mathcal{B}^{(\mu)}}^{+} \exp\left(-\beta\Delta\epsilon_{i'j}^{(\mu)}\right)} = \frac{\prod_{(i,j)\in\mathcal{B}^{(\mu\nu)}}^{+} \exp\left(-\beta\Delta\epsilon_{i'j}^{(\nu)}\right)}{\prod_{(i,j)\in\mathcal{B}^{(\mu\nu)}}^{+} \exp\left(-\beta\Delta\epsilon_{i'j}^{(\mu)}\right)} \frac{\prod_{(i,j)\in\mathcal{B}^{(\overline{\mu}\nu)}}^{+} \exp\left(-\beta\Delta\epsilon_{i'j}^{(\nu)}\right)}{\prod_{(i,j)\in\mathcal{B}^{(\mu\overline{\nu})}}^{+} \exp\left(-\beta\Delta\epsilon_{i'j}^{(\mu)}\right)}. \tag{B10}$$

Similar to the above, $+$ denotes products over those boundary pairs (i,j) for which the corresponding energy differences are positive, i.e., for which $\Delta\epsilon_{i'j}^{(\nu)} > 0$ or $\Delta\epsilon_{i'j}^{(\mu)} > 0$. An analogous notation is also used in what follows. By using Eq. (B4a), the first fraction in (B10) can be expressed as

$$\prod_{(i,j)\in\mathcal{B}^{(\mu\nu)}}^{+} \exp\left(-\beta\Delta\epsilon_{i'j}^{(\nu)}\right) \prod_{(i,j)\in\mathcal{B}^{(\mu\nu)}}^{-} \exp\left(-\beta\Delta\epsilon_{i'j}^{(\nu)}\right) = \prod_{(i,j)\in\mathcal{B}^{(\mu\nu)}} \exp\left(-\beta\Delta\epsilon_{i'j}^{(\nu)}\right) = \frac{\prod_{(i,j)\in\mathcal{B}^{(\mu\nu)}} \exp\left(-\beta\epsilon_{ij}^{(\mu)}\right)}{\prod_{(i,j)\in\mathcal{B}^{(\mu\nu)}} \exp\left(-\beta\epsilon_{ij}^{(\nu)}\right)}, \tag{B11}$$

and the second fraction in (B10) can be expressed as

$$\frac{\prod^{+}_{(i,j)\in\mathcal{B}^{(\overline{\mu}\nu)}}\exp\left(-\beta\Delta\epsilon^{(\nu)}_{i'j}\right)}{\prod^{+}_{(i,j)\in\mathcal{B}^{(\mu\overline{\nu})}}\exp\left(-\beta\Delta\epsilon^{(\mu)}_{i'j}\right)}=\frac{\prod^{-}_{(i,j)\in\mathcal{B}^{(\overline{\mu}\nu)}}\exp\left(\beta\epsilon^{(\nu)}_{ij}\right)}{\prod^{-}_{(i,j)\in\mathcal{B}^{(\mu\overline{\nu})}}\exp\left(\beta\epsilon^{(\mu)}_{ij}\right)}. \tag{B12}$$

Hence,

$$\frac{\prod_{(i,j)\in\mathcal{B}^{(\nu)}}\mathcal{Q}^{(\nu)}_{i'j}}{\prod_{(i,j)\in\mathcal{B}^{(\mu)}}\mathcal{Q}^{(\mu)}_{i'j}}=\frac{\prod_{(i,j)\in\mathcal{B}^{(\mu\nu)}}\exp\left(-\beta\epsilon^{(\mu)}_{ij}\right)}{\prod_{(i,j)\in\mathcal{B}^{(\mu\nu)}}\exp\left(-\beta\epsilon^{(\nu)}_{ij}\right)}\frac{\prod^{-}_{(i,j)\in\mathcal{B}^{(\overline{\mu}\nu)}}\exp\left(\beta\epsilon^{(\nu)}_{ij}\right)}{\prod^{-}_{(i,j)\in\mathcal{B}^{(\mu\overline{\nu})}}\exp\left(\beta\epsilon^{(\mu)}_{ij}\right)}. \tag{B13}$$

By combining expressions (B9) and (B13), the acceptance probability (B2) reduces to

$$W^{(\mu\to\nu|R)}_{\rm acc}=\min\left\{1,\frac{\prod^{+}_{(i,j)\in\mathcal{B}^{(\overline{\mu}\nu)}}\exp\left(-\beta\epsilon^{(\nu)}_{ij}\right)}{\prod^{+}_{(i,j)\in\mathcal{B}^{(\mu\overline{\nu})}}\exp\left(-\beta\epsilon^{(\mu)}_{ij}\right)}\right\}, \tag{B14a}$$

provided there is no frustrated link in the boundary $\mathcal{B}^{(\mu)}$. If $\mathcal{B}^{(\mu)}$ contains a frustrated link, the cluster is rejected, i.e.,

$$W^{(\mu\to\nu|R)}_{\rm acc}=0. \tag{B14b}$$

Expressions (B14) are identical to the original expression for the cluster move acceptance probability [9], although the notation here is slightly different. The notation here is more explicit, in that the product in the numerator runs only over those pairs in the boundary of $\mathcal{C}$ that are outside the interaction region in the original state, but end up in the interaction region in the final state. Again, this set of pairs is denoted by $\mathcal{B}^{(\overline{\mu}\nu)}$. Moreover, the notation also explicitly restricts the product to run only over those pairs in $\mathcal{B}^{(\overline{\mu}\nu)}$ such that $\epsilon^{(\nu)}_{ij}>0$. Similarly, the product in the denominator runs over boundary pairs (i,j) which are interacting in the original state but not interacting in the final state, and have $\epsilon^{(\mu)}_{ij}>0$.

Recall that Eq. (B14) was derived under the assumption of free cluster selection. Let us now restrict the class of pairs to which a link is proposed in the recursive selection of $\mathcal{C}$. If links are proposed only to pairs interacting in state μ, and $R^{(\mu)}_{\mathcal{C}}$ is the corresponding realization of $\mathcal{C}$, then it is clear that there exists a realization $R^{(\nu)}_{\mathcal{C}}$ such that $\mathcal{L}^{(\nu)}=\mathcal{L}^{(\mu)}$ and $\mathcal{F}^{(\nu)}=\mathcal{F}^{(\mu)}$; however, one can not expect $\mathcal{B}^{(\nu)}$ equal to $\mathcal{B}^{(\mu)}$. Since links proposed to pairs $\mathcal{B}^{(\nu)}\setminus\mathcal{B}^{(\mu)}$ or more generally to the corresponding subset of pairs $\mathcal{A}\setminus\mathcal{B}^{(\mu)}$ are doomed to fail by definition (B1), it is practical not to propose links to those pairs, i.e., to the pairs that do not interact in state μ. We can thus assume that links were proposed to all pairs (i,j), $i\in\mathcal{C}$, $j\notin\mathcal{C}$, although they were not, and we can still use the acceptance probability (B14). Note that to evaluate the denominator in Eq. (B14a), the set of pairs $\mathcal{B}^{(\nu)}\setminus\mathcal{B}^{(\mu)}$ still needs to be detected. Since $\mathcal{B}^{(\nu)}\setminus\mathcal{B}^{(\mu)}$ consists of pairs (i,j), $i\in\mathcal{C}$, $j\notin\mathcal{C}$, such that (i,j) is not interacting in μ but interacting in μ_i, the computational cost of this algorithm is comparable to the cost of the algorithm generating realizations of clusters with symmetric boundary and asymmetric core (Sec. V) in the limit of high cluster acceptance probability.

APPENDIX C: VALIDATION OF THE EARLY REJECTION SCHEMES

In what follows, we validate the early rejection schemes used in this paper in a way which is similar to that derived in Ref. [19] for a single-particle move.

1. Algorithm of Sec. IV

Here, we attempt to clarify why rejection of clusters selected via the free cluster selection, and having frustrated links in the boundary, does not violate sampling from the Boltzmann distribution. Let us first explain why clusters with frustrated boundary pairs are rejected. If a boundary pair is frustrated in μ under M, then $p^{(\mu)}_{i'j}>0$, and Eq. (9) implies that $p^{(\nu)}_{i'j}=0$, which means that (i,j) is necessarily outright failed in state ν under M^{-1}. It is thus impossible to construct the realization of $\mathcal{C}$ in state ν with the same boundary pair, which would be frustrated, and the cluster must be rejected. Now, pair (i,j) is frustrated in μ with probability lower than 1, and it might not be completely obvious why rejection of clusters with frustrated links in the boundary preserves the correct sampling. To demonstrate this more clearly, let us compare the cluster move acceptance probabilities for the early rejection scheme in a way which is analogous to Ref. [19]. It can be easily seen that the cluster move acceptance probability (27) is equivalent to the probability

$$W^{(\mu\to\nu|R)}_{\rm acc}=\prod_{(i,j)\in\mathcal{B}^{(\mu)}}q^{(\mu)}_{i'j}, \tag{C1}$$

which can be understood as the probability of not having any frustrated link in the boundary. Similarly, the acceptance probability for the reverse move can be written as

$$W^{(\mu\to\nu|R)}_{\rm acc}=\prod_{(i,j)\in\mathcal{B}^{(\nu)}}q^{(\nu)}_{i'j}. \tag{C2}$$

Since links between $(i,j), i,j\in\mathcal{C}$, can be seen to be selected to $\mathcal{C}$ with the same probability in states μ and ν, relation (26) implies that

$$\frac{W^{(\mu\to\nu|R)}_{\rm acc}}{W^{(\nu\to\mu|R)}_{\rm acc}}=\exp[-\beta(E_\nu-E_\mu)], \tag{C3}$$

which is what is expected in a valid early rejection scheme.

2. Algorithm of Sec. VI

We will show that rejecting the proposed clusters with frustrated links in the boundary, selected by the procedure described in Sec. VI, still leads to the correct sampling. We define the probability of accepting a realization $R_{\mathcal{C}}^{(\mu)}$ in a different way than in Eqs. (22) and (34) as

$$W_{\mathrm{acc}}^{(\mu\to\nu|R)} = \prod_{(i,j)\in\mathcal{B}^*}^{+} \exp\left(-\beta\Delta\epsilon_{i'j}^{(\mu)}\right) \min\left\{1, \prod_{(i,j)\in\mathcal{B}^\dagger} \exp\left(-\beta\Delta\epsilon_{i'j}^{(\mu)}\right)\right\}, \tag{C4}$$

which is easily seen to be equivalent to Eq. (34a). Indeed, the first product determines the probability of generating a boundary formed of outright failed links, and the second term (conditional upon the first) is the acceptance probability, provided $\mathcal{B}^*$ is without frustrated links. By using relation (8) we can express similarly the acceptance probability for the reverse move as

$$W_{\mathrm{acc}}^{(\nu\to\mu|R)} = \prod_{(i,j)\in\mathcal{B}^*}^{-} \exp\left(\beta\Delta\epsilon_{i'j}^{(\mu)}\right) \min\left\{1, \prod_{(i,j)\in\mathcal{B}^\dagger} \exp\left(-\beta\Delta\epsilon_{i'j}^{(\nu)}\right)\right\}. \tag{C5}$$

Now, it follows from Eq. (9) that

$$\text{if} \quad \prod_{(i,j)\in\mathcal{B}^\dagger} \exp\left(-\beta\Delta\epsilon_{i'j}^{(\mu)}\right) < 1, \quad \text{then} \quad \prod_{(i,j)\in\mathcal{B}^\dagger} \exp\left(-\beta\Delta\epsilon_{i'j}^{(\nu)}\right) > 1, \tag{C6}$$

$$\text{and if} \quad \prod_{(i,j)\in\mathcal{B}^\dagger} \exp\left(-\beta\Delta\epsilon_{i'j}^{(\mu)}\right) > 1, \quad \text{then} \quad \prod_{(i,j)\in\mathcal{B}^\dagger} \exp\left(-\beta\Delta\epsilon_{i'j}^{(\nu)}\right) < 1. \tag{C7}$$

Let us consider the case (C6); then Eqs. (C4), (C5), (29), and (31) imply that

$$\frac{W_{\mathrm{acc}}^{(\mu\to\nu|R)}}{W_{\mathrm{acc}}^{(\nu\to\mu|R)}} = \frac{\prod_{(i,j)\in\mathcal{B}^*}^{+} \exp\left(-\beta\Delta\epsilon_{i'j}^{(\mu)}\right) \prod_{(i,j)\in\mathcal{B}^\dagger} \exp\left(-\beta\Delta\epsilon_{i'j}^{(\mu)}\right)}{\prod_{(i,j)\in\mathcal{B}^*}^{-} \exp\left(\beta\Delta\epsilon_{i'j}^{(\mu)}\right)} = \prod_{(i,j)\in\mathcal{B}} \exp\left(-\beta\Delta\epsilon_{i'j}^{(\mu)}\right) = \exp[-\beta(E_\nu - E_\mu)], \tag{C8}$$

which is what must be valid in a correct early rejection scheme. One can show the same for the case (C7). This guarantees that the scheme samples from the Boltzmann distribution.

3. Algorithm of Sec. VIII

We now verify the validity of the early rejection scheme of the algorithm in Sec. VIII. It can be seen that the cluster move acceptance probability (B14) is equivalent to the probability

$$W_{\mathrm{acc}}^{(\mu\to\nu|R)} = \prod_{(i,j)\in\mathcal{B}^{(\mu)}} Q_{i'j}^{(\mu)} \min\left\{1, \frac{\prod_{(i,j)\in\mathcal{B}^{(\overline{\mu}\nu)}}^{+} \exp\left(-\beta\epsilon_{ij}^{(\nu)}\right)}{\prod_{(i,j)\in\mathcal{B}^{(\mu\overline{\nu})}}^{+} \exp\left(-\beta\epsilon_{ij}^{(\mu)}\right)}\right\}, \tag{C9}$$

which can be understood as the probability of accepting a cluster move, conditional upon not having any frustrated link in the boundary. Similarly, the acceptance probability for the reverse move can be written as

$$W_{\mathrm{acc}}^{(\nu\to\mu|R)} = \prod_{(i,j)\in\mathcal{B}^{(\nu)}} Q_{i'j}^{(\nu)} \min\left\{1, \frac{\prod_{(i,j)\in\mathcal{B}^{(\mu\overline{\nu})}}^{+} \exp\left(-\beta\epsilon_{ij}^{(\mu)}\right)}{\prod_{(i,j)\in\mathcal{B}^{(\overline{\mu}\nu)}}^{+} \exp\left(-\beta\epsilon_{ij}^{(\nu)}\right)}\right\}. \tag{C10}$$

By using Eqs. (B13) and (B9), and distinguishing between the two cases

$$\prod_{(i,j)\in\mathcal{B}^{(\mu\overline{\nu})}}^{+} \exp\left(-\beta\epsilon_{ij}^{(\mu)}\right) \leqslant \prod_{(i,j)\in\mathcal{B}^{(\overline{\mu}\nu)}}^{+} \exp\left(-\beta\epsilon_{ij}^{(\nu)}\right),$$

$$\prod_{(i,j)\in\mathcal{B}^{(\mu\overline{\nu})}}^{+} \exp\left(-\beta\epsilon_{ij}^{(\mu)}\right) > \prod_{(i,j)\in\mathcal{B}^{(\overline{\mu}\nu)}}^{+} \exp\left(-\beta\epsilon_{ij}^{(\nu)}\right),$$

one can show that

$$\frac{W_{\mathrm{acc}}^{(\mu\to\nu|R)}}{W_{\mathrm{acc}}^{(\nu\to\mu|R)}} = \exp[-\beta(E_\nu - E_\mu)], \tag{C11}$$

as desired.

[1] R. H. Swendsen and J. S. Wang, Phys. Rev. Lett. **58**, 86 (1987).
[2] F. Niedermayer, Phys. Rev. Lett. **61**, 2026 (1988).
[3] U. Wolff, Phys. Rev. Lett. **62**, 361 (1989).
[4] D. Wu, D. Chandler, and B. Smit, J. Phys. Chem. **96**, 4077 (1992).
[5] J. W. Liu and E. Luijten, Phys. Rev. Lett. **92**, 035504 (2004).
[6] J. W. Liu and E. Luijten, Phys. Rev. E **71**, 066701 (2005).
[7] S. Whitelam and P. L. Geissler, J. Chem. Phys. **127**, 154101 (2007).
[8] S. Whitelam and P. L. Geissler, J. Chem. Phys. **128**, 219901 (2008).
[9] S. Whitelam, E. H. Feng, M. F. Hagan, and P. L. Geissler, Soft Matter **5**, 1251 (2009).
[10] S. Whitelam, I. Tamblyn, P. H. Beton, and J. P. Garrahan, Phys. Rev. Lett. **108**, 035702 (2012).
[11] T. K. Haxton and S. Whitelam, Soft Matter **8**, 3558 (2012).
[12] J. Grant, R. L. Jack, and S. Whitelam, J. Chem. Phys. **135**, 214505 (2011).
[13] J. Russo, P. Tartaglia, and F. Sciortino, Soft Matter **6**, 4229 (2010).
[14] F. Romano, A. Hudson, J. Doye, T. E. Ouldridge, and A. A. Louis, J. Chem. Phys. **136**, 215102 (2012).
[15] N. S. Bieler, T. Knowles, D. Frenkel, and R. Vácha, PLoS Comput. Biol. **8**, e1002692 (2012).
[16] P. Šulc, F. Romano, T. E. Ouldridge, L. Rovigatti, J. Doye, and A. Louis, J. Chem. Phys. **137**, 135101 (2012).
[17] D. Fusco, J. J. Headd, A. De Simone, J. Wang, and P. Charbonneau, Soft Matter **10**, 290 (2014).
[18] Š. Růžička and M. P. Allen (unpublished).
[19] D. Frenkel and B. Smit, *Understanding Molecular Simulation: From Algorithms to Applications*, 2nd ed. (Academic, New York, 2002).
[20] D. Frenkel, Proc. Natl. Acad. Sci. USA **101**, 17571 (2004).
[21] S. Whitelam, Mol. Simul. **37**, 606 (2011).
[22] A. Troisi, V. Wong, and M. A. Ratner, J. Chem. Phys. **122**, 024102 (2005).
[23] T. Biyikoglu and J. Leydold, J. Comb. Theory, Ser. B **97**, 159 (2007).
[24] S. Whitelam (private communication).
[25] G. Vliegenthart, J. Lodge, and H. Lekkerkerker, Phys. A **263**, 378 (1999).
[26] R. L. Jack, M. F. Hagan, and D. Chandler, Phys. Rev. E **76**, 021119 (2007).
[27] T. Perez, Y. Liu, W. Li, J. Gunton, and A. Chakrabarti, Langmuir **27**, 11401 (2011).
[28] F. Sciortino, S. Mossa, E. Zaccarelli, and P. Tartaglia, Phys. Rev. Lett. **93**, 055701 (2004).
[29] W. Krauth, *Algorithms and Computations* (Oxford University Press, Oxford, UK, 2006).
[30] A. Bhattacharyay and A. Troisi, Chem. Phys. Lett. **458**, 210 (2008).
[31] P. Charbonneau and D. R. Reichman, Phys. Rev. E **75**, 050401 (2007).
[32] B. Chen and J. Siepmann, J. Phys. Chem. B **104**, 8725 (2000).
[33] R. H. Walmsley, J. Chem. Phys. **88**, 4473 (1988).
[34] E. P. Bernard and W. Krauth, Phys. Rev. E **86**, 017701 (2012).
[35] E. P. Bernard, W. Krauth, and D. B. Wilson, Phys. Rev. E **80**, 056704 (2009).
[36] E. A. J. F. Peters and G. de With, Phys. Rev. E **85**, 026703 (2012).
[37] D. Klotsa and R. Jack, Soft Matter **7**, 6294 (2011).
[38] E. Sanz and D. Marenduzzo, J. Chem. Phys. **132**, 194102 (2010).
[39] P. ten Wolde and D. Frenkel, Science **277**, 1975 (1997).
[40] G. Foffi, C. De Michele, F. Sciortino, and P. Tartaglia, J. Chem. Phys. **122**, 224903 (2005).
[41] P. Lu, E. Zaccarelli, F. Ciulla, A. Schofield, F. Sciortino, and D. Weitz, Nature (London) **453**, 499 (2008).
[42] P. Royall and A. Malins, Faraday Discuss. **158**, 301 (2012).