A parallel algorithm for implicit depletant simulations

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(Dated: 31 August 2015)

We present an algorithm to simulate the many-body depletion interaction between anisotropic colloids in an implicit way, integrating out the degrees of freedom of the depletants, which we treat as an ideal gas. Because the depletant particles are statistically independent and the depletion interaction is short-ranged, depletants are randomly inserted in parallel into the excluded volume surrounding a single translated and/or rotated colloid. A configurational bias scheme is used to enhance the acceptance rate. The method is validated and benchmarked both on multi-core CPUs and graphics processing units (GPUs) for the case of hard spheres, hemispheres and discoids. With depletants, we report novel cluster phases, in which hemispheres first assemble into spheres, which then form ordered hcp/fcc lattices. The method is significantly faster than any method without cluster moves and that tracks depletants explicitly, for systems of colloid packing fraction $\phi_c < 0.50$, and additionally enables simulation of the fluid-solid transition.

I. INTRODUCTION

The self-assembly of anisotropic particles into complex structures has emerged as a promising strategy towards the fabrication of materials with novel properties. Methods for the synthesis of anisotropic nano- and colloidal particles are becoming available, and enable experiments that study their phase behavior. Anisotropic particles, such as proteins, are also emerging building blocks for biomaterials. Simulations predict a wealth of different crystal structures that hard shapes form through maximization of entropy. In addition to particle shape, attractive interactions between patchy particles can be important in achieving desired target structures. Towards that end, the main routes that are actively being explored include surface functionalization of nanoparticles using short DNA molecules, and exploiting the depletion interaction between colloids in the presence of small polymer chains. Here we focus on the depletion interaction, since it is of entropic origin and arises without the need for engineering particle surface chemistry, emerging in mixtures of colloids with non-adsorbing polymer.

Depletion describes the emergent attraction between colloids in solution that maximize the free volume available to a small-particle cosolute via overlap of their excluded volume shells. It has been demonstrated that depletion enhances the directional entropic force resulting from anisotropic particle shape, and that it promotes the contact between large facets. The depletion interaction can promote binding between lock and key colloids and lead to the formation of porous phases. Because depletion mediates an additional attraction of entropic origin, this interaction can be thought of as competing with contact (excluded volume) interactions resulting from particle shape. Depletion thus enables novel phase behavior through the additional parameters of depletant shape and density. Therefore, it is desirable to have a method to investigate the self-assembly of anisotropic shapes in the presence of depletants. Results for the phase behavior of binary hard sphere mixtures have been reported using thermodynamic integration. In general, however, such results are challenging to obtain because of the size disparity between the colloid and the depletant. If one is interested in the phase behavior of the colloids, a customary approximation treats the depletant particles as an ideal gas. This approximation would, in principle, allow integrating out the depletant to arrive at an effective colloid-colloid interaction; however, the resulting interaction is a many-body interaction and we are not aware of any prior implementation that treats many-body effects exactly. Here, we propose a novel, parallel Monte Carlo algorithm to simulate the depletion interaction between arbitrarily shaped colloids in an efficient manner that includes many-body effects.

Figure 1 shows the effect of depletion interactions between two hard tetrahedra in solution with small penetrable hard spheres. The small spheres mediate an at-
tractive interaction between the colloids that drives them to aggregate face to face. For two particles only, the depletion interaction can be easily simulated explicitly (left panel) or implicitly (right panel). However, implicit simulation of depletion interactions allow for a tremendous performance benefit, particularly for dilute systems of colloids and high densities of depletants, as we demonstrate below.

This paper is organized as follows. In section II we discuss previous numerical methods for the simulation of depletion interactions. We describe our algorithm in section III and validate it against published data for hard spheres in the following section IV. Section V contains new results for depletants, obtained with the new algorithm. Finally, in Sec. VI we summarize and give an outlook on future applications of the method.

II. BACKGROUND

Previous numerical treatments of depletion interactions employ cluster moves. Biben, Bolhuis and Frenkel proposed a configurational bias approach\cite{Biben, Bolhuis, Frenkel}, where depletants overlapping with a moved colloid are reinserted to enhance the acceptance probability of colloid moves. A geometric cluster algorithm has also been proposed by Dress and Krauth\cite{Dress, Krauth}, which is rejection-free and can therefore greatly enhance the equilibration of dilute systems of colloids. However, when the system is dense in colloids, clusters can span the system and the algorithm ceases to be efficient\cite{Dress, Krauth}. To explore the phase behavior of a system of hard spheres in penetrable hard-sphere depletants, Vink and Horbach proposed grand-canonical simulation of both the colloids and the depletants, and they could efficiently sample the gas-liquid coexistence curve\cite{Vink, Horbach}. However, their scheme does not generalize well beyond to the fluid-solid transition, because it is based on particle insertion.

All these methods have in common that they track the small depletant particles explicitly, which are stored in memory. An interesting alternative was proposed by Dijkstra et al\cite{Dijkstra}, who proposed a Monte Carlo integration of the free volume around every single moved colloid. However, their scheme does not obey detailed balance, and achieving sufficient accuracy comes at the expense of computation time, as we discuss in more detail below. Another implicit implementation of the depletion interaction between octahedra was proposed by Henzie et al\cite{Henzie}, where the generally anisotropic many-body interaction is reduced to an isotropic pair potential. We note that such a drastic simplification, while rendering the problem computationally tractable, is insufficient to allow the study of arbitrary shapes.

The scheme we describe in the following section is a completely general treatment of depletion interactions between anisotropic particles due to an ideal gas of depletants, and works well both for dilute and dense systems. In the ideal gas treatment, depletants interact with colloids but not with each other. The algorithm is rigorous, i.e. it obeys detailed balance, and it can be efficiently implemented on multi-core processors and graphics processing units (GPUs).

III. DESCRIPTION OF THE ALGORITHM

A. Semigrand $N_T$VT ensemble

We simulate a semigrand ensemble of $N$ colloids in a grand-canonical bath of penetrable depletants of chemical potential $\mu_p$. The partition sum for the depletants is

$$e^{-\beta \Xi(\mathbf{r}_c, \mathbf{r}_p)} = \sum_{N_p=0}^{\infty} \frac{e^{\beta \mu_p N_p}}{N_p!} \int d^3 \mathbf{r}_p e^{-\beta H_{cc} - \beta H_{cp}} \tag{1}$$

$$= \sum_{N_p=0}^{\infty} \frac{e^{\beta \mu_p N_p}}{N_p!} \int d^3 \mathbf{r}_p e^{-\beta H_{cc}} V_f^{N_p} \tag{2}$$

where $V_f = V_f(\mathbf{r}_p)$ is the free volume available to depletants and $\lambda_p$ the thermal de Broglie wavelength associated with the depletants. We denote the colloid-colloid contribution to the Hamiltonian as $H_{cc} = \sum_{i,j\in\text{colloids}} U_{ij}$, where $U_{ij} = \infty$ for two colloids that overlap, and $U_{ij} = 0$ otherwise. The colloid-polymer contribution to the Hamiltonian $H_{cp}$ is defined analogously. Summation over the number $N_p$ of depletants in the system results in

$$e^{-\beta \Xi(\mathbf{r}_c, \mathbf{r}_p)} = e^{z_p V_f - \beta H_{cc}}, \tag{3}$$

where $z_p = \frac{e^{\beta \mu_p}}{\lambda_p}$ is the depletant fugacity.

B. Basic idea

Our central algorithmic result is the following Monte Carlo scheme to integrate the colloids under the action of the effective potential $H_{eff} \equiv -\beta^{-1} z_p V_f [\mathbf{r}_c, \mathbf{r}_p]$ occurring in Eq. (3). The basic idea of the algorithm, which we present here, is very simple, and we describe optimized versions of it in ensuing sections.

1. Propose a trial move for the colloids $M \rightarrow M'$.
2. Generate $N_p$ random depletant positions $\mathbf{r}_p^{(p)}$ uniformly in the free volume of the old configuration $M$, where $N_p$ is chosen according to $P_{z_p V_f} (N_p) \sim \text{Poisson}(V_f z_p)$, where Poisson($\lambda$) is the Poisson distribution of mean and variance $\lambda$. One possibility is to use rejection sampling in a larger volume $V_0 \gtrsim V_f$.
3. Reject the trial move if any depletant overlaps with the new colloid configuration $M'$, otherwise accept.
where the probability of surrounding colloids (light shaded square) are not considered. Depletants that overlap with the colloid in the old position or with only overlap volume at the old position are ignored. Depletants that overlap with the colloid in the old position or with surrounding colloids (light shaded square) are not considered.

In other words, we have an a priori move generation probability

$$P_{\text{trial}}^{(N_p)}(M \rightarrow M') = P_{\text{coll}}^{(M \rightarrow M')}(z_p V_f N_p^{f})$$

$$= P_{\text{coll}}^{(M \rightarrow M')}(z_p V_f N_p^{f}) e^{-z_p V_f},$$

where $P_{\text{coll}}^{(M \rightarrow M')}$ is symmetric in $\Delta \vec{r}_{c,i} \leftrightarrow -\Delta \vec{r}_{c,i}$. In Eq. (4), we have used the definition of the Poisson distribution $P_{z_p V_f}(N_p)$ with average $z_p V_f$, the number of depletants in the free volume. We impose the following acceptance probability

$$P^{(N_p)}_{\text{acc}}(M \rightarrow M') = \min(1, e^{-\beta \Delta H_{cc}}) e^{-\beta H_{cc}'(N_p)}.$$  

Figure 2 contains a graphical summary of the algorithm. Here, a square colloid is moved from configuration $M$ to configuration $M'$, by some translation and/or rotation, and depletants are placed in the free volume. As we detail below in Sec. III C, the sampling can be restricted to the circle (or sphere, in three dimensions) containing the colloid in the new colloid position. By using rejection sampling, any depletants falling into the excluded volume at the old position are ignored. Depletants that overlap only in the new configuration lead to a rejection of the colloid move.

Next, we show that the above scheme obeys detailed balance, which is required for correctly sampling the ensemble defined by Eq. (3) in the statistical sense. The transition probability $\pi$ from the old configuration $M$ to the new configuration $M'$ obeys

$$\pi_{M \rightarrow M'} = e^{-\beta \Pi(\vec{r}_{c,i})} P_{\text{trial}}^{(N_p)}(M \rightarrow M') P_{\text{acc}}^{(N_p)}(M \rightarrow M')$$

$$= e^{-\beta H_{cc} + \beta V_f} P_{\text{trial}}^{(M \rightarrow M')} (z_p V_f) N_p^{f}$$

$$\times e^{-z_p V_f} \min(1, e^{-\beta \Delta H_{cc}}) e^{-\beta H_{cc}'(N_p)}.$$

We require for detailed balance that $\pi_{M \rightarrow M'} = \pi_{M' \rightarrow M}$, and average over all realizations $(N_p, \{V_f^{N_p}\})$ of depletants, in the free volume $V_f$,

$$\lim_{N_p \rightarrow \infty} \int dV_f^{N_p} \frac{dV_f^{N_p}}{V_f^{N_p}} \pi_{M \rightarrow M'} = e^{-\beta H_{cc}} P_{\text{coll}}^{(M \rightarrow M')} e^{-\beta H_{cc}'(N_p)} \times \min(1, e^{-\beta \Delta H_{cc}})$$

$$\times \int dV_f^{N_p} \frac{dV_f^{N_p}}{V_f^{N_p}} e^{-\beta H_{cc}'(N_p)}.$$ 

Note that in order to obtain Eq. (7), we observe that the Poisson distribution is normalized in such a way so as to cancel out the depletant contribution, $e^{V_f z_p}$ to the ensemble weight. The integrand in the last line of Eq. (7) is non-zero exactly for $\vec{r}_{p,i} \in V_f^f$; hence, after performing the summation over $N_p$, the transition probability becomes

$$\pi_{M \rightarrow M'} = e^{-\beta H_{cc}} P_{\text{coll}}^{(M \rightarrow M')} \min(1, e^{-\beta \Delta H_{cc}}) e^{-z_p \mu(V_f \cap V_f^f)}$$

$$e^{-z_p \mu(V_f \cap V_f^f)},$$

where the volume $\mu(V_f \cap V_f^f)$ is the intersection of the free volume $V_f$ in the old configuration and the free volume $V_f^f$ in the new configuration. This term arises because of the symmetry of the Metropolis criterion,

$$e^{-\beta H_{cc} \min(1, e^{-\beta \Delta H_{cc}})} = e^{-\beta H_{cc} \min(e^{-\beta \Delta H_{cc}}, 1)}$$

and the symmetry property of the set intersection, the product in Eq. (8) is symmetric under the exchange $M \leftrightarrow M'$. Consequently, our integration scheme obeys detailed balance.

C. Improved formulation

The above integration scheme conveys the general idea of the algorithm. However, this algorithm is impractical to implement as is in an actual program, because it would require computation of the free volume $V_f$ in the entire simulation box for every single colloid move. Without loss of generality, we can restrict the sampling volume $V_f$ for depletants to a smaller volume $V_0 \supseteq V_f^c \setminus V_{\text{excl}}$, i.e. containing the excluded volume $V_{\text{excl}}$ of the colloids in the system in the new configuration minus the excluded volume $V_{\text{excl}}$ in the old configuration. The improved scheme is the same as the old scheme (Sec. III B), as are the move generation and acceptance probabilities, with the exception that $V_f$ is replaced by $V_f^c \setminus V_0$. The proof of detailed balance is only slightly more complicated for this algorithm.

We rewrite the ensemble weight

$$\Pi(\vec{r}_{c,i}) = e^{-\beta H_{cc} - \beta H_{cc}^f}$$

$$= e^{-\beta H_{cc} + \beta z_p V_f}$$

$$= e^{-\beta H_{cc} + \beta \mu(V_f \cap V_0) + \mu(V_f \cap V_0)},$$

(10)
where $V_0$ denotes the complement $V \setminus V_0$ with respect to the simulation volume $V$. Using Eq. (10), integrating over $V_0 \cap V_f$ and using transformations analogous to Eqs. (11)-(15), the transition probability $M \to M'$ averaged over the number of test depletants and their positions becomes

$$
\pi_{M \to M'} = e^{-\beta H_{cs}} \min \left(1, e^{-\beta \Delta H_{cs}}\right) \frac{P_{\text{trial}}(M \to M')}{e^{\beta \mu(V_f)}},
$$

(11)

It is straightforward to show that this transition probability is symmetric for forward and reverse moves. Since $V_0 \supseteq V_{\text{excl}} \setminus V_{\text{excl}}$, it follows that

$$
V_0 \subseteq V_{\text{excl}} \setminus V_{\text{excl}} \subseteq V_{\text{excl}} \cap V_{\text{excl}} = V_f \cap V_{\text{excl}}
$$

(12)

and therefore $V_0 = V_0 \cap (V_f \cup V_{\text{excl}})$. Hence, applying the distributive law,

$$
V_f \cap V_0 = V_f \cap V_0 \cap (V_f \cup V_{\text{excl}}) = V_f \cap V_0 \cap V_f
$$

(13)

because $V_f \cap V_{\text{excl}} = \emptyset$.

Using Eq. (13) we rewrite the transition probability Eq. (11) as

$$
\pi_{M \to M'} = e^{-\beta H_{cs}} \min \left(1, e^{-\beta \Delta H_{cs}}\right) \frac{P_{\text{trial}}(M \to M')}{e^{\beta \mu(V_f)}},
$$

(14)

and because the measures in the exponent are taken from disjoint sets we can simplify this equation as

$$
\pi_{M \to M'} = e^{-\beta H_{cs}} \min \left(1, e^{-\beta \Delta H_{cs}}\right) \frac{P_{\text{trial}}(M \to M')}{e^{\beta \mu(V_f)}}
$$

(15)

This is the same transition rate as Eq. (15), consequently our restricted sampling algorithm obeys detailed balance.

We may choose $V_0$ as the smallest region with $V_0 \supseteq V_{\text{excl}} \setminus V_{\text{excl}}$ that is convenient to sample from. E.g., we can sample in the excluded volume $V_{\text{excl},i}$ of the single moved colloid $i$ at the position of the new configuration $M'$ only, ignoring depletants that overlap with the colloid in the old configuration $M$. For anisotropic colloids, we will choose the circumsphere of diameter $d_{\text{colloid}} + d_{\text{depletant}}$ around the colloid in the new configuration, as done in Fig. 2.

We remark that a further possible optimization consists in restricting the sampling to the excluded volume shell of the moved colloid $V_{\text{excl},i} \setminus V_{\text{core},i}$, and it can be shown, using steps analogous to above, that such a choice also fulfills detailed balance.

D. Configurational bias moves

The algorithm described above gives finite acceptance rates for translation step sizes $\delta \lesssim z_p^{-1} R^{-2}$, where $R$ is the size of the colloid, which is in general anisotropic. However, when there is more than one depletant in the excluded volume shell around the colloid particle on average, moves will be rejected most of the time. Equilibration of colloids in very dense depletant systems is therefore difficult.

To ameliorate this situation, we apply the configurational bias move of Biben, Bolhuis and Frenkel\cite{biben1996, biben1997} to implicit depletants, the idea of which we briefly summarize. Figure 3 depicts the basic idea. For every depletant overlapping in the new configuration $M'$, we attempt to reinsert it $n_{\text{trial}}$ times such that it overlaps with the shape in the old configuration $M$, but does not overlap with any other colloid. Such a cluster move obeys detailed balance because when performing the reverse move from $M'$ to $M$, the reinserted colloid will overlap in the old configuration. To correct for the configurational bias generated in this way\cite{biben1996}, we modify the acceptance probability

$$
P_{\text{acc}} = \min \left(1, \prod_{i=1}^{n_{\text{overlap}}} \frac{N_{\text{insert},i}(N_i + 1)}{(N_{\text{insert},i} + 1) N_i} \right),
$$

(16)

in which $N_{\text{insert},i}$ and $N'_{\text{insert},i}$ are the number of times the overlapping depletant $i$ could be reinserted without overlap into the old and new configuration, respectively. The numbers $N_i, N'_i \leq n_{\text{trial}}$ count the valid insertion attempts in which the depletant overlaps with the moved shape in the old (new) configuration, without overlapping in the other. All other insertion attempts are ignored. The increment of one ($N_{\text{insert}} + 1$) is necessary because the depletant the colloid was overlapping with originally can be reinserted at old position and it can be ignored, the depletant the colloid was overlapping with originally can be reinserted at old position and it can be ignored.
E. Parallel implementation

An important feature of our algorithm is that the depletant insertions are independent and can be performed in parallel. We exploit this feature to implement the algorithm on the GPU. Some details of the GPU implementation are described in App. A.

In addition, depletants are inserted only in a local neighborhood of the particle, reflecting the short-ranged nature of the depletion interaction. This means the parallelization scheme for particle based Monte Carlo that has recently been introduced within the Hard Particle Monte Carlo (HPMC) framework\cite{34,35} in HOOMD-blue\cite{33,35} can be generalized to our implicit depletion algorithm. HPMC uses a checkerboard decomposition to allow parallelization of the MC simulation on a graphics processor (GPU). The checkerboard is colored in such a way that simultaneously active cells are separated by a layer of inactive cells of width $d_{\text{colloid}} + d_{\text{depletant}}$, which allows the active cells to be updated independently. Particles are not allowed to move outside their cells. The checkerboard coloring is permuted randomly. In order to maintain ergodicity, the grid lines are randomly shifted. HPMC also runs on the CPU, using an efficient tree-based particle data storage for overlap checks in combination with a sequential algorithm. Both the CPU and the GPU code path can be combined with spatial domain decomposition\cite{37} using the same same concept of an inactive layer for parallel execution. A reference implementation of the algorithm described in this paper will be released open-source as part of HOOMD-blue\cite{35}.

IV. VALIDATION

A. Equation of state of the penetrable hard sphere model

To validate our method, we compare results for hard spheres with the previously obtained results by Dijkstra et al.\cite{32} We note that even though their implicit algorithm for depletion does not obey detailed balance, it relies on minimizing errors from the violation of detailed balance through increasing the discretization of the MC integration step, which is a trade-off between accuracy and performance. In order to obtain an accurate equation of state, Dijkstra et. al had to restrict themselves to fairly small systems of $N = 128$ spheres. Fig. 1 compares results obtained with our algorithm (filled symbols) to those from Fig. 2 of Ref. \cite{32} (stars). We show the measured free volume fraction $\phi_p$ available to the penetrable hard spheres of same size, as a function of the reservoir volume fraction $\phi_p^r$ for different colloid volume fractions $\phi_c$ at constant simulation volume. For a system size of $N = 128$ colloids, our and Dijkstra’s results are in essentially perfect agreement, mutually validating both algorithms (top panel). However with our new algorithm we can easily perform simulations for a larger system of $N = 1000$ spheres. We do see slight deviations from the results for the $N = 128$ system (lower panel), particularly at high depletant reservoir densities $\phi_p^r$, indicating the presence of finite size effects for this system size.

B. Coexistence curve of the penetrable hard sphere model

We also tested the capability of our algorithm to equilibrate hard sphere systems at gas-liquid coexistence, and especially near the critical point. We carried out Gibbs ensemble simulations of hard spheres in penetrable hard sphere depletants\cite{10}. These types of simulations require insertion of the colloid at random positions in the simulation box, which is nearly impossible for high depletant fugacities. To overcome this difficulty, we resort to the configurational bias scheme discussed in Sec. \ref{sec:config-bias} and originally introduced in the context of the Gibbs ensem-
ble of hard spheres with depleting rods in Ref. [27]. For every exchange of a colloid between boxes, depletants are randomly inserted at the new position, and overlapping depletants are attempted to be reinserted in the old box. The move is accepted with the probability that accounts for the configurational bias weight.

In Fig. 5 we compare the coexistence curve thus obtained to published data by Vink and Horbach [31]. Those authors did not use the Gibbs ensemble, but performed direct simulation in the grand-canonical ensemble of the colloids and depletants in a single box. Their method is advantageous to sample the gas-liquid separation, which takes place at intermediate densities \( \phi_c \lesssim 0.4 \), because it relies exclusively on particle insertion and deletion at random positions in the simulation box. Thus, in this regime their scheme can be at least as efficient as single particle moves, if the particle deletions are combined with depletant insertions, and vice versa. However, the grand-canonical method is not easily applicable to solid phases, for which particle insertion in a crystal lattice is nearly impossible. Our method, in contrast, computes depletion interactions for single-particle translations and rotations.

As shown in Fig. 5 our data for the total system size \( N = 256 \), corresponding to the larger of the two system sizes studied by Vink and Horbach, generally reproduces their data for a depletant-colloid size ratio of \( q = 0.8 \), at which many-body effects are important. However, we see some scatter in our data, which is likely a consequence of surface effects that make it notoriously hard to study coexistence near the critical point in Gibbs ensemble simulation [31]. Vink and Horbach improved their sampling using the umbrella method and thermodynamic integration. Overall, however, our data obtained without using advanced free energy techniques is in agreement with the published data, validating the method.

V. RESULTS

A. Aggregation of hemispheres into superlattices

Equilibrium data of anisotropic particles aggregating into crystals with depletants is scarce [32]. Here, we present new results on the hierarchical assembly of hemispheres into FCC/HCP-cluster phases. Hard hemispheres for self-assembly have been the subject of previous investigations. Marechal and Dijkstra predicted the stability of a cluster-FCC (fcc\(^2\)) phase for hemispheres, but they were unable to find it in self-assembly simulations of sufficient size [33]. Cinacchi presented the phase diagram of hard spherical caps, which does not include an fcc\(^2\) phase [34]. Neither study involved depletants.

We analyze the phase behavior of hemispheres in the presence of penetrable hard sphere depletants. Figure 6 shows the kinetic phase diagram as a function of depletant reservoir density \( \phi^{r}_{p} \) and colloid density \( \phi_{c} \), for a depletant-hemisphere diameter ratio of \( q = 0.15 \). Remarkably, we observe the formation of the fcc\(^2\) and hcp\(^2\) phases at finite depletant densities \( \phi^{r}_{p} \geq 0.30 \), and the inset shows a snapshot of such a configuration of hemispheres. However, at zero depletant fugacity, which corresponds to the case studied previously, we did not observe any ordered phase, even after 6 \( \times \) 10\(^{8}\) MC sweeps. Instead, we find a cluster fluid. In the phase diagram, we find close-packed crystals with both HCP and FCC stacking, and we suspect the fact that both occur indicates that the free energy difference is small [35]. We compare the implicit method against two other schemes, an explicit grand-canonical ensemble for the depletants [36] and a canonical ensemble with fixed concentration of depletants. Figure 7 shows the number of hemisphere pairs that have formed after time \( t \). Because Monte Carlo simulations do not have a time scale, we choose the wall-clock time of the simulation as an ad-hoc measure of time. By analyzing bond order, we found that the time scale of crystallization corresponds to the time when all 512 hemispheres in the simulation box have paired up. This event occurs earliest for the implicit depletion algorithm. The simulation with explicit grand-canonical depletants also orders at a later time. However, the simulation with fixed number of depletants does not equilibrate into an ordered phase within the wall-clock time limit of 48h or 7.8 \( \times \) 10\(^{7}\) sweeps. Our findings show that the implicit algorithm leads to the fastest assembly of hemispheres into cluster crystal phases.
The effect of increasing the step size due to a higher additional effort to carry out the depletant reinsertions, while drops off slowly, as a result of the increased computational bias moves. The effect is dramatic and similar in orders of magnitude compared to not using configurational bias moves. The upper panel of Figure 8 shows the effect of $n_{\text{trial}}$ on the diffusivity $D$ of discoids. The colloid particles are uniaxial ellipsoids with semi axes $a = b = 0.5$ and $c = 0.25$, the depletants are of radius $r = 0.25$, and the simulations are performed in a dilute system at colloid density $\phi_c = 0.01$ and depletant reservoir density $\phi^*_p = 0.40$, below the coexistence density for metastable clusters. From the graph, it can be clearly seen that using configurational bias moves with a modest value of $n_{\text{trial}} \gtrsim 10$ speeds up the equilibration by almost three orders of magnitude compared to not using configurational bias moves. The effect is dramatic and similar in magnitude between running the simulation on the CPU vs. the GPU. At peak diffusivity, there is a slight advantage to using the GPU, compared to CPU socket performance. For higher values of $n_{\text{trial}}$, the performance drops off slowly, as a result of the increased computational effort to carry out the depletant reinsertions, while the effect of increasing the step size due to a higher acceptance ratio is weaker. We note that we carried out simulations with finite values of $n_{\text{trial}}$ at higher colloid densities as well (data not shown) and found the effect to be less pronounced at these densities.

We further measure the performance at different colloid densities $\phi_c$ between the dilute regime and the regime of a dense liquid, for the same parameters as above, with $n_{\text{trial}} = 0$ (Fig. 8 lower panel). For simulations with implicit depletants, either using the CPU or the GPU, the performance depends only slightly on the colloid volume fraction, directly confirming the beneficial effect of implicit calculation of the interaction in the dilute system, where the number of depletants would be very high with an explicit treatment. Indeed, the performance of the explicit depletant simulations in the grand-canonical ensemble drops noticeably when going from $\phi_c = 0.50$ towards lower densities, and the system becomes practically impossible to equilibrate when $\phi_c < 0.30$. Looking at GPU vs. CPU performance, we note that GPUs are advantageous for very dilute systems, but do not provide better performance when the system is dense in colloids. This is because the checkerboard parallelization scheme implemented for performing the colloid moves on the GPU (Sec. III E and Ref. 35) requires a large simulation box to operate efficiently.
We see applications for our method in the simulation of anisotropic colloid phase behavior. Even without depletants, polyhedra have been shown to order into a multitude of different structures\cite{22}. With depletion interactions, additional phases can be stabilized\cite{21,21,23}. The algorithm can also be used to study the aggregation of entropically patchy colloids into colloidal polymer chains, held together by strong depletion bonds\cite{22}. In this context, it would be interesting to study solutions as well as melts of such colloidal polymers. An interesting open question concerns whether depletant entropy can stabilize not only close-packed but also open ordered structures\cite{22}. In protein crystallization, depletant polymers are commonly used as precipitants. An important limitation of our algorithm is that it treats only non-interacting depletants, and the validity of that approximation remains to be investigated for specific systems. In contrast to enthalpically patchy models, our algorithm does not require implementation of shape-specific attractive patches to study aggregation of colloids, and the algorithm is therefore highly robust and generic.

**ACKNOWLEDGMENTS**

We are thankful to Werner Krauth for a discussion that led to the development of this algorithm. We also thank Michael Engel for fruitful discussions and careful reading of the manuscript.

This material is based upon work supported in part by the U.S. Army Research Office under Grant Award No. W911NF-10-1-0518 and by a Simons Investigator award from the Simons Foundation to Sharon Glotzer. This research used the Extreme Science and Engineering Discovery Environment\cite{45} (XSEDE), which is supported by National Science Foundation grant number ACI-1053575; XSEDE award DMR 140129. The Glotzer Group at the University of Michigan is an NVIDIA GPU Research Center. Hardware support by NVIDIA Corp. is gratefully acknowledged.

**Appendix A: GPU implementation**

In the GPU implementation, we perform the colloid trial moves in the active cell\cite{49} and the depletant insertions in different kernels. To insert depletants, we draw a random number of depletants for every moved colloid, as described in Sec. III B. We use a one-to-one mapping between depletants and thread groups of size \(n \leq n_{\text{max}}\). Here, \(n_{\text{max}} = 32\) is the maximum number of threads that can perform overlap checks synchronously, and we tune \(n\) at run-time. When any thread detects an overlap between the depletant and any particles in the old configuration, the depletant is ignored. In the other case, if the depletant overlaps with the moved colloid, that colloid move is flagged for rejection.
When the configurational bias scheme is used ($\text{trial} > 0$), a second kernel with a similar thread mapping is launched, however,-deletants are assigned to whole thread blocks of size $s \leq 1024$, which is an auto-tuned parameter, so that the bias weights of different reinsertions belonging to the same depletant can be summed in shared memory.

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