Designing colloidal ground state patterns using short-range isotropic interactions

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Abstract

DNA-coated colloids are a popular model system for self-assembly through tunable interactions. The DNA-encoded linkages between particles theoretically allow for very high specificity, but generally no directionality or long-range interactions. We introduce a two-dimensional lattice model for particles of many different types with short-range isotropic interactions that are pairwise specific. For this class of models, we address the fundamental question whether it is possible to reliably design the interactions so that the ground state is unique and corresponds to a given crystal structure. First, we determine lower limits for the interaction range between particles, depending on the complexity of the desired pattern and the underlying lattice. Then, we introduce a 'recipe' for determining the pairwise interactions that exactly satisfies this minimum criterion, and we show that it is sufficient to uniquely determine the ground state for a large class of crystal structures. Finally, we verify these results using Monte Carlo simulations.

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I. INTRODUCTION

Micrometer-sized colloidal particles have the desirable property that they are small enough to undergo thermal motion, yet large enough to be accessible to direct manipulation and controlled fabrication. This makes them into an ideal class of systems to investigate the relation between particle interactions and the large-scale properties of the structures they form. Rather than the traditional approach of determining the nature of the interactions between particles in existing materials and reconstructing the material properties from these interactions, we can now attempt to use tailor-made colloidal particles to *design* new materials. The question then becomes whether the interactions between particles can be chosen in such a way that they form a system with the required emergent properties. Because the desired interactions (inputs) are determined for a given system (output), this approach has also been named 'inverse' statistical-mechanics (see [1] for a recent overview).

A promising model system for particles with extensively tunable interactions is that of DNA-coated colloids. In this system, first proposed by Mirkin *et al.* [2], DNA is grafted onto micro-meter-sized colloids. The two strands forming the DNA are designed to differ slightly in length, so that a short stretch of single stranded DNA is exposed at the far end of the strand. This creates what is called a 'sticky' end, to which another single DNA strand can bind through hybridization. The multitude of possible binding sequences provided by DNA's four-letter alphabet combined with the specificity of base pair binding means that the binding affinity can be precisely manipulated. This specificity is not limited to a single pair of DNA strands, but pairwise-specific interactions can be defined simultaneously for a large number of sticky ends. In principle, it is possible to create a system with many different types of colloids, each of which has tunable interactions with every other type of colloid. The sticky ends of two different colloids can either bind directly (see figure 1), or mediated by a piece of linker DNA that has preferential affinities for both types of colloids. The latter provides more flexibility to control the interactions in the system, especially when many colloids with different sticky ends are involved. The ultimate goal of the research on DNA-coated colloids is to design materials that will, in the proper circumstances, self-assemble from their constituents.

The range of possibilities offered by DNA-mediated interactions is fundamentally different from electrostatic interactions, for which the control is limited to the sign, strength and
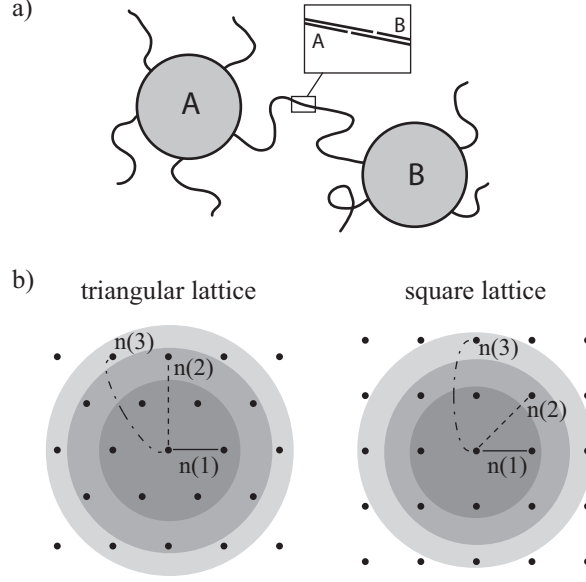
Figure 1: a) Schematic overview of colloid-colloid binding through DNA interactions. b) Overview of the nearest neighbor ($n(1)$), next-nearest neighbor ($n(2)$) and next-next-nearest neighbor ($n(3)$) interactions on triangular and square lattices.

range of the interactions without further possibilities for discrimination. Patterns composed of charged colloids are therefore generally limited to two colloidal species (see, for example [3]). Arguably, the potential of DNA-mediated interactions has so far not even been fully utilized, as experiments have only been done on systems with single [4, 5] or two species of colloids [6, 7, 8]. Also, theoretical work [9] and simulations [10, 11] have predominantly focused on systems with two types of colloids. Notable exceptions are the work by Licata and Tkachenko [12], which was limited to a single particle per colloid type, and the lattice model by Lukatsky *et al.* [13] that used four species of colloids, and provided the basis for this work.

In order for a collection of DNA-coated colloids to self-assemble into a complex pattern, every colloid – through its interactions – should contain enough information to 'find' its target position. A complication is that the distribution of the sticky DNA ends that mediate the interactions is to a first approximation isotropic [14] so that the interactions can only be a function of the distance between colloids. Furthermore, for practical purposes, this distance is constrained by the length of the DNA [8]. Therefore we may ask ourselves whether it is at all possible to design large-scale patterns using only short-range isotropic interactions, and,

if so, whether there is a lower limit to this interaction range. We address this question in the context of a two-dimensional lattice model with isotropic interactions and we investigate whether the interactions between the colloids on this lattice can be designed in such a way that the colloids self-assemble into a complex crystal structure.

A necessary requirement for self-assembly is that the target structure represents the unique minimum energy ground state of the system, so that it will be the preferred state for $T \rightarrow 0$. For the basic theoretical work presented here we therefore restrict ourselves to the design of a unique ground state for non-trivial crystal structures, using only isotropic interactions.

After introducing the model, we derive a requirement for the minimum interaction range between colloids, depending on the symmetry of the underlying lattice and the size of the desired pattern. Subsequently, we present a minimal recipe for the interactions that allows for the design of arbitrarily large periodic patterns. Besides periodic patterns, this recipe can also be used to construct patterns with glide reflections and two-fold rotations. Finally, these results are illustrated by means of Monte Carlo simulations that demonstrate the self-assembly of the designed patterns from random initial conditions.

II.   MODEL DEFINITION

We define a simple geometrical lattice model for the interactions in a system of DNA-coated colloids, as a generalization of the model by Lukatsky *et al.* [13]. Let us consider a lattice on which every site may be occupied by at most one colloid, corresponding to an excluded volume effect with the size of a lattice unit. Each colloid is of a particular type that is characterized by its sticky end and labelled by an alphabetical index (A, B, etc.). Formally, every lattice site i is in a state

$$s(i) \in \{\texttt{A}, \texttt{B}, ..., \texttt{Z}\} \cup \emptyset, \tag{1}$$

in which Z is the final element of the set of distinguishable colloids (not necessarily containing 26 elements) and $\emptyset$ denotes an empty site. Empty sites can be regarded as an additional non-interacting colloid species. We can trivially assign a vector in a Z dimensional vector

space to each of the possible states through the identification

$$
\mathtt{A} = \begin{pmatrix} 1 \\ 0 \\ \vdots \\ 0 \end{pmatrix}, \quad \ldots, \quad \mathtt{Z} = \begin{pmatrix} 0 \\ \vdots \\ 0 \\ 1 \end{pmatrix}; \quad \emptyset = \begin{pmatrix} 0 \\ \vdots \\ 0 \\ 0 \end{pmatrix} \tag{2}
$$

The colloids on the lattice have DNA-mediated interactions that give rise to an effective two-body interaction energy that is both isotropic and short-ranged. This interaction will therefore be a function of the distance on the lattice. It is convenient to introduce the shorthand notation $n(r)$, $r \in \mathbf{N}$, for the set of particles with identical site-to-site distances on the lattice, ordered by increasing distance for increasing r. $n(1)$ thus contains all nearest-neighbor pairs, $n(2)$ all next-nearest-neighbor pairs, etc. In the context of this work, we restrict ourselves to two-dimensional lattices, but the language used to describe the interactions is also applicable to lattices in higher dimensions. See figure 1 for the interaction ranges for the square and triangular lattices used in this work.

The Hamiltonian for the system is defined as

$$
H = \frac{1}{2} \sum_{r=1}^{R} \sum_{(i,j) \in n(r)} J_{mn}^{(r)} s_m(i) s_n(j), \tag{3}
$$

with an implicit summation over the vector indices m and n. R indicates the maximum range of the particle interactions, as measured along the lattice links, and we introduce a symmetric interaction matrix $J^{(r)}$ for every lattice distance r. The aim is to design the interaction matrices $J^{(r)}$ in such a way that the Hamiltonian is uniquely minimized for a predetermined crystal lattice – up to global transformations corresponding to the symmetries of the underlying lattice (rotations, translations and reflections).

At this point, it will be clear that the above model can easily be used to describe *any* multi-state lattice model with pairwise interactions that are both short-ranged and isotropic. However, for conceptual clarity, we refer only to the DNA-coated colloid system and leave further applications up to imagination of the reader.

III. LOWER LIMITS TO THE INTERACTION RANGE

So far, the maximum interaction range R has not been specified. For practical applications this interaction range should be as short as possible. However, it is reasonable to expect that

a very short interaction range may impose limitations on size or complexity of the patterns that can be designed. In this section we determine lower limits for the interaction range, depending on the underlying lattice type (square, triangular) and the desired complexity of the designed pattern.

The square and triangular lattices have a large number of intrinsic symmetries: translations, rotations, reflections and glide reflections (reflections accompanied by a translation along the reflection axis). The collection of these symmetries is summarized by the corresponding wallpaper groups: *p4m* for the square lattice, *p6m* for the triangular lattice [15]. Applying any of these symmetry operations to a configuration of colloids *on* the lattice produces another valid (on-lattice) configuration. Furthermore, for any given configuration and symmetry operation, a number of *symmetrized configurations* can be constructed that are invariant under the given symmetry operation. For example, a pair of reflection-symmetrized configurations is created by copying the pattern on one side of a reflection axis over to the other side, and vice-versa.

The goal of this work is to design the interaction matrices in such a way that the system has a unique ground state for a configuration of colloids that is equal to an *a priori* specified pattern. Naturally, this means the energy of this distribution should be lower than that of every other distinguishable distribution, including all possible symmetrized forms. We conclude that the ground state can only possibly be unique if each of the possible symmetrized distributions either (a) has a larger energy or (b) is indistinguishable from the original distribution (i.e. it was already symmetric).

This observation gives us a handle on the relation between ground state design and interaction range. Figure 2 gives a graphical overview of this relation on a square lattice. Starting on the left, for an interaction range of $n(0)$ (no interactions) the interaction energy is always zero. Obviously, any symmetrized solution will have the same energy, so a solution can only be a unique ground state if it itself is symmetric under all symmetry operations on the lattice (*p4m*). This is shown as the maximum complexity pattern on the bottom left, consisting of only A-type colloids.

Increasing the interaction range to $n(1)$, the nearest-neighbor interactions along lattice links can be used to distinguish a colloid from its neighbors, as shown in the interaction patch by the different labels 0 and 1. The presence of these interactions can cause a symmetry-generated state to have a higher energy than the original state. Graphically speaking, this

range	n(0)	n(1)	n(2)	n(3)
interaction patch	⓪	① ① ⓪ ① ①	② ① ② ① ⓪ ① ② ① ②	③ ② ① ② ③ ① ⓪ ① ③ ② ① ② ③
unsuppressible lattice symmetries				
group	p4m	p4m (larger)	p2m	0
maximum complexity pattern	a a a a a a a a a a a a a a a a	a b a b b a b a a b a b b a b a	a b a b c d c d a b a b c d c d	∞

Legend (unsuppressible lattice symmetries):
— reflection
---- glide reflection
◇ 2-fold rotation
□ 4-fold rotation

Figure 2: Table relating the interaction range, the unsuppressible lattice symmetries and the corresponding maximum complexity patterns on a square lattice.

happens when, for a given symmetry operation, the interaction patch can be placed on a position such that either (a) the 0 is mapped onto a 1 or vice-versa, or (b) the patch is split by a glide reflection. A large fraction of the intrinsic lattice symmetries can be suppressed this way, such as the reflection symmetry between columns and rows of colloids. The remaining symmetries are shown in the second row of figure 2 (the glide symmetries are a resultant of the remaining symmetries). Again, the symmetry group is $p4m$, but this time with a unit cell of two lattice sites. Every ground state should by symmetric under this group, so that the most complex ground state pattern is given by the checkerboard pattern of A and B type colloids.

Increasing the range yet again to $n(2)$ further reduces the symmetries that cannot be suppressed to the $p2m$ wallpaper group, corresponding to a 2×2 repeated pattern of colloids. This class of interactions and the corresponding solutions have been used by Lukatsky *et al.*

7

[13]. When the interactions include $n(3)$, all lattice symmetries can be suppressed and this method does not indicate any remaining symmetry-derived limitations. An interaction range of $n(3)$ or longer is therefore a necessary condition for the design of patterns that are larger than 2×2. In the next section, we will show that this interaction range is also sufficient.
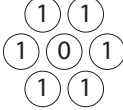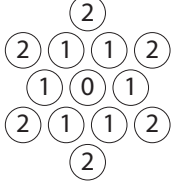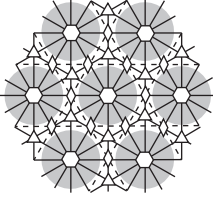

Figure 3: Table relating the interaction range, the unsuppressible lattice symmetries and the corresponding maximum complexity patterns on a triangular lattice.

Figure 3 shows a similar derivation on the triangular lattice. Starting from the full symmetry of the lattice ($p6m$), symmetries are suppressed by increasing the interaction range. For $n(1)$ interactions the remaining lattice symmetries are of group $p3m$, corresponding to a triangular 3-colloid pattern. In contrast to the square lattice, $n(2)$ interactions are already sufficient to suppress all lattice symmetries on the triangular lattice. The design recipe that is presented in the following section will prove that the $n(2)$ interaction range is not only necessary, but also sufficient for designing unique ground states with arbitrarily large numbers of colloids.

IV.   PROOF OF DESIGNABILITY

The results from the previous section indicate that non-trivial patterns can only be reliably designed if interaction range is at least $n(2)$ (on a triangular lattice) or $n(3)$ (on a square lattice). Building on this generic result we now introduce a simple recipe for interactions between the colloids that is both minimal in terms of the interaction range and still guaranteed to produce a unique ground state for a large class of patterns.

The prescription for the interactions consists of a mixture of positive and negative design elements. First, each pair of colloids that should form a nearest-neighbor pair in the final pattern is assigned a negative interaction energy $-\alpha < 0$ in the nearest-neighbor matrix $J^{(1)}$ (positive design). In addition, we introduce a repulsive interaction at longer distances, represented by a contribution $\varepsilon > 0$ for all diagonal elements in the next-nearest neighbor matrix $J^{(2)}$ and, for square lattices, also the next-next-nearest neighbor matrix $J^{(3)}$. The remaining interactions are set to zero. This choice of the interaction matrices is far from unique, but it is simple, leading to sparse matrices, and it is sufficient to guarantee a unique ground state with an energy of $-\alpha n/2$ per particle, where n is the coordination number (the number of nearest-neighbors per site) of the lattice. A motivation and proof for this design strategy is given below, for both lattice types under consideration.

1.   One dimension

It is instructive to initiate our analysis with a one-dimensional system (see figure 4a). The symmetry argument from the previous section suggests that the interactions should range up to $n(2)$ in order to suppress the reflection symmetry through the center of each colloid. Suppose we wish to design a linear pattern containing the sequence ...ABC.... Using only nearest-neighbor interactions this requires a preferential binding of B to both A and C. However, when B is bound to A on one side, there is nothing to stop another A from binding on the other side of L, producing the sequence ABA. Hence, as expected, the only sequence that can reliably be designed using next-neighbor interactions alone is an alternating sequence.

This restriction can be circumvented by extending the range of interactions to $n(2)$. This allows us to include a *self-repulsion* at range $n(2)$ for both A and C. Suppose A binds to B

first, forming the complex `AB`. The long-range self-repulsion of `A` will prevent it from also binding to the other side of `B`, or it can only do so with a reduced affinity. In both cases, if `C` has approximately the same nearest-neighbor affinity for `B` as `A` does, the ground state will contain the sequence `...ABC...`, or its reverse, which is allowed by a global symmetry operation. The same argument can be applied iteratively to each position in the sequence, from which we conclude that a ground state sequence of infinite length can indeed be designed. Using the interaction recipe defined above, all repulsive interaction $(n(2))$ are avoided and only the attractive interactions $(n(1))$ remain. This way, every link in the lattice obtains an energy $-\alpha$, corresponding to the lowest possible energy state of the lattice, which proves that it it indeed the ground state.

This argument shows that it is theoretically possible to design arbitrarily long unique strings of letters, but it may be more desirable to form a string of a limited length, say `AB...YZ`, and to create a repeated 'tiling' based on this fragment. Implementing this periodic boundary condition is straightforward, as we can simply instruct `A` and `Z` to become nearest neighbors by setting their interaction energy to $-\alpha$ (positive design).

2. Triangular lattice in two dimensions

We now address the more interesting case of two-dimensional designs, starting with the triangular lattice. As in the one-dimensional case, a minimum interaction range extending to the next-nearest neighbors $(n(2))$ is required to design crystals with more than three colloids (see section III). That the design recipe is also sufficient can be seen as follows.

Consider a single particle `A`, having six nearest-neighbors, and suppose we wish to design a ring of particles `BCDEFG` around `A` (see figure 4b, left). Attractive nearest-neighbor interactions between colloid `A` and the other particles cause the ring of particles around `A` to be made up of the correct colloids in the ground state, but does not yet specify their order.

However, let us now view this ring of six colloids around `A` as a periodic line. Figure 4b (right) shows that the $n(2)$-interactions on the triangular lattice also correspond to the next-nearest neighbor interactions along this ring. The implication is that the one-dimensional argument for designability carries over directly to this situation, meaning that the sequence `BCDEFG` will reliably form around colloid `A`, up to a global rotation or reflection. By iterative application of this argument to the points in the outer ring of the hexagon (`B`, `C`, etc.),

target patterns   **interactions**

a) one-dimensional lattice

b) triangular lattice

c) square lattice

d) target pattern with two-fold rotation
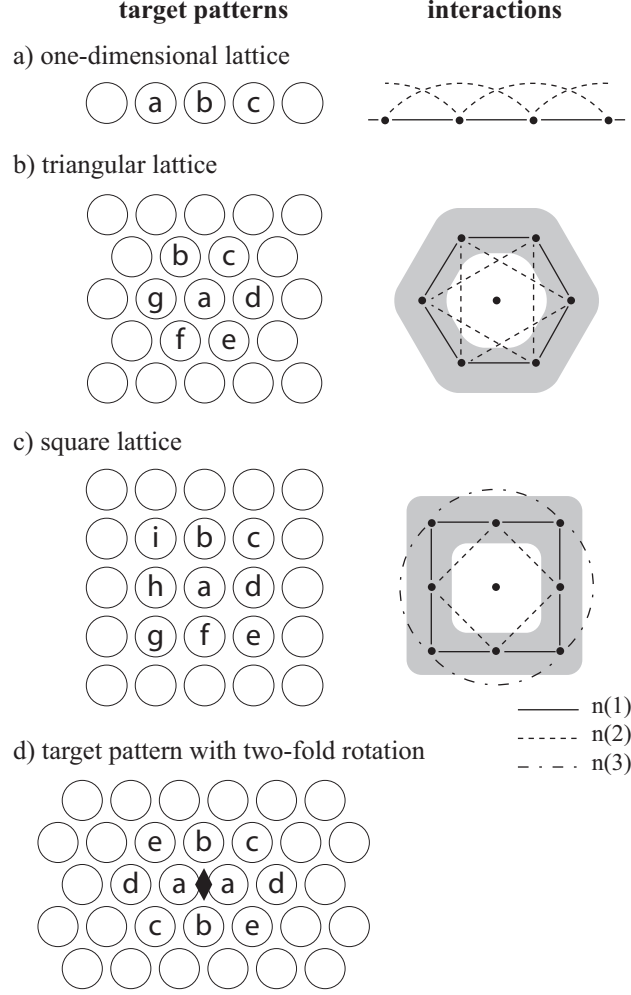
n(1)
n(2)
n(3)

Figure 4: Overview of the local target patterns for one- and two-dimensional lattices and corresponding interactions between lattice sites. The shaded areas in (b) and (c) indicate the mapping of local neighborhoods onto a one-dimensional periodic structure. Panel (d) depicts the local neighborhood of a two-fold rotation center on a triangular lattice.

the proof scales to arbitrarily large systems. Note that the orientation of the subsequent hexagons is completely fixed with respect to the initial patch. There are only *global* degrees of freedom to orient the pattern.

3. Square lattice in two dimensions

On the square lattice the self-repulsion energy ε of the design recipe should be extended to the $n(3)$ range (the $J^{(3)}$ matrix). The proof then follows along the same lines as that for

the triangular lattice. We pick any lattice location and consider the 8-vertex square around it (see figure 4c). This square can be represented as a line with periodic boundary conditions and next-nearest neighbor interactions, proving the local uniqueness of the ground state. By repeating this process iteratively for points on the edge of the square the proof is extended to arbitrarily large systems.

V.   CRYSTAL STRUCTURES

We have shown that the design recipe produces a unique ground state locally, and, by extension, for larger patches consisting entirely of unique colloids. Of course, the ability to construct a macroscopic materials that must consist of colloids with unique DNA sequences is of limited use. Rather, one would like to use a limited number of colloids to form a complex crystal that can grow to arbitrary size. In this section, we show that the design recipe can be used to construct various crystal structures.

Every crystal structure exhibits symmetries; at least two independent translations. The 17 crystallographic *wallpaper groups* provide an exhaustive set of all such possible symmetry groups on the two-dimensional plane [15]. It should be noted that a crystal structure can only exist on our lattice model if its symmetry group is compatible with that of the lattice itself. Specifically, the 5 wallpaper groups containing a 3-fold rotation are not compatible with a square lattice and the 3 groups with a 4-fold rotation are not compatible with the triangular lattice. Formally, the symmetry group of the crystal should be a subgroup of that of the lattice (*p4m* or *p6m*), and at least contain two independent translations on the lattice (*p1*). For a pattern with symmetry group g, we have $p1 \subseteq g \subseteq p4m$ (square) or $p1 \subseteq g \subseteq p6m$ (triangular).

The interaction recipe outlined above can be successfully applied to generate patterns representing 4 out of the 17 wallpaper groups by selectively enabling symmetries. The simplest wallpaper group, p1, represents a periodic crystal with only translation symmetries. The ground state for such a pattern can be reliably designed simply by instructing the colloids on one side of a patch to connect to those on the opposite side. There is, however, a lower limit to the translation distances that can be used. The proof for the existence of a unique ground state in section IV assumes that the colloids that form a ring around any colloid A (see figure 4b) do not have attractive interactions with the colloids on the opposite

side of the ring. However, if one of the two translation vectors becomes so short that the ring of colloids around colloid A has nearest-neighbor interactions with another copy of itself, the design recipe leads to spurious attractions that can cause a degeneracy of the ground state. An example of a regular periodic pattern on a triangular lattice is given in figure 5 (top). Note that this pattern has the shortest repeat length that is possible without creating spurious interactions within a single colloid's local neighborhood.

Another symmetry that can be implemented in a straightforward fashion is the glide reflection: a reflection followed by a translation along the reflection axis. Again, if the translation is large enough so that the local neighborhoods of identical colloids do not touch one another, the glide reflection is simply achieved by applying the interaction recipe to the desired pattern. Producing a periodic pattern based on the glide reflection generates the *pg* wallpaper group, an example of which is shown in figure 5 (bottom). For this symmetry group, the unit cell is twice the size of the fundamental domain, the patch of uniquely designed colloids.

As a final step we implement a non-trivial symmetry operation that forces us to revisit the uniqueness proof of section IV. This symmetry operation is the two-fold rotation around the center point of two colloids on the triangular lattice. An example of the local target pattern for this symmetry is given in figure 4d. For all the colloids outside this region, the local neighborhood is qualitatively unaffected, so the (local) ground state remains unique. For each of the colloids *inside* the region, one can enumerate the possible local neighborhoods and verify that the target configuration is the only one that corresponds to attractive interactions on all lattice links and is therefore a good candidate for the ground state. There is, however, an energy penalty associated with the presence of two B colloids at a next-nearest neighbor distance from each other. As long as this energy penalty is similar in magnitude to the attractive interactions – and it's likely to be much smaller in practical applications – this penalty is outweighed by the attractive interactions and the target pattern represents the unique ground state. Obviously, a very large repulsive energy between the B-colloids will disrupt the target pattern, but the exact threshold value will generally depend on non-local interactions. The use of a two-fold rotation allows us to generate patterns from two other wallpaper groups: the group *p2* with only two-fold rotation symmetries (and resulting translations) and the group *pgg* that combines two-fold rotations with glide reflections. An example of the latter is given in figure 6. For the group *pgg*, the unit cell is four times the

13

p1 symmetry group

pattern and symmetries

a	b	c	g	h	i	a	b	c
d	e	f	j	k	l	d	e	f
g	h	i	a	b	c	g	h	i
j	k	l	d	e	f	j	k	l
a	b	c	g	h	i	a	b	c
d	e	f	j	k	l	d	e	f
g	h	i	a	b	c	g	h	i
j	k	l	d	e	f	j	k	l
a	b	c	g	h	i	a	b	c
d	e	f	j	k	l	d	e	f

tiling

P		P
	P	
P		P
	P	

simulation results

a g j
b d h k
c e i l
f

pg symmetry group

tiling

P	P	P	P
q	q	q	q
P	P	P	P
q	q	q	q

simulation results

a b c d
e f g h
i j k l
m n o p

pattern and symmetries

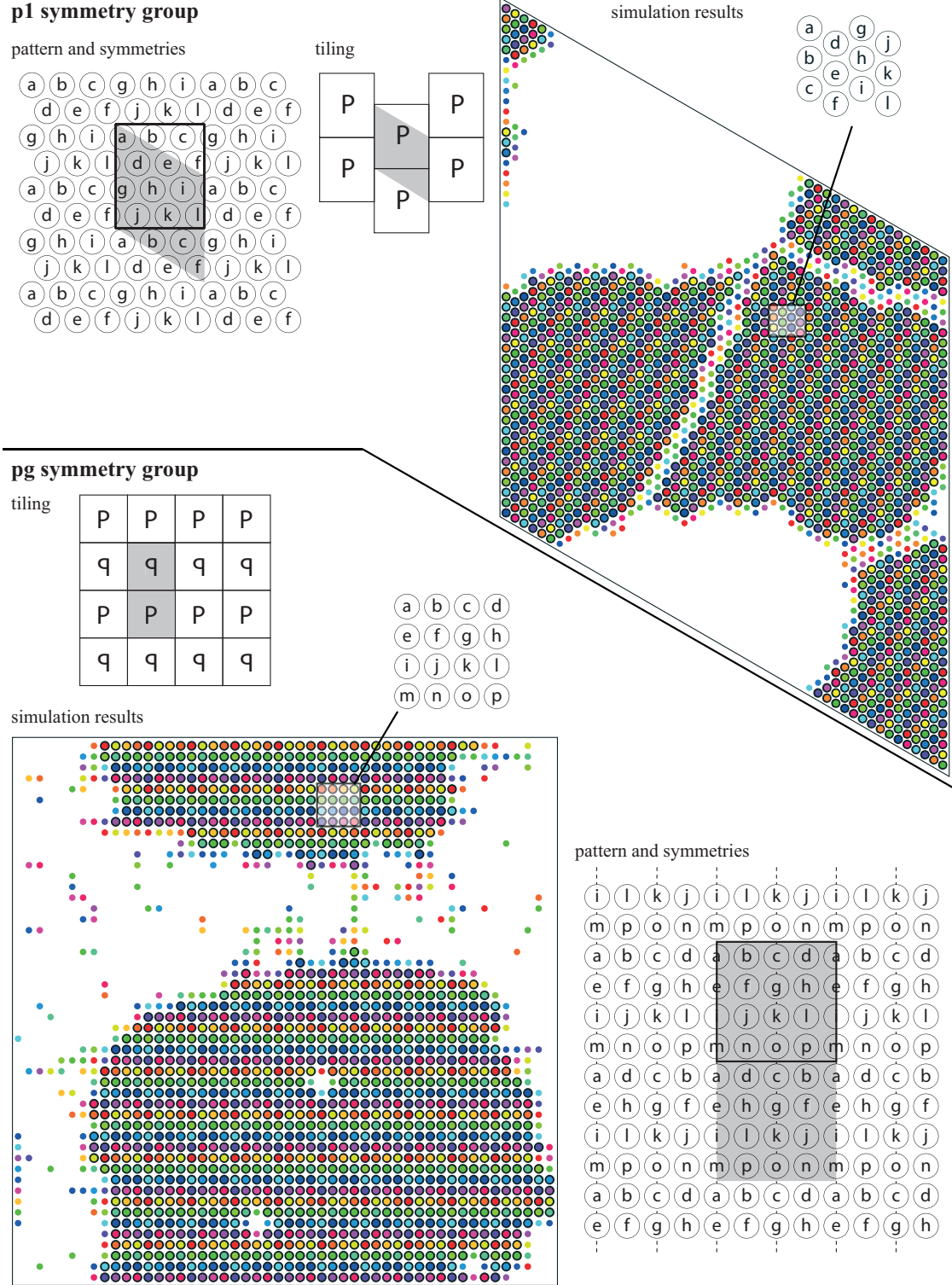| i	l	k	j	i	l	k	j	i	l	k	j
m	p	o	n	m	p	o	n	m	p	o	n
a	b	c	d	a	b	c	d	a	b	c	d
e	f	g	h	e	f	g	h	e	f	g	h
i	j	k	l	i	j	k	l	i	j	k	l
m	n	o	p	m	n	o	p	m	n	o	p
a	d	c	b	a	d	c	b	a	d	c	b
e	h	g	f	e	h	g	f	e	h	g	f
i	l	k	j	i	l	k	j	i	l	k	j
m	p	o	n	m	p	o	n	m	p	o	n
a	b	c	d	a	b	c	d	a	b	c	d
e	f	g	h	e	f	g	h	e	f	g	h

Figure 5: Examples of a simple periodic crystal on a triangular lattice (top; group *p1*) and one with glide symmetries (dashed lines) on a square lattice (bottom; group *pg*). The basic tile of colloids is delineated by the black rectangle, and the unit cell is indicated by the gray parallelogram/rectangle. The resulting tilings are shown with a P in each tile to indicate its intrinsic orientation. In the simulation results, colloids with locally ordered nearest-neighbors are indicated with a dark ring.

pgg symmetry group
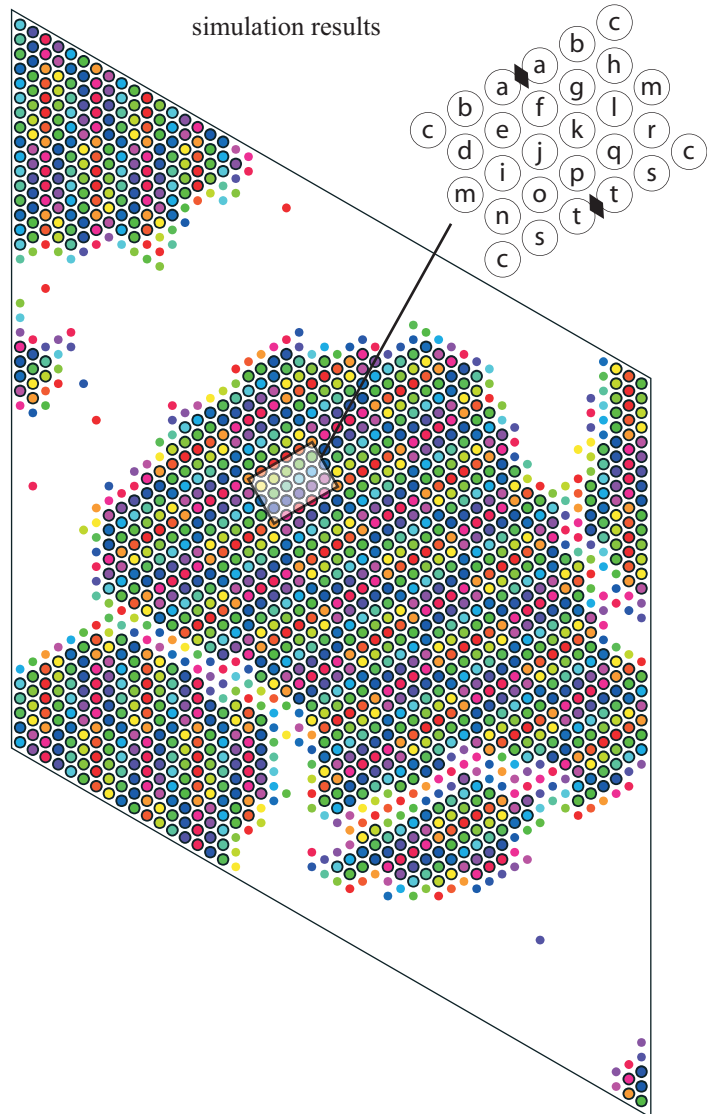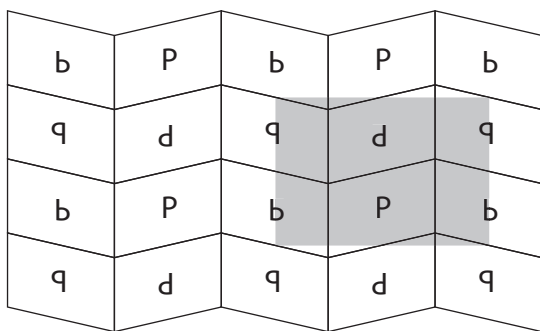
pattern and symmetries

tiling

simulation results
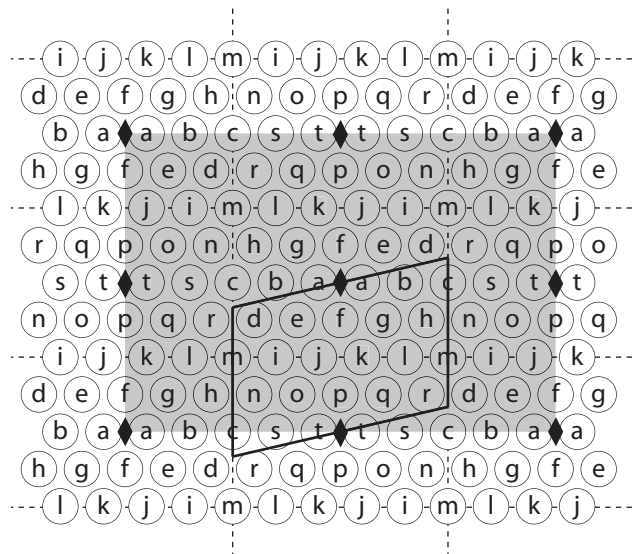
Figure 6: Example of a periodic crystal (group *pgg*) with 2-fold rotational (diamonds) and glide symmetries (dashed lines) on a triangular lattice. The basic tile of colloids is delineated by the black parallelogram, and the unit cell is indicated by the gray rectangle. The resulting tiling is shown with a P in each tile to indicate its intrinsic orientation. In the simulation results, colloids with locally ordered nearest-neighbors are indicated with a dark ring.

size of the fundamental domain.

VI. SIMULATION RESULTS

To illustrate our findings, we have run Monte Carlo simulations starting from random initial conditions for the target patterns shown in figures 5 and 6. Snapshots of the resulting configurations are shown alongside the patterns. These clearly indicate a strong tendency to assemble into the designed target patterns.

For the simulations, the interaction energies were chosen according to the interaction recipe described above, with $\alpha = 3k_BT$, $\varepsilon = 3k_BT$. The system dimensions were 50×50, forming a square for a square lattice and a parallelogram for a triangular lattice, both with periodic boundary conditions between opposing edges. The systems were initialized with 2/3 of the sites occupied by colloids of all types in equal proportions, and at random positions. For the evolution of the system a Metropolis algorithm was used with 10^9 steps in which a swap of two random colloids was attempted. In all cases, this led to sufficient (local) equilibration of the system. Local order was determined by detecting whether a colloid had all the correct nearest neighbors in the appropriate order. Colloids with locally ordered neighborhoods are indicated by a black ring around them. Connected regions of these colloids therefore indicate macroscopic crystal structures of the correct type. In figures 5 (top) and 6 distinct grain boundaries are visible between macroscopic ordered patches with incompatible orientations.

VII. DISCUSSION

In this work we have introduced a two-dimensional lattice model for the interactions between DNA-coated colloids. The model allows for a multitude of colloid types that interact according to pair-specific interaction energies that are isotropic and of finite range. For this system we have shown that it is possible to choose the interaction energies in such a way that a predetermined periodic pattern is the unique ground state.

Essential for the establishment of a non-trivial pattern as a unique ground state is the ability of the interactions between colloids to suppress the symmetries of the underlying lattice. This has lead to the derivation in section III of a lattice-dependent minimum interaction range. On a square lattice, interactions need to extend to the next-next-nearest neighbors, whereas on a triangular lattice, interactions up to and including the next-nearest neighbors

are sufficient.

Building on this result, we have introduced a simple recipe for choosing the interactions between colloid species that is minimal in terms of the interaction range between particles and guarantees the local uniqueness of the ground state. The prescription consists of an attractive nearest-neighbor potential for particles that should become nearest neighbors in the final pattern and a self-repulsion at larger distances (up to the required interaction range) between particles of the same type. This recipe has been shown to work for simple periodic patterns, patterns with glide reflections and patterns with two-fold rotations on a triangular lattice.

The choice of interaction energies that has been made for the simple recipe is presented as a proof of concept and is certainly not unique. This is especially true for the choice for the long-range self-repulsion that does not contribute to the energy of the ground state, but merely prevents lattice symmetries from disrupting the pattern. Another valid choice would be to add an offset to all long-range interaction energies, whilst maintaining a slightly more repulsive (or less attractive) interaction for colloids of the same type.

Any such adjustments to the interaction recipe will need to be made in the light of the kinetic aspects of self-assembly, which have been ignored in the context of this work. For example, the ground state of a system, however well designed, may be kinetically inaccessible. On the other hand, judiciously chosen interactions could speed up the formation of the ground state pattern, for example through a 'staged' ordering process [13].
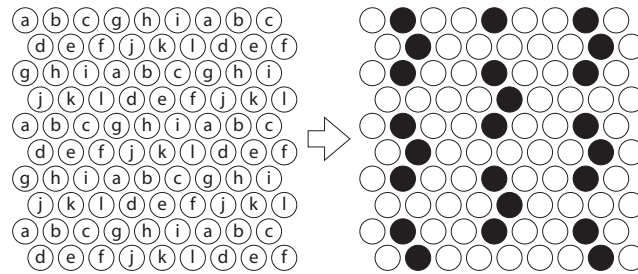

Figure 7: Demonstration of the use of a periodic pattern of unique colloids as a template. Colloids `b`, `e` and `h` are colored black, the others are white.

In section V various crystal structures have been created by enabling specific symmetries: translations, glide reflections and two-fold rotations. These crystals have fundamental

domains that consist of colloids that are all unique in terms of their interactions. One of the distinct advantages of more complex crystal structures over the simple periodic crystals is that the fundamental domain, the basic unit of the tiling, is smaller than the unit cell, limiting the number of uniquely designed colloids that is required to make a pattern of a given periodicity. For example, the unit cell of the *pgg* symmetry group is four times larger than its fundamental domain (see figure 6).

In addition, it is important to stress that the requirement for all colloids in a tile to be unique only pertains to their DNA-mediated interactions. The other properties of the colloids can be chosen independently and can be used to create a higher level pattern on top of the periodic crystal that now serves as a template. For example, some colloids could have additional chemical binding sites, or fluorescent or electrical properties. The ability to use the underlying crystal as a template is visualized in figure 7 for the simple periodic pattern shown in figure 5 (top).

In future work, the interaction recipe presented in this work could be extended to allow for additional symmetries, enabling even more complex crystals to be designed. Furthermore, the techniques that have been introduced in this work can be applied to three-dimensional lattices, which have many more symmetries, but are not fundamentally different from the two-dimensional lattices discussed here.

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