

New methods for developing design strategies for self-assembling patchy particles

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Utilizing bottom-up building block assembly, we efficiently generate energy-minimizing structures and assembly pathways for a family of complex, interacting patchy particles. Grouping the generated configurations into motifs, we discern important characteristics for assembling a desired configuration. We find the structures self-assembled by patchy particles with Monte Carlo simulations and compare with the energy-minimizing configurations. Comparing the self-assembled structures with the ordered, energy-minimizing clusters we develop design heuristics for robust self-assembly and we utilize the assembly pathways to propose strategies for overcoming poor propensity.

INTRODUCTION

Nanoparticles with specific, custom shapes and strong anisotropic interactions can now be manufactured in large quantities and with great precision due to advances in chemical synthesis techniques[1]. To use these particles as the building blocks of next-generation materials and devices, however, we must understand how they can be made to robustly self-assemble target structures[2]. Strong interactions and complex shapes can be used to stabilize desired configurations and can be exploited to assist in self-assembly, but they also present new challenges. In Brownian systems, strong interactions can cause jamming and gelation that prevent the system from rearranging and reaching its energetically favored configuration[1, 3]. These kinetic traps occur in both experiments and simulations and can prevent energetically stabilized organized structures from forming from complex building blocks. In order to avoid these traps, methods like bottom-up building block assembly (BUBBA) are used to generate energy minimizing structures efficiently[4].

In this paper we use BUBBA as a screening tool for complex building blocks. By quickly generating energy-minimizing configurations of patchy particles we can identify building blocks with energetically stabilized useful structures. We show that the configurations generated by these 25 building blocks fall into a set of motifs that include stripes, porous arrays and redundant networks. We use cluster Monte Carlo simulations to assess the ability of a building block to self-assemble via thermodynamic processes into the energy-minimizing structure predicted by BUBBA and we quantify this ability. Finally, we show how building blocks with low propensity for self-assembly might benefit from a limited amount of directed assembly intervention.

MODEL

We use a model introduced by Troisi *et al.*[5], in which systems of lattice animals whose shapes resemble Tetra-

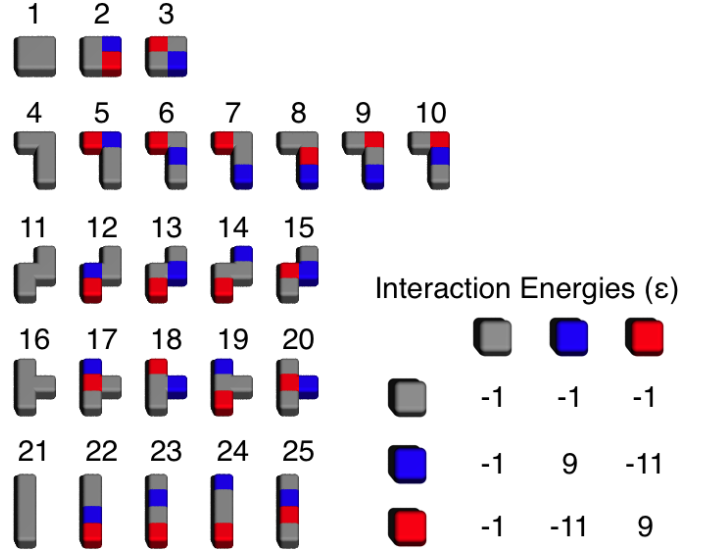


FIG. 1: The 25 primitive particles studied in this work, as in Troisi *et al.*[5] and the interactions between their subunits. Gray represents neutral subunits, red represents positive subunits, and blue represents negative subunits. Interactions are only between nearest neighbors

minoes (Figure 1) are confined to a two-dimensional surface. In their model, the four subunits that make up each particle are either positive, negative, or neutral. The dimensionless potential energies between nearest neighbor subunits are modeled after van der Waals interactions ($U_{VDW} = -\epsilon$) and electrostatic interactions ($U_{\pm} = \pm 10\epsilon$). When two like charges share an edge, the associated potential energy is $U = -9\epsilon$. For opposite charges the potential energy is $U = -11\epsilon$. The potential energy for a neutral subunit sharing a face with any other subunit type is $U = -\epsilon$. These primitive building blocks can translate and rotate on the lattice, but particle overlaps and inversions are prohibited.

METHODS

In this paper we utilize BUBBA to mimic directed assembly and cluster Monte Carlo to mimic thermodynamic self-assembly. The time required to generate a 40-particle cluster with BUBBA can vary significantly between different building blocks and depends upon the number of clusters stored as the algorithm is executed. Here, when we record only energy-minimizing clusters, a BUBBA run takes between 4 seconds and 4 minutes on a 2.8GHz iMac, depending on the building block. Cluster Monte Carlo simulation of 40 identical particles on a 32×32 lattice with periodic boundary conditions and 10^7 time steps require 2 hours of run time on the same machine.

RESULTS

From the structures generated by BUBBA, we find seven common motifs. Simple striped structures such as Figure 2 are common, while complex networks and porous arrays are relatively rare. Potential applications for the striped structures include nanoscale electronic wires if the red and blue cells are conducting and the grey cells are made of an insulating material. Of the particles that form porous arrays, all are “L”-shaped, suggesting this is an important characteristic in the energetic stabilization of non-close packed structures. While we find common surface patterns stabilized by multiple patchy particles, cluster Monte Carlo simulations show the particles have a wide variety of self-assembly propensities. Patchy particle 8, for example, can easily self-assemble the striped structure generated by BUBBA, but patchy particle 24 gets trapped in disordered configurations.

Analyzing the assembly pathways generated by BUBBA, we find characteristics of the pathways that correspond to high and low propensity. In the case of patchy particle 8, the assembly pathway is simple with few energy minimizing clusters of each size, but many paths to the large clusters (Figure 3). In the case of patchy particle 24, we observe multiple clusters of different configurations at a given size, some of which are inconsistent with the wide stripe motif (indicated by squares in Figure 4). These inconsistent clusters, as well as the relatively low number of pathways that lead to large energy-minimizing clusters contribute to the lower self-assembly propensity for patchy particle 24.

In the case of patchy particle 19, for which BUBBA generates an interesting redundant array, the self-assembly propensity of the basic building block is low. However, we find that if a mesoblock made from two copies of the particle is used for self-assembly, the desired array can be formed. The $N = 2$ mesoblock is the energy-minimizing cluster made from two copies of patchy particle 19. This mesoblock has higher self-assembly propen-

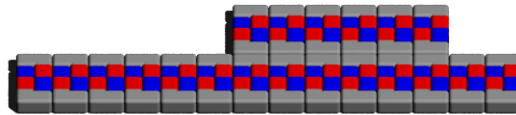


FIG. 2: Stripes formed by patchy particle 8

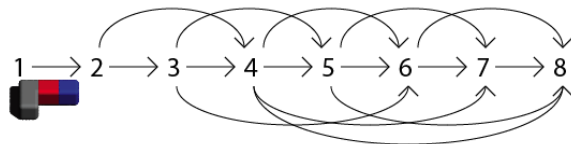


FIG. 3: Energy minimizing assembly pathway for patchy particle 8

sity because the odd-numbered clusters in the assembly pathway for patchy particle 19 were inconsistent with the desired motif and hindered self-assembly. Because the $N = 2$ mesoblock can only form even-numbered clusters, these kinetic traps are avoided.

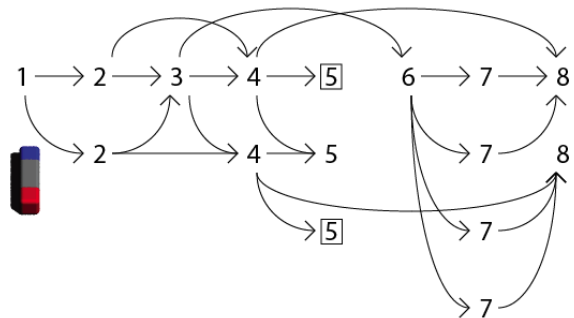


FIG. 4: Energy minimizing assembly pathway for patchy particle 24. Clusters that are not present in the energy-minimizing motif of 40 particles are indicated with a square

CONCLUSIONS

Using BUBBA to efficiently generate energy-minimizing configurations of complex building blocks, we identify structures with practical applications. By comparing self-assembled configurations with their energy-minimizing counterparts, we identify building blocks with high self-assembly propensity. We show correlations between assembly pathway networks and the propensities of patchy particles, namely that the presence of small clusters outside of the desired motif prevent substantial self-assembly barriers. For systems with low self-assembly propensity we demonstrate that informed directed assembly of larger mesoblocks can limit the effect of assembly pitfalls and improve a

system's ability to self-assemble.

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