MATERIALS

Driving Structure Selection in Colloidal Particles Through Confinement

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Abstract:

We use Monte Carlo simulations of hard tetrahedral particles to examine the effects of external confinement and particle shape on the self-assembly process. We examine a set of particles related to tetrahedra by vertex truncation. Through simulating self-assembly in a spherical container, we show that confined tetrahedral particles assemble in distinct concentric shells up to hundreds of particles. We also show that the curvature of the container can drive the local environment of particles towards specific motifs, allowing researchers to selectively induce the self-assembly of particular structures.

Summary of Research:

This work uses numerical simulations to explore the effect of confinement on the self-assembly behavior of hard colloidal particles — in particular tetrahedral particles. In experiment, advancements in synthesis of anisotropic particles have allowed the development of an array of shaped nanoparticles [1]. This raises the question: what structures do these different shapes assemble?

Computational studies enable the exploration of the bulk behavior of particles with different shapes [2], replicating, for example, an experiment with particles floating in solution. However, the non-bulk case is less well explored. Here, we investigate the behavior of hard (non-attractive) tetrahedral particles confined in spherical walls, and the effects of wall curvature and particle shape on interparticle motifs. In experiment, this mimics assembly mechanisms such as confinement in an evaporating droplet [3].

To explore shape space, we apply vertex truncation to hard tetrahedra. Three shapes were given particular attention: the Platonic tetrahedron, the Archimedean truncated tetrahedron (ATT), and the space-filling truncated tetrahedron (STT). These shapes mark different regions in self-assembly space: the Platonic tetrahedra assemble a dodecagonal quasicrystal, the ATTs a diamond-type crystal, and the STTs lie on the boundary between to the two structures, in a region of structural competition [4]. We use a continually shrinking, hard spherical wall, compressed to high pressure to induce assembly. Simulations were performed with the HOOMD-blue Hard-Particle Monte Carlo (HPMC) package [5-7], using the resources provided by the CNF Computer Cluster, among others.

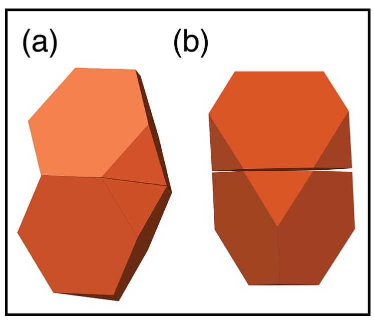

Figure 1: (a) The aligned motif (ca. 70.5°) vs. (b) the anti-aligned motif (90°).

To explore the effects of container size — and therefore curvature — at equal pressure, we increase the number of particles in the system. We observe that concentric shells of particles form, conforming to the curvature of the wall. At small N, the vertices cluster in the center. Additional particles are added in the outer shell until the container is large enough that a two-shell structure forms. We have shown that this process repeats for a third shell, and organization into distinct layers continues up to thousands of particles.

The core-shell structure drives the particles towards local motifs that conform to the container wall. In tetrahedral particles, there are two dominant motifs, characterized by their misorientation angle: the angle through which a particle must be rotated in order to match the orientation of a reference particle. For tetrahedral particles, there are two important local motifs, both with facet-to-facet alignment (Figure 1): in one motif, the vertices of both particles align with one another (misorientation angle = *ca.* 70.5°), while in the second motif, the vertices of one particle align with the edge midpoints of the other (misorientation angle = 90°) [8]. The "anti-aligned" misorientation angle is characteristic of a diamond-type structure formed in the bulk by ATTs, whereas Platonic tetrahedra favor the "aligned" motif, characteristic of a dodecagonal quasicrystal.

Plotting the change in predominant motif as the system size increases gives information on how the container drives the assembled structure. At small *N*, the clustering of vertices near the center of the containers drives the particle motif towards aligned for all shapes. For Platonic tetrahedra, the bulk motif is identical, so there is no overall transition with increasing *N* (Figure 2a).

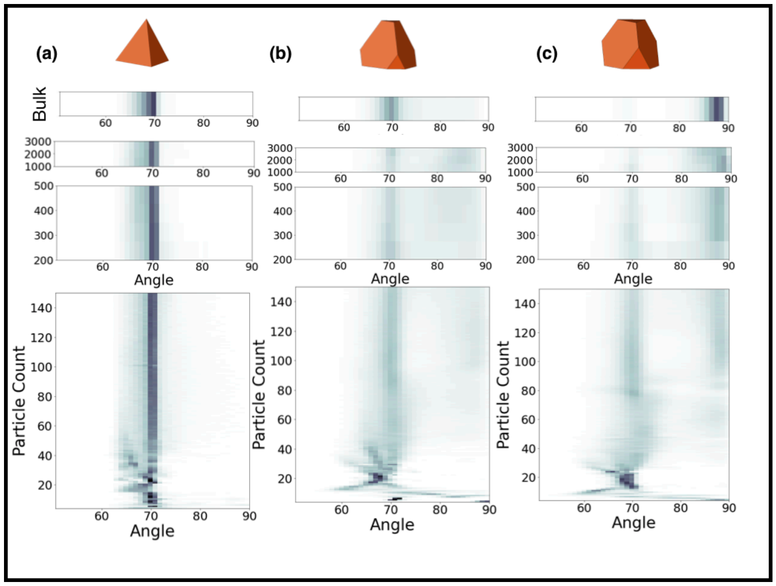

Figure 2: The distribution of misorientation angles for (a) Platonic tetrahedra, (b) space-filling truncated tetrahedra, and (c) Archimedean truncated tetrahedra with increasing container size. Color intensity corresponds to the frequency of that angle.

In contrast, the ATT bulk motif is anti-aligned, leading to a gradual transition in which the frequency of the anti-aligned motif increases and the aligned motif decreases (Figure 2c). The intermediate shape — STT — lies in a region that exhibits both aligned and anti-aligned motifs in the bulk.

In confined systems, we see first an increase in the frequency of the anti-aligned motif, followed by a decrease towards the bulk system, again persisting up to thousands of particles (Figure 2c). By mapping where different motifs occur, we see that in very large containers, the anti-aligned motif is clustered near the surface. This indicates that low-curvature walls favor the diamond-type structure.

Conclusions and Future Steps:

We have shown that it is possible to influence structure selection through changing the curvature of the walls of confined systems, driving assembly towards desirable structures. Going forward, we intend to study the effects of other confinement geometries.

References:

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