

Modeling morphology: Solid-solid phase transitions based on colloidal particle shape changes

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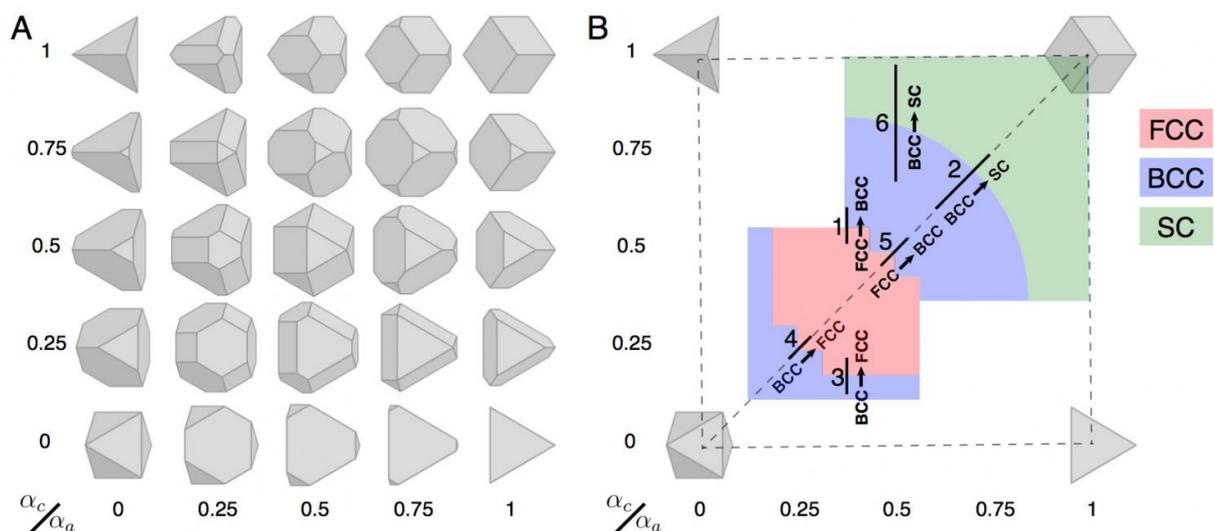


Fig. 1. (A) Spheric triangle invariant (Δ_{323}) polyhedra form a continuous two-parameter (α_a, α_c) family of symmetric convex shapes that are bounded by the octahedron [$(\alpha_a, \alpha_c) = (0,0)$], tetrahedron [$(0,1)$ and $(1,0)$], and cube $(1,1)$. (B) We show six lines indicating regions of shape space in which there is a change in the equilibrium structure at a packing density of $\eta = 0.55$. The lines are annotated with the relevant structural transition and direction. The colors indicate the self-assembled structures, where FCC is red, BCC is blue, and SC is green. The self-assembled phases indicated are an approximated representation from the actual phase diagram (45). Phases in the white region are not of interest in this paper. Results for transitions 1 and 2 are given in Figs. 4 and 5, respectively. Results for transitions 3–6 are in *SI Text*. Credit: Du CX, van Anders G, Newman RS, Glotzer SC (2017) Shape-driven solid–solid transitions

in colloids. *Proc Natl Acad Sci USA* 114:E3892-E3899.

(Phys.org)—Phase transitions are transformations that occur between states of matter—that is, between solid, liquid, gas, and less commonly between gas and plasma. What may be surprising is that solid-solid phase transitions, which are essential in metallurgy, ceramics, earth science, reconfigurable materials, and colloidal matter, are the *most* common. (Examples of solid-solid phase transitions include transformations between the three primary crystalline states of pure iron and self-organizing anisotropic colloidal suspensions—that is, colloidal suspensions having different properties along different axes.) Despite their ubiquity, however, high pressure and/or high temperature contexts and the need to employ high-resolution imaging technology have made studying solid-solid phase transition intermediate transformational states significantly challenging. Recently, scientists at the University of Michigan have devised computer models demonstrating solid-solid phase transitions based on colloidal particle shape changes as the control variable, reporting both discontinuous and continuous transitions (i.e., those that require and do not require thermal activation, respectively). The researchers state that by establishing a new method for studying solid–solid phase transitions, their models may support the design and generation of reconfigurable colloidal materials.

Doctoral candidate Chrisy Xiyu Du and Prof. Greg van Anders discussed the paper that they, Dr. Richmond S. Newman, and Prof. Sharon C. Glotzer, and their co-authors published in *Proceedings of the National Academy of Sciences* with *Phys.org*. Describing the main challenges in designing models that capture solid–solid phase transition thermodynamics and determining that a thermal activation barrier is not universally required in solid-solid transitions, van Anders tells *Phys.org* that "Solid-solid transitions have been important in technology for

thousands of years—in fact, since the beginning of the iron age—and are also important in geological processes. Moreover," he adds, "the pattern of symmetry breaking that exists in solids means that these transitions are not only technologically important, but that there are a lot of them. The problem in understanding the transitions is that they typically happen under extreme conditions (high temperature or pressure), which makes them hard to study."

Before their study, Du says, no other paper has done a thorough investigation of the thermodynamics for any colloidal solid-solid transitions. "This void in knowledge meant that regardless of the results we found, we needed to perform enough validation to convince ourselves that we were not observing artifacts from our simulations." She adds that anisotropic colloidal nanoparticles are perfect building blocks for crystal structure self-assembly—and researchers have been experimentally able to self-assemble these nanoparticles into colloidal crystal structures ranging from the basic and ubiquitous face-centered cubic phase to complicated phases such as clathrates.

Another challenge was finding order parameters that had appropriate signal-to-noise behavior—a particular concern, van Anders points out, because the systems they studied are entropically stabilized (that is, thermal fluctuations are fundamentally implicated in system behavior, but can complicate order parameter measurements). "Balancing these effects and checking that the behavior we observed was not an artifact of our parametrization required substantial effort."

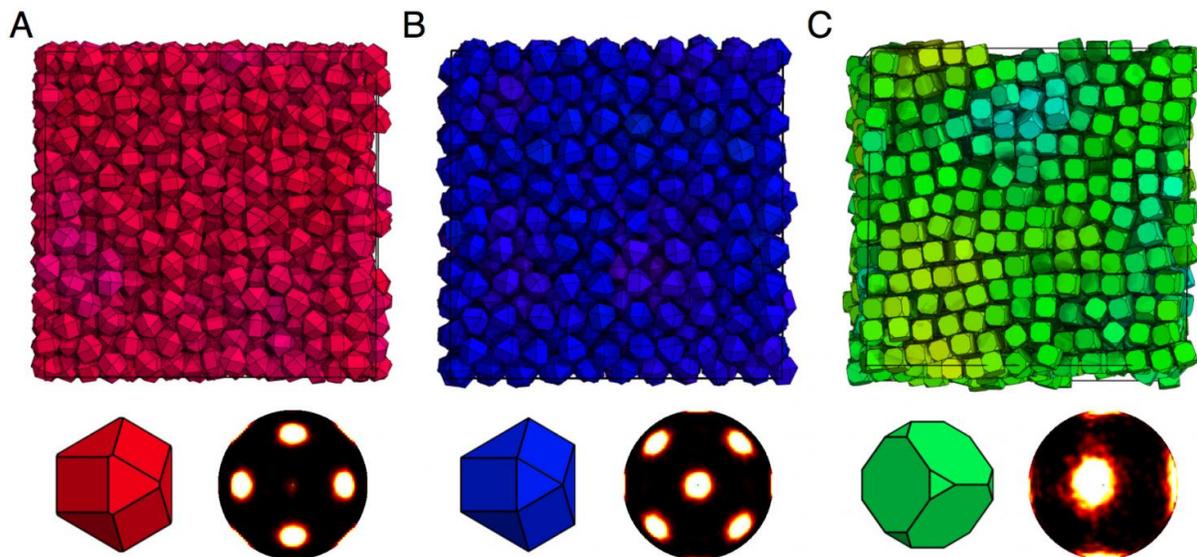


Fig. 2. Sample self-assembled colloidal crystals formed by shapes in the Δ_{323} triangle-invariant family of hard polyhedra, with images showing particle shape and bond order diagram. (A) An FCC crystal self-assembled from shape $(\alpha_a, \alpha_c) = (0:4, 0:525)$. (B) A BCC crystal self-assembled from shape $(\alpha_a, \alpha_c) = (0:4, 0:59)$. (C) An SC crystal self-assembled from shape $(\alpha_a, \alpha_c) = (0:76, 0:76)$. Note the similarity of shapes in A and B; even small shape differences can affect the bulk self-assembly of hard polyhedra. Shapes in A and B are both on line 1 in Fig. 1, and the shape in C is on line 2 in Fig. 1. Credit: Du CX, van Anders G, Newman RS, Glotzer SC (2017) Shape-driven solid–solid transitions in colloids. *Proc Natl Acad Sci USA* 114:E3892-E3899.

Du notes that while studying the thermodynamics of two stable phases individually is straightforward, simultaneous comparisons are difficult. "Due to the brief timescale and low probability of the system being in a transition state, we had to apply bias forces to study it. In addition to finding the right order parameter to distinguish different crystal phases—a challenge in its own right—we carefully tuned the strength of the bias force sampling intervals to reduce noise, thereby achieving a statistically significant conclusion."

Addressing these challenges, van Anders explains, involved measuring the change in the nearest-neighbor environment for particles before and after the transition, which is usually characterized using *coordination polyhedra* that provide a geometric division of the local environments. "We realized that if we could come up with systems in which it is possible to directly manipulate the coordination polyhedra, it could be possible to have solid-solid transitions that occur under less extreme conditions. To do this, we realized that in suspensions of anisotropically shaped colloidal nanoparticles it is possible to manipulate the particle shape, which in turn could allow control of the shape of the coordination polyhedra in the crystal." Changing colloid shape allows for solid-solid transitions in simulations that mimic normal laboratory conditions.

Du describes two key, prior insights used in this work: entropy can lead to order, and particle shapes can be included as a thermodynamic variable similar to temperature or pressure. "In our work, we combined these two insights and extended the study of solid-solid [phase transitions](#) to include building block properties such as shape. As to technical difficulties, we searched through the literature to select a good order parameter to distinguish different crystal structures, and then adapted it to meet our needs." The scientists also extended the NVT (or canonical) statistical ensemble—a constant-temperature, constant-volume ensemble—in [HOOMD-blue](#) (a general-purpose particle simulation toolkit) to better reduce noise in their simulations.

"Our work has two sets of implications," van Anders tells *Phys.org*. "Firstly, we showed that it is simple to construct minimal models of solid-solid transitions that occur in systems that can be studied in real time, simple, tabletop experiments using optical microscopy. This should give us new ways of getting detailed insight into how solid-solid transitions happen. Secondly, we demonstrated that solid-solid transitions driven by shape change occur on sufficiently brief timescales, allowing them to be used for making reconfigurable materials."

		Transition from Solid		Assembly from Fluid		
Initial Phase	Discontinuous	Metastable	 FCC	 BCC	 Fluid	 Fluid
Final Phase			BCC	FCC	BCC	FCC
Timescale τ			$\gg 10^7$		$\approx 10^6$	
Initial Phase	Discontinuous	Unstable	 FCC	 BCC	 Fluid	 Fluid
Final Phase			BCC	FCC	BCC	FCC
Timescale τ			$\lesssim 10^7$		$\approx 10^6$	
Initial Phase	Continuous	Unstable	 SC	 BCC	 Fluid	 Fluid
Final Phase			BCC	SC	BCC	SC
Timescale τ			$\lesssim 10^6$		$\approx 10^6$	

Fig. 7. Shape-driven solid–solid reconfiguration and self-assembly timescales for BCC, FCC, and SC structures. Thermodynamically discontinuous FCC↔BCC solid–solid phase transitions occur dynamically in MC simulations on timescales ($\tau \gtrsim 10^7$ MC sweeps) that are similar to self-assembly timescales ($\tau \approx 10^6$ MC sweeps) beyond the metastable region. In the metastable region, solid–solid reconfiguration does not occur on timescales ($\tau \gg 10^7$ MC sweeps) that are much longer than typical self-assembly times. Thermodynamically continuous BCC↔SC solid–solid phase transitions occur dynamically in MC simulations on timescales (τ

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