

Shape-sensitive crystallization in colloidal superball fluids

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Guiding the self-assembly of materials by controlling the shape of the individual particle constituents is a powerful approach to material design. We show that colloidal silica superballs crystallize into canted phases in the presence of depletants. Some of these phases are consistent with the so-called “ Λ_1 ” lattice that was recently predicted as the densest packing of superdisks. As the size of the depletant is reduced, however, we observe a transition to a square phase. The differences in these entropically stabilized phases result from an interplay between the size of the depletants and the fine structure of the superball shape. We find qualitative agreement of our experimental results both with a phase diagram computed on the basis of the volume accessible to the depletants and with simulations. By using a mixture of depletants, one of which is thermosensitive, we induce solid-to-solid phase transitions between square and canted structures. The use of depletant size to leverage fine features of the shape of particles in driving their self-assembly demonstrates a general and powerful mechanism for engineering novel materials.

superballs | phase behavior | dense packings | depletion interactions | Monte Carlo simulations

Determining the relationship between the macroscopic structure of a material and the properties of its microscopic constituents is a fundamental problem in condensed matter science. A particularly interesting aspect of this problem is to understand how the self-assembly of a collection of particles is determined by their shape. These so-called “packing problems” have long interested physicists, mathematicians, and chemists alike and have been used to understand the structures of many condensed phases of matter (1–3). Computational and experimental advances continue to enable new explorations into fundamental aspects of these problems today (4–13). Recent discoveries include dense packings of tetrahedra into disordered, crystalline, and quasi-crystalline structures (14, 15), as well as the singular dense packings of ellipsoids (16).

Technologically speaking, these discoveries are becoming increasingly crucial as new synthesis techniques are allowing for the creation of more and more complex shaped nanoscopic and microscopic particles (17, 18). The self-assembly of these particles into ordered structures creates new possibilities for the fabrication of novel materials (19–23). Moreover, advances in synthesis techniques have created new capabilities for experimentally investigating how the shapes of particles can be exploited in their self-assembly (24–26).

Here, we experimentally and computationally explore the self-assembly of colloidal superballs interacting with depletion forces. We find that monolayers of superballs can be tuned to equilibrate into both their densest known packings—so-called “ Λ_0 ” and “ Λ_1 ” lattices (12)—as well as into less dense structures of different symmetries depending on an interplay between the subtle features of the particle shapes and the size of the depletants. The family of superballs can smoothly interpolate shapes between spheres and cubes (Fig. 1E) and is modeled as

$$(x)^m + (y)^m + (z)^m \leq 1, \quad [1]$$

where m is the shape parameter. For $m = 2$, this parameterization describes a purely isotropic sphere. As m is increased, the shape increasingly resembles a cube, as shown in Fig. 1. The amorphous colloidal superballs were prepared via controlled deposition of silica on the surface of hematite templates, using a synthetic technique (27) that yields high amounts of monodisperse (3% polydispersity) particles. Each batch of particles, which were made from the same initial hematite cores, contains superballs of comparable sizes ($\sim 1.3 \mu\text{m}$), but differing shape parameters as a result of differing amounts of silica precipitated on the surface. Size and shape of superballs were analyzed using scanning electron microscopy (SEM) and transmission electron microscopy (TEM) micrographs (Fig. 1). Analyzing the particle shape from TEM images, we find agreement between the contour of the particle and the superball shape as shown in Fig. 1B, in which the red contours correspond to the superball fits. More information on the fitting procedure and shape polydispersity can be found in *SI Text*.

Fig. 1 shows SEM and TEM images of the silica superballs used for the experiments. Although the particles still possess a distinct cubic symmetry, they have rounded edges whose curvatures are consistent with superballs of shape parameters $m = 2.0$, $m = 3.0$,

Significance

Since antiquity it has been known that particle shape plays an essential role in the symmetry and structure of matter. A familiar example comes from dense packings, such as spheres arranged in a face-centered cubic lattice. For colloidal superballs, we observe the transition from hexagonal to rhombic crystals consistent with the densest packings. In addition, we see the existence of square structures promoted by the presence of depletion attractions in the colloidal system. By using a mixture of depletants, one of which is size tunable, we induce solid-to-solid phase transitions between these phases. Our results introduce a general scenario where particle building blocks are designed to assemble not only into their maximum density states, but also into depletion-tunable interaction-dependent structures.

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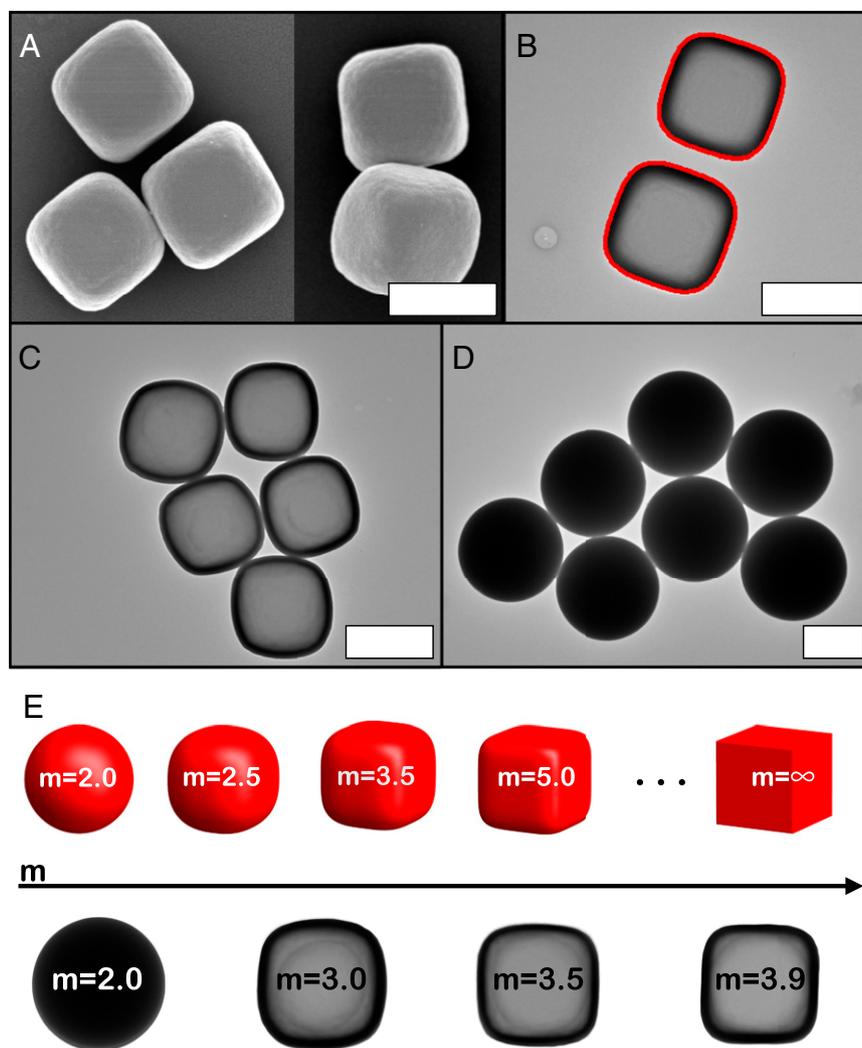


Fig. 1. (A) SEM images of sample $m = 3.9$. The particles have a cubic shape with rounded edges. (B–D) TEM micrographs of samples with $m = 3.5$, $m = 3.0$, and $m = 2.0$, respectively. All samples are uniform with a size polydispersity as low as 3%. (Scale bars: $1 \mu\text{m}$.) In B the particles are shown with their corresponding superball fit highlighted in red (see also Fig. S1). (E, Top) Computer-generated models of colloidal superballs with different shape parameters m . A gradual increase of the absolute value of the shape parameter from $m = 2$ (spheres) results in a gradual alteration of the particle shape to resemble more cube-like particles. (E, Bottom) TEM images of silica superballs with different m values.

$m = 3.5$, and $m = 3.9$. The spherical particles with shape parameters $m = 2$ were purchased from Bangs Laboratoires.

To perform the experiments, silica superballs were dispersed in slightly alkaline water ($\text{pH} = 9$) and were stabilized against aggregation by surface charges. Sodium chloride (10 mM, final concentration) was added to the dispersion to screen the charges and lower the Debye length down to a thickness of about 3 nm, small enough to allow the particles to fully experience their anisotropic shape. Attractive forces between superballs arise by addition of depletion agents with gyration radii of $R_g = 57$ nm, 65 nm, 70 nm, 210 nm, 228 nm, and 329 nm. Flat optical capillaries were filled with aqueous mixtures of superballs and depletants and were monitored in time with bright-field microscopy. More experimental details as well as information on depletants and sample preparation can be found in *SI Text*.

At low particle concentration, the superballs first sediment to the bottom of the capillary where they are attracted to the glass wall by depletion forces. While diffusing in the plane, the particles cluster together into monolayers. Once clusters are formed, time-lapsed images are collected and analyzed. The images show the appearance of several qualitatively distinct phases (Fig. 2).

The particles are found to arrange into crystallite islands, often possessing grain boundaries, which we separate by orientation and analyze independently. We do not exclude a priori the possibility that a cluster does not have a coherent crystal structure.

To characterize the structure of each cluster, the positions of the constituent particles are identified for every time-lapsed image. The relative positions of nearest neighbors are then computed for each particle. For spherical superballs the distribution of these positions are found to be consistent with triangular lattices (Fig. 2C). For superballs with intermediate shape parameters ($2 < m < \infty$), however, the behavior becomes more interesting. Experimentally, we observe that the particles often form canted structures (Fig. 2A) characterized by interparticle bond angles distinct from 60° , indicative of triangular lattices, and 90° , which are characteristic of square lattices. Recently, the densest packings of superdisks with these intermediate shape parameters were predicted to fall into two families of lattices, referred to as Λ_0 and Λ_1 packings (12). Testing the distribution of relative nearest-neighbor positions in the experiment for consistency with the lattice vectors of these structures confirms, for the first time to our knowledge,

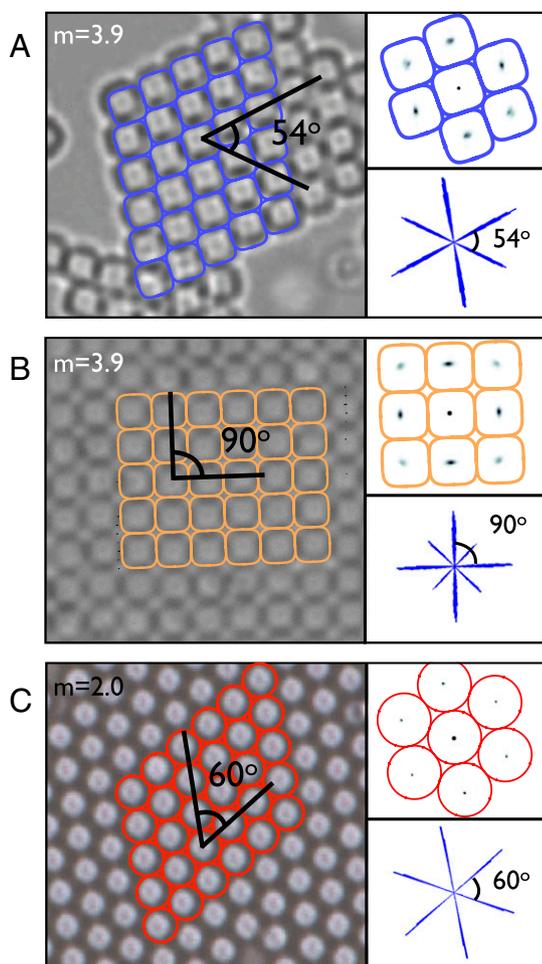


Fig. 2. Representative optical microscope images showing three different ordered structures found in superball samples. (A–C, *Right*) Histogram of the relative positions of nearest neighbors for each particle in a crystallite (*Top*) and a histogram of the interparticle bond angles (*Bottom*) (see also Fig. S2). The structures of the crystallites are characterized by bond angles of 54° (A), 90° (B), and 60° (C). Note that the superballs in A and B have the same shape. The different lattice structures in these two samples result from different depletant sizes.

the observation of an equilibrium Λ_1 lattice of superballs in experiments (Fig. 2). We also find that, for superballs with these same intermediate shape parameters ($m = 3.5$ and $m = 3.9$), the equilibrium structure transitions to a square lattice as the depletant size is decreased, suggesting that the resulting phases are determined by an interplay between the shape of the particle and the size ratio $q = 2R_g/L$ between the depletant and the superball.

To understand this interplay, we look at the depletion interactions between the superballs. Each superball is surrounded by an exclusion zone of thickness R_g that is unavailable for the centers of the depletants to occupy. Superball configurations that minimize the volume excluded from the depletants by overlapping exclusion zones increase the overall entropy of the system. To understand the favorability of the three lattices for a given choice of parameters, we compute the free energy of a depletion-stabilized bound state of a particle for each crystal type. For a number density n of depletants, this energy is given by $U = -nK_B T \Delta V_{\text{ex}}$, where ΔV_{ex} is the change in volume excluded when a particle is removed from the interior of an otherwise filled lattice. By computing and comparing ΔV_{ex} for the Λ_0 , Λ_1 , and square lattices, we estimate which lattice is energetically

favorable for a particular value of m (Fig. 3). In this model, the magnitude of ΔV_{ex} , and thus the overall bound state energy, will generally scale with R_g . We note that this model neglects the entropy of the superballs. It has been suggested that the role of rotational entropy of the particles can be significant in stabilizing canted phases (25), although the relative importance of this effect is debated (13). Fig. 3B shows that, for fixed-sized depletants and superballs, ΔV_{ex} varies smoothly for each lattice type as m is varied. For a particular combination of m and q , the lattice with the highest value of ΔV_{ex} represents the preferred phase. Using this principle, a 2D phase diagram is approximated in Fig. 3C. The interplay between the particle shape and the size ratio q suggested by this diagram is qualitatively apparent in the experimentally realized structures (Fig. 4).

Indeed, the calculations agree with the experimental result that for sufficiently small depletants and sufficiently large m , square lattices, although they are not the densest packings for any finite value of m , are preferred. Square lattices occur when m is large enough such that the overlap in exclusion zones resulting from face-to-face contact is considerable and for q small enough such that depletants are able to fit into the interparticle pores made where the rounded edges of the superballs meet. When the osmotic pressure exerted by a depletant within an interparticle pore is substantial, the cubic phase is stabilized. However, when intermediate-sized depletants, which can no longer fit into the spaces within the lattice, are dispersed with superballs possessing these larger values of m (3.5 and 3.9), the densely packed Λ_1 phase emerges. As the size ratio gets larger, we note the distribution of bond angles within a crystallite begins to broaden. In the case of $m = 3.9$, for the highest size ratio q we tested, the distribution was too broad to identify the experimental structure with one of the three lattices, leaving the structure undetermined.

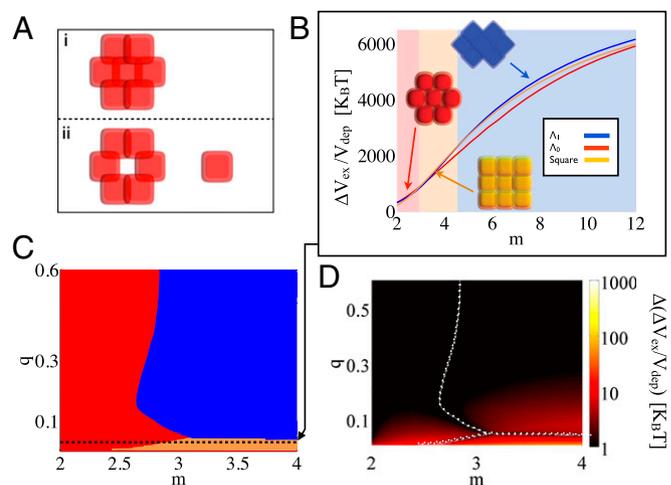


Fig. 3. Two-dimensional predicted diagram for depletion-stabilized superball phases. The favorability of each lattice type is determined by calculating the bound state energy of a particle. (A) Operationally, the bound state energy is found by computing the difference in the excluded volume for a particular lattice (A, *i*) and the excluded volume of that lattice when a particle is removed from the interior (A, *ii*). (B) Change in excluded volume for each lattice type with varying m but fixed $q = 2R_g/L$, where R_g is the radius of gyration of the depletant and L is the diameter of the superball. To illustrate the behavior of ΔV_{ex} , the range of m used in this plot is larger than the experimentally investigated range. Background color indicates the preferred phase. (C) Two-dimensional phase diagram for experimental range of q and m . (D) Difference in ΔV_{ex} between two most favorable lattice types. Near phase boundaries, the phases become degenerate. In addition, for large depletants, the benefit of choosing a particular phase is small (see also Fig. S3). Recent molecular dynamics simulations (12) of convex superdisks have shown that the critical value of m when the densest packings change from Λ_1 to Λ_0 is at $m \approx 2.572$.

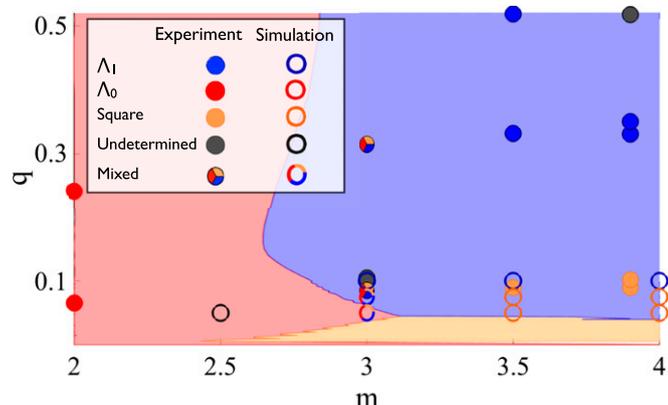


Fig. 4. Comparison between experimental observations, bulk crystal simulations, and calculated phase diagram for superballs at different m and q values. Circles indicate the experimental results, open circles indicate simulation results, and the background color indicates the predicted phase. The approximated phase diagram qualitatively agrees with our experimental and simulation results.

Whereas our calculations suggest that the Λ_1 phase is energetically favorable, Fig. 3D shows that the difference in ΔV_{ex} between the lattices with the two highest values becomes negligible for large q . This suggests that the energetic benefit of choosing a particular phase decreases, which is consistent with our observation that the variance in experimental bond angle distributions increases for high q .

As mentioned previously, spherical superballs form triangular lattices, which are equivalent to the Λ_0 lattice for $m=2$. For small deviations from spheres, our calculations suggest that the Λ_0 lattice also tends to maximize ΔV_{ex} . As the deformation parameter is increased, however, the value of ΔV_{ex} for a different

lattice, depending on q , surpasses that of the Λ_0 lattice. This can be seen, for example, in Fig. 3B where the curve representing the square lattice intersects the curve representing the Λ_0 lattice. At this intersection point, the lowest energy state becomes degenerate. Near these regions, the difference in energy between the most favorable lattices is small (Fig. 3D). As a result, we find experimental structures near phase boundaries fail to conform to a single coherent crystal type. Again, here we find some experimental structures are characterized by broad variances in bond angle distributions, which disallow the identification of a particular crystal type. Often, however, although there are insufficient statistical data to make a precise classification, we find the appearance of mixed assortments of crystallites (*SI Text*) of both cubic structures and undetermined, noncubic structures within a single sample cell.

To more carefully probe the stability of our observed lattices, we perform idealized simulations of superballs and depletants (*SI Text* and Fig. S4). We first simulate finite crystallites and find the results qualitatively agree with experiments (Figs. S5 and S6). A particular choice of initial conditions, however, may influence the vulnerability of the resulting assembly to fall into kinetic traps. To probe the true stability of our candidate lattices, and to remove surface effects that exist in finite crystallites, we perform bulk crystal simulations, using periodic boundary conditions of each candidate lattice (Fig. S7). Fig. 4 shows the resulting stable lattices determined from these simulations. The results qualitatively agree with our excluded volume calculations. It is interesting to note that near phase boundaries both Λ_1 and square lattices often can be stable for the same parameters, as suggested by the appearance of mixed crystallites in experimental structures. In addition, we find that, for m values between 2 and 3, particles often assemble with irregular orientations with respect to their neighbors, consistent with the observation of indeterminate experimental structures.

It is particularly interesting to note that for both experiment and simulation, we identify different crystalline structures as q is

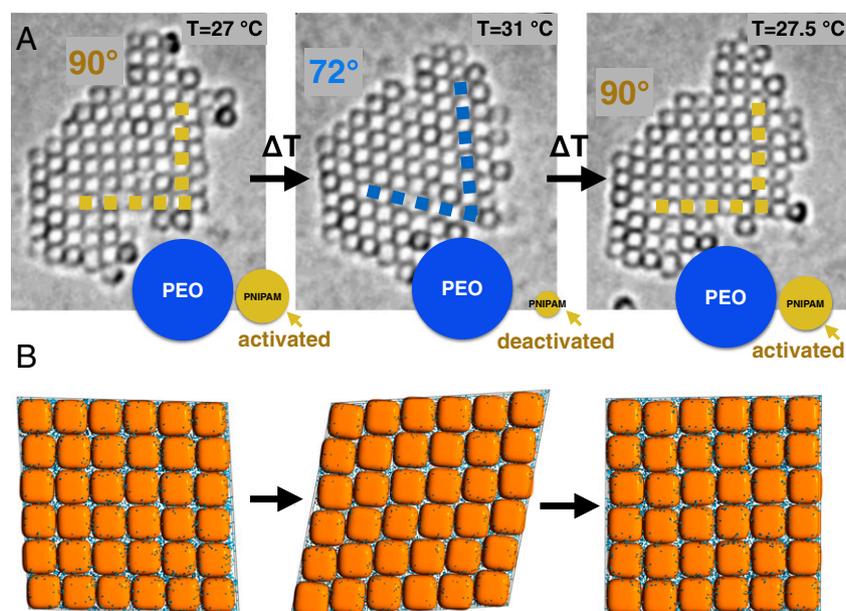


Fig. 5. Demonstration of reversible solid–solid phase transition of superballs. (A) Colloidal superballs with shape parameter $m = 3.9$ dispersed in depletant mixture of PEO and pNIPAM. At 27.5 °C, superballs assemble into a square lattice. At 31 °C, energetic contribution of pNIPAM becomes negligible, while that of PEO stays fixed, resulting in the transition into a Λ_1 lattice. (B) Simulated phase transition in a bulk crystal of superballs and depletants. A periodic lattice of superballs is simulated along with a mixture of two species of depletants, one with fixed size ratio of $q_1 = 0.35$ (which favors a Λ_1 lattice) and a smaller depletant (which favors a square lattice) of size ratio varying from $q_2 = 0.04$ to 0.032. As the smaller depletant is reduced in size, its overall energetic contribution decreases and the lattice transitions to a Λ_1 structure. When the size of the smaller depletant is once again increased, the square lattice once again emerges.

varied for $m \geq 3.5$. In principle, it is thus experimentally possible to use size-variable depletants to reversibly switch the lattice structure within a single sample. To explore this possibility, we use thermosensitive poly(*N*-isopropylacrylamide) (pNIPAM) microgel spheres as depletants. Although we find inducing a structural transition with pNIPAM depletants alone is difficult (*SI Text*), we find that, using a bidepletant mixture, we are able to entropically drive a solid–solid transition. This transition demonstrates a powerful mechanism in which leveraging different geometric features of individual particles enables one to controllably and reversibly tune their assembly.

To drive this transition, we use superballs with shape parameter $m = 3.9$ and a mixture of polyethylene oxide (PEO) and pNIPAM as depletant. Using the pNIPAM alone, the superballs form square lattices at 25 °C. When they are heated to 29 °C, we find the overall superball interactions induced by pNIPAM decrease sufficiently to melt this square lattice (*Movie S1*). Moreover, when the superballs are dispersed with PEO (molecular weight of 8 M) alone as depletant, we find we are able to stabilize a Λ_1 lattice of superballs (*Movie S2*).

Using a mixture of the two depletants, however, allows us to reversibly switch between the two lattice types by varying the temperature. At room temperature, the interactions induced by the pNIPAM are activated, and the superballs once again favor a square lattice. As the temperature is increased, the relative energetic contribution of the pNIPAM depletant decreases, while the contribution of the PEO remains the same. Because the PEO dominates the overall energy at high temperatures, the Λ_1 lattice emerges. Fig. 5 and *Movie S3* demonstrate this reversible solid–solid phase transition.

By performing simulations of bidepletant superball dispersions we provide further evidence of the simple entropic nature of the geometric mechanism that induces this solid–solid transition. Again we perform periodic simulations of a bulk crystal as well as simulations of finite crystallites. Superballs are dispersed with two species of depletant, one with fixed size ratio $q_1 = 0.35$, which is found to stabilize a Λ_1 lattice, and a variable-size depletant with initial size ratio $q_2 = 0.04$, which is found to stabilize a square lattice.

When dispersed in a mixture with number densities $n_1 = 24.9L^{-3}$ and $n_2 = 596.8L^{-3}$ for the large and small depletant, respectively, superballs with shape parameter $m = 4$ arrange into a square lattice. Here L is the diameter of the superball. As the smaller depletant is shrunk by 20% at fixed number density, its induced pressure remains fixed while its overall energetic contribution is lowered. We find, consistent with our experimental observations, that the lattice becomes canted. Upon increasing q_2 once again, we find the square lattice is restored (*Figs. S8 and S9* and *Movie S4*).

In this article we have demonstrated the reversible assembly of the same superball-shaped colloidal particles into both a square phase and the recently predicted Λ_1 phase. We show depletant size can be used to tune interparticle interactions. As a result, both particle shape and depletant size are used to determine the resulting phases. By mixing large depletants and small thermosensitive depletants we demonstrate a fully reversible solid-to-solid transition between square and Λ_1 superball phases. The sensitivity of the assembled phase to a fine feature of the particle shape, combined with a mechanism to reversibly activate a depletant on that scale, demonstrates that depletants can be used to tune interactions. These results create previously unidentified opportunities for controlling the reversible self-assembly of colloidal particles and controlling phases, for example through solid-to-solid phase transitions.

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