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. 1*E*) and is modeled as

$$(x)^m + (y)^m + (z)^m \le 1, \qquad [1]$$

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 (~1.3 μm), 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. 1*B*, 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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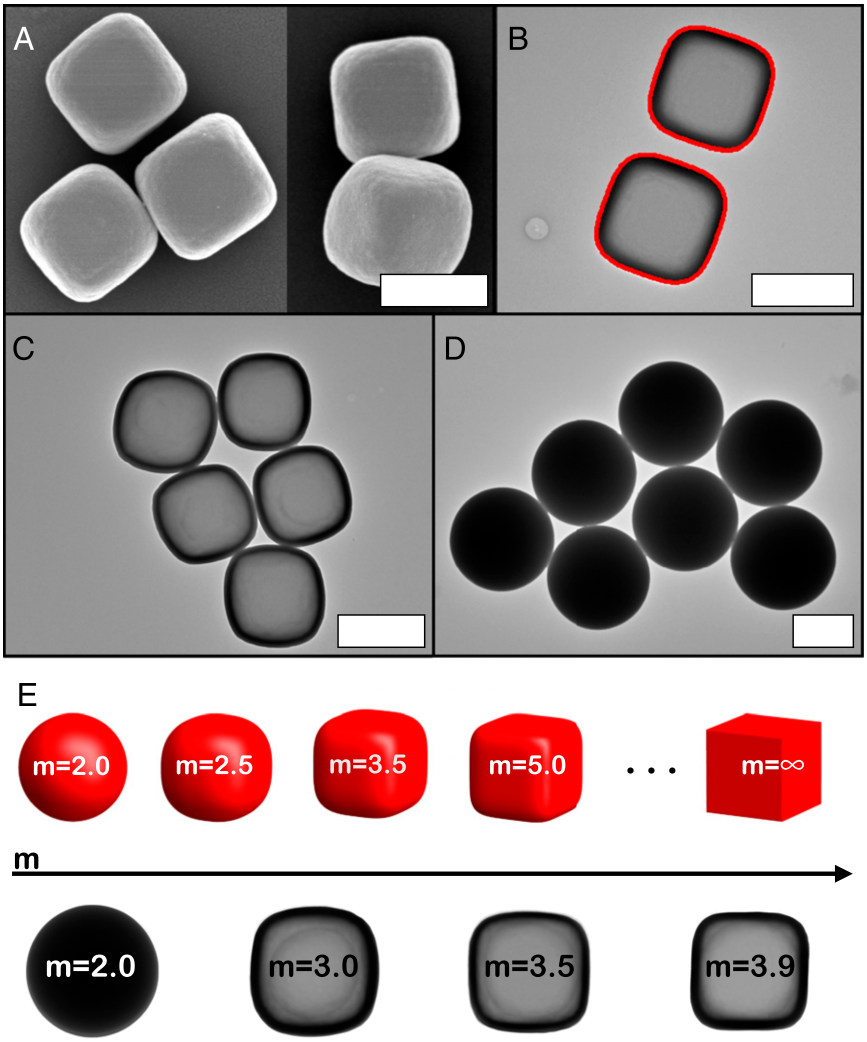

Fig. 1. (*A*) SEM images of sample $m = 3.9$. The particles have a cubic shape with rounded edges. (*B–D*) TEM micrographs of samples with $m = 3.5$, $m = 3.0$, and $m = 2.0$, respectively. All samples are uniform with a size polydispersity as low as 3%. (Scale bars: 1 μm.) In *B* the particles are shown 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 (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. 2*C*). 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. 2*A*) 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,

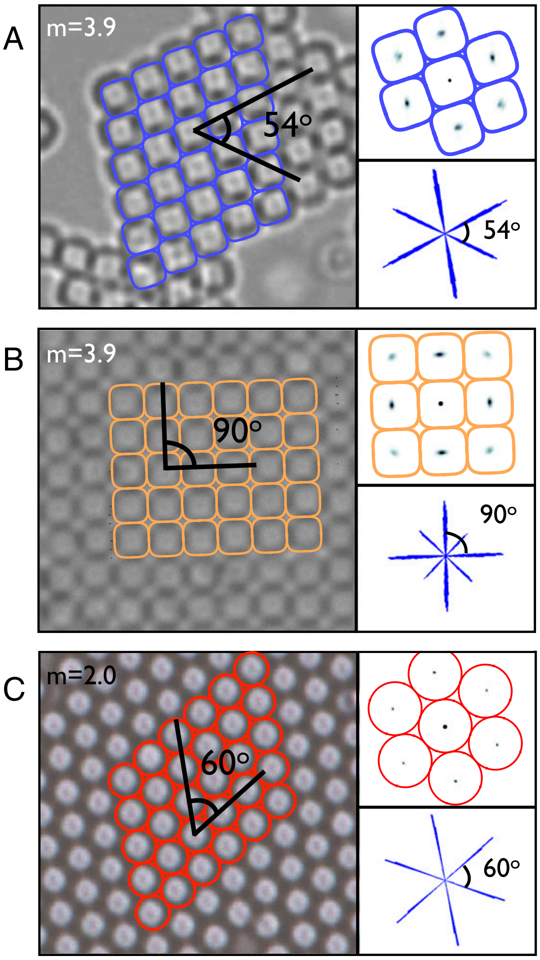

Fig. 2. Representative optical microscope images showing three different ordered structures found in superball samples. (*A*–*C*, *Right*) Histogram of the relative positions of nearest neighbors for each particle in a crystallite (*Top*) and a histogram of the interparticle bond angles (*Bottom*) (see also Fig. S2). The structures of the crystallites are characterized by bond angels 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 $U = -nK_BT\Delta V_{\mathrm{ex}}$, 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. 3*B* 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. 3*C*. 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.

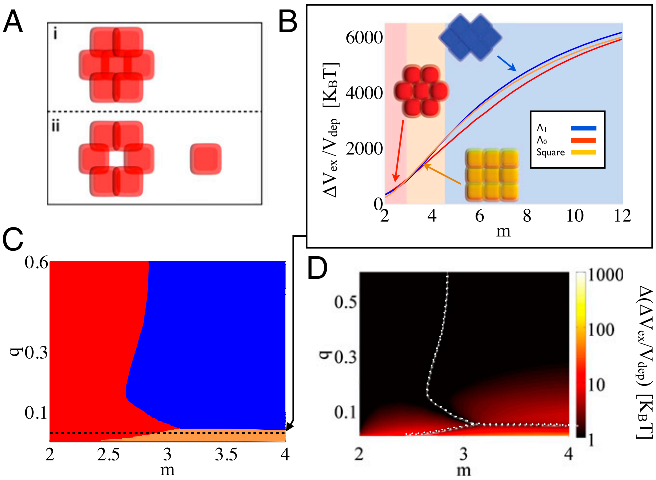

Fig. 3. Two-dimensional predicted diagram for depletion-stabilized superball phases. The favorability of each lattice type is determined by calculating the bound state energy of a particle. (*A*) Operationally, the bound state energy is found by computing the difference in the excluded volume for a particular 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 $m \approx 2.572$.

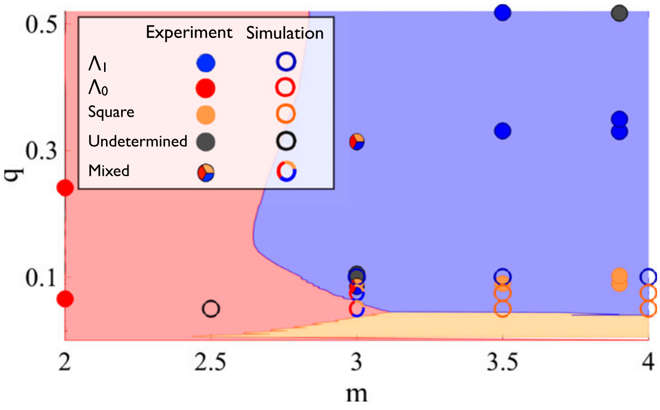

Fig. 4. Comparison between experimental observations, bulk crystal simulations, and calculated phase diagram for superballs at different *m* and *q* values. Circles indicate the experimental results, open circles indicate simulation results, and the background color indicates the predicted phase. The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

Whereas our calculations suggest that the Λ_1 phase is energetically favorable, Fig. 3*D* 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. 3*B* 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. 3*D*). 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

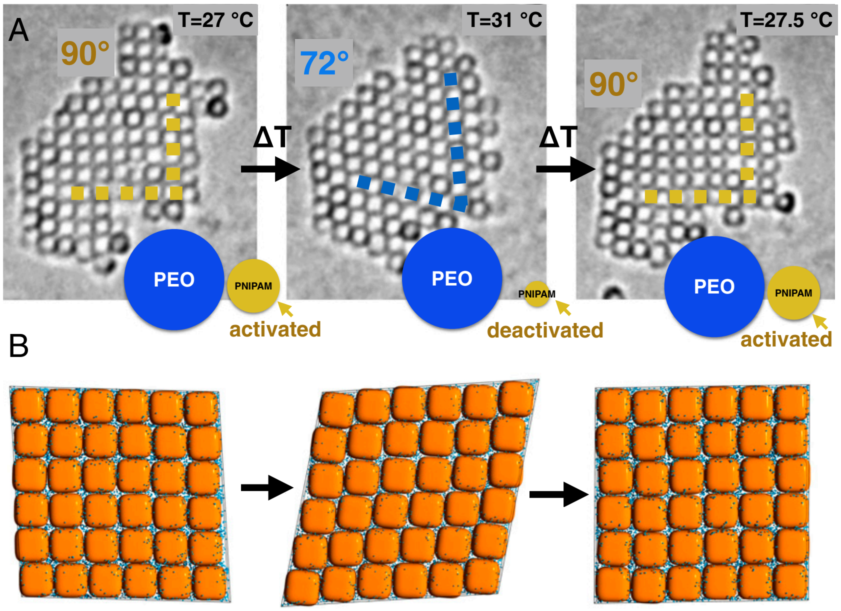

Fig. 5. Demonstration of reversible solid–solid phase transition of superballs. (*A*) Colloidal superballs with shape parameter $m = 3.9$ dispersed in depletant mixture of PEO and pNIPAM. At 27.5 °C, superballs assemble into a square lattice. At 31 °C, energetic contribution of pNIPAM becomes negligible, 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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Supporting Information

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SI Text

Depletant Solutions

Attractive forces between superballs were induced by addition of depletion agents with different gyration radii. The depletant dispersions consisted of polymers, microgels, and colloidal particles and each dispersion was prepared and stored as indicated below.

Poly(ethylene oxide). We used poly(ethylene oxide) (PEO) polymer with two different molar masses, namely 6×10^5 g/mol (PEO 600 k) and 7×10^6 g/mol (PEO 7 M), corresponding to a radius of gyration R_g of, respectively, 57 nm and 210 nm (1). The polymer stock solutions of 2 g/L were prepared by dissolving PEO in 10 mM aqueous sodium chloride (NaCl) and they were freshly prepared before microscopy experiments.

Xanthan. Xanthan is a wormlike double-helical polysaccharide with a diameter of ca. 2.2 nm and a persistence length of 120 nm. The stock solution with a final xanthan concentration of 1 g/L was prepared by dissolving xanthan powder (Sigma Aldrich) in water containing 10 mM NaCl and 2 mM sodium azide (NaN_3), the latter to prevent bacterial growth. The mechanically stirred solution was heated to 85 °C using an oil bath and then slowly cooled for about 15 h (2). The xanthan batch used here has a weight-average molar mass M of 3×10^6 g/mol, contour length L_c of about 1.5 μm, and radius of gyration R_g of 329 nm.

Poly(*N*-isopropylacrylamide). Poly(*N*-isopropylacrylamide) (pNIPAM) microgel particles with a radius of 65 nm were prepared following ref. 3. The particles were stored in Millipore water. The total measured mass concentration of the particles in the stock dispersion was 1.22% wt.

Colloidal Akaganèite. Akaganèite (β-FeOOH) rods were prepared following ref. 4. The particles were stored in ethanol at a concentration of about 13% wt. The average length of the rod-like particles was estimated to be 140 nm with a polydispersity of about 30%.

Sample Preparation for Optical Microscopy

Samples with superballs and depletion agents were prepared following the same procedure independently on what depletant was used. First, a small amount of silica superballs (~1 mL), usually stored in ethanol, were sedimented using a microcentrifuge (Beckman Coulter Microfuge 16, typical working speed 1,300 × *g* for about 20 min) and dispersed in water at pH 9; this pH was reached by adding 20–30 μL tetramethylammonium hydroxide 1% wt to 1 mL water. If a dispersion appeared stable under the optical microscope, particles were sedimented and dispersed in 1 mL aqueous solution of 10 mM NaCl, pH 9, containing different depletant dispersions. In samples containing PEO depletant, to prevent PEO adsorption on the surface on the particles, Pluronics F 127 was added to the sample to reach a final Pluronics F 127 concentration of 500 μg/mL. Superballs were dispersed very well and occasionally briefly sonicated. The dispersions were placed into flat VitroCom optical capillaries (0.1 mm × 2 mm × 5 cm) and sealed with UV-sensitive epoxy glue onto clean microscope slides. The samples were allowed to equilibrate for about 20 min before imaging.

Crystal–Crystal Transition

Using pNIPAM depletants alone to induce a crystal–crystal transition poses challenges due to the narrow parameter range that supports suitable interparticle interactions. As the particles shrink at high temperatures, the overall interaction energies decrease considerably, often melting the resulting crystals. Moreover, increasing the number density of the depletant to compensate for the energy loss results in too strong interactions between particles when the depletant is in the expanded state. As a result, it is difficult to achieve the proper conditions for assembly at both the shrunken and expanded states for pNIPAM alone. Thus, crystal–crystal transition experiments were performed using a mixture of pNIPAM and PEO depletants. We used PEO with a molecular weight of 8×10^6 g/mol (PEO 8 M), corresponding to a radius of gyration of ~228 nm (1). pNIPAM microgel particles used in these crystal transition experiments were prepared with no added cross-linker, following ref. 5, and the stock dispersion consisted of the whole reaction dispersion brought to a final NaCl concentration of 10 mM by adding 280 mM NaCl.

Because we were unable to characterize pNIPAM particles using dynamic light scattering, we instead characterized their effect on the assembly of silica superballs. To do that we added 6 μL pNIPAM stock dispersion to 7 μL of a diluted superball suspension, resulting in a total dispersion volume of 13 μL, which was kept at pH 9 and 10 mM NaCl. We find superballs robustly form square lattices at 25.5 °C. When heated to 28.5 °C, we find that depletion interactions weaken considerably, resulting in the complete melting of crystallites. When cooled down once again, the square lattices begin to assemble back (Movie S1).

To test the behavior of superballs dispersed in PEO 8 M we prepared an aqueous dispersion of superballs in 0.31 g/L PEO 8 M, keeping the NaCl concentration at 10 mM and the pH at 9. To prevent adsorption of the PEO onto the surface of the superballs, Pluronics F 127 was added to the sample to reach a final concentration of 500 μg/mL. We find the superballs assemble into Λ_1 lattices (Movie S2).

To perform crystal transition experiments we used a mixture of PEO 8 M and pNIPAM with the same final concentration used for the single depletant experiments reported above. A total of 13 μL of superball dispersion with a final PEO concentration of 0.31 g/L was prepared by mixing 6 μL of the pNIPAM stock dispersion to 7 μL of a superball–PEO 8 M mixture (Movie S3).

Shape Parameters of Silica Superballs

The silica superballs reported in this work (except silica spheres) were obtained by depositing an amorphous silica layer with varying thicknesses starting from the same hematite cores. As the shape parameter m decreased with increasing silica thickness we obtained superballs with $m = 3.9$, $m = 3.5$, and $m = 3.0$, starting from hematite cores having $m \approx 4.0$. Growing an even thicker silica layer would result in superballs with $m < 3.0$. Using these hematite seeds, it is not possible to prepare superballs with $m < 2$.

The contour of a superball is mathematically represented by the formula

$$(x)^m + (y)^m + (z)^m = 1, \qquad \textbf{[S1]}$$

where x, y, and z are Cartesian coordinates and m is the shape parameter, which indicates the extent of deformation. Fig. 1*E* of the main text shows computer-generated models of colloidal superballs with different shape parameters. It is possible to recognize two special cases, which are represented by the sphere for $m = 2$ and the perfect cube for $m = \infty$. All of the intermediate shape parameters ($m > 2$) correspond to particles having a shape that interpolates between the sphere and the cube. Shape parameters between 2 and 1 correspond to a different family of square-symmetric superballs, whereas shape parameters smaller than 1 correspond to convex solids (6).

To determine the parameters that uniquely characterize the shape of our synthetic particles, we took as a starting point transmission electron microscopy (TEM) images, such as the ones shown in Fig. 1 *B* and *C* of the main text. We then used a standard algorithm to find the edges of the particle and subsequently fitted the edges with the equation

$$\left(\frac{x}{a}\right)^m + \left(\frac{y}{b}\right)^m = 1, \qquad \textbf{[S2]}$$

where a and b are the semiaxes of the particles. Eq. **S2** differs from Eq. **S1** because the analysis is done on TEM images, which are essentially 2D projections of the superballs, and also because Eq. **S2** should account for deviations in the particle aspect ratio (a/b) that, by definition, is 1 for a superball. A typical fit is shown in Fig. 1*B* in the main text and a plot of the results obtained by fitting an ensemble of images (about 100 fits) for different m values is shown in Fig. S1. The average value of m obtained for each superball sample can therefore be used to characterize the roundness of the shape and consequently how much the shape deviates from the cubic shape. The dense cloud of data for the superballs with highest m (sample S3.9, purple points in Fig. S1) indicates that particles are highly monodisperse in shape. The data spread out more for decreasing shape parameter, which is apparently related to the (still poorly understood) mechanism of silica growth on a superball surface. The plot in Fig. S1*B* exhibits for sample S3.0 a curious relation between particle size and shape. The graph shows that for small particle size the sample is monodisperse in shape until a critical particle length is reached (L_c, in this case corresponding to 1.26 μm) at which the shape polydispersity increases. Upon further silica growth beyond the critical length, the shape becomes again monodisperse. The nature of this growth behavior remains to be clarified; the important point here is that despite the polydispersity of samples S3.0 and S3.5, the average position of the data points in Fig. S1 clearly demonstrates that the various superball samples have significantly different average shape parameters.

Bond-Angle Distributions

After particles are allowed to relax, time-lapsed images are collected and analyzed. The particles are identified using an algorithm based on circular Hough transforms. After identifying the positions, we cluster the particles and separate the clusters based on their apparent orientation. For each particle within a cluster, we compute the angles between adjacent nearest-neighbor bonds. An ensemble of bond angles is collected over time and over each particle within a cluster.

The bond-angle distributions are used to identify which of the lattice type of interest are statistically most similar to the experimental structures. This is accomplished by comparing the resulting distributions to the values of the bond angles expected for the square, Λ_0, and Λ_1 lattices for the particular value of m. Fig. S2*A* shows the distribution of bond angles for experimental data corresponding to a variety of shape parameters. For experiments characterized by broad distributions of bond angles (Fig. S2 *C* and *D*), a clear identification may not be possible.

Predicted Phase Diagram

The bound state energy of a superball inside of a depletion-stabilized lattice is given by $U = -nK_BT\Delta V_{\mathrm{ex}}$, where ΔV_{ex} is the change in volume excluded when a particle is removed from the interior of an otherwise filled lattice and n is the number density of depletants. This volume change is computed by first constructing a finely pixelated binary image of an arrangement of filled outlines of superballs of length $L + R_g$ placed at the lattice sites corresponding to square, Λ_0, and Λ_1 lattices for fixed L and shape parameter m. Similar images are produced corresponding to the same arrangement with one particle removed from the interior of the lattice. ΔV_{ex} is computed by subtracting the total number of nonzero pixels for the full lattice by the lattice with one particle missing and then subsequently subtracting the number of nonzero pixels for an isolated superball of length $L + R_g$. 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. S3 *A* and *C*).

To quantify how energetically favorable a particular lattice is for a particular m and q, we also compute the difference in energy between the two lattices that have the lowest values. This difference characterizes the energetic benefit of choosing one particular lattice. When the difference is zero, the most favorable lattices becomes degenerate.

To compare the energetics in different regions of the phase diagram, however, a consistent definition of the number density of depletants n must to be used. Fig. S3*E* shows the diagram computed using a constant depletant density between experiments. In our experiments, the depletant concentration is typically on the order of C^*, where C^* is maximum density in which the depletants can maintain their radius of gyration. We thus use $n \propto 1/V_{\mathrm{dep}}$, where V_{dep} is the volume of the depletant. Fig. S3 *B* and *D* shows the resulting diagram, which corresponds to normalizing the difference in ΔV_{ex} by the volume of the depletant. We note that this simple model neglects to account for the rotational and vibrational entropy of the superballs.

Fig. S3 *C* and *D* corresponds to diagrams computed for 2D arrangements of 3D superballs. The complementary diagrams for purely 2D superdisks are shown in Fig. S3 *A* and *B*. The qualitative similarity reflects the quasi-2D nature of the system.

Simulation Details

We consider colloidal superballs with a surface satisfying the equality

$$|x|^m + |y|^m + |z|^m = \left(\frac{\sigma_c}{2}\right)^m, \qquad \textbf{[S3]}$$

where σ_c is the superball diameter at its narrowest point and m controls the particle shape as described in the main text. The rounded cubes are treated as hard particles with no attraction or repulsion and are confined to move in a 2D plane to mimic moving on a substrate. The depletants may move in all three dimensions and are modeled as penetrable spheres of diameter $\sigma_d = 2R_g$, with R_g the radius of gyration of the polymer depletant, that may overlap with one another but not with the superballs. Overlap is detected using the algorithm of Donev (7) as implemented in ref. 8.

For all simulations described here we study a fixed number, N, of superballs and the depletant particles are treated grand canonically with a constant chemical potential, μ_d, corresponding to a fixed reservoir volume fraction, η_d^r. Instead of the depletant diameter we quote the size ratio, $q = \sigma_d/\sigma_c$, which we study in the range $0.04 \le q \le 0.35$. The volume fraction, η_d^r is related to reservoir number density by

$$\eta_d^r = \frac{n_d^r \pi \sigma_c^3 q^3}{6} \qquad \textbf{[S4]}$$

and from here on we quote reservoir number density.

The difficulty in simulating highly size-asymmetric binary mixtures is that rearrangements of the large particles (the ones we are most interested in) are limited by the length scales of the smaller particles. To remediate this problem we use the geometric cluster algorithm (GCA) of Dress and Krauth (9), later extended by Liu and Luijten (10). In this method a large particle is added to the cluster and moved using a self-inverse operation, such as reflection in a point pivot. After this move, any particles overlapping are also added to a cluster. At each iteration a particle is taken off the bottom of the stack and moved, repeating until all particles have been moved or no overlaps remain. Clusters may move an arbitrary number of large particles or can be limited to one large particle. Rearrangement of large clusters is vital in the early stages of self-assembly, whereas single-particle moves are more efficient for relaxing particles within an assembled structure.

Special consideration is required for moving anisotropic particles such as the superballs considered here. As described in ref. 11, we include a GCA move that reflects a large particle in a plane instead of a point pivot as shown in Fig. S4. If the plane lies close to one of the superball's axes, then the rotation can be arbitrarily small. This allows the large particles to fully explore their orientational degrees of freedom. Our full move set is as follows: Each Monte Carlo sweep we attempt on average one large cluster move and N single-particle moves. For the single-particle moves the reflection pivots and planes are chosen close to the target particle to increase the acceptance rate.

Even using the GCA simulations is challenging for a number of reasons: The interactions are strong and short ranged, which makes assembly difficult with very long physical timescales. Computationally the overlap checks with superballs are expensive and often require slowly converging numerical solvers. The large number of depletants means that many overlap checks need to be made. In particular, to observe transitions between states in a reasonable timescale, care has to be taken to choose parameters that do not create interactions that are too strong, leading to kinetic trapping, while strong enough to allow assembly.

Self-Assembly Simulations

To study the formation of self-assembled structures we place $N = 169$ superballs evenly distributed in a periodic box of dimensions $L_x = L_y = 30\sigma_c$ and $L_z = 1.05\sigma_c$. The box is filled with depletants grand canonically before the large particles are allowed to move. The simulation is then run until the assembled structures are stable to rearrangement. We studied a range of particle shapes, m, and depletant size ratios, q, and for each combination scanned a range of depletant number densities, n_d^r to find the point of best assembly. We found that the window between the interactions being too weak for assembly and too strong for good assembly (kinetic trapping) was quite narrow due to the short-ranged nature of the depletion interaction.

The final configurations are shown in Fig. S5, indicating the different structures that assemble for different combinations of shape and depletant size. The simulations suffer from kinetic trapping, in particular when the depletant is small, in a manner quite similar to that seen in experiments. The stable structures from these simulations generally agree with the experimental results. The results are summarized and compared with the experiment in Fig. S6.

Bulk Phase Simulations

To better understand which phase, square or Λ_1, is truly thermodynamically stable we also performed simulations in the bulk to remove surface effects. Simulations were performed in the $NPT\mu_d$ ensemble at a constant pressure, P, and fluctuating box size. The box shape was also allowed to fluctuate (sometimes referred to as a "floppy box") to accommodate crystal structures that do not tile in a square box. The pressure, P, is set by the depletant pressure in the reservoir, that of an ideal gas $\beta P = n_d^r$ where n_d^r is the reservoir depletant number density and β is the inverse of temperature multiplied by Boltzmann's constant, $\beta = (k_B T)^{-1}$, which is far higher than the pressure from the superballs. In this ensemble it is possible for the box to increase to an arbitrarily large size if the depletion interaction is not strong enough. If the superballs are started sufficiently close together, this does not represent a practical problem.

We placed $N = 6 \times 6 = 36$ superballs in a periodic box. The values for n_d^r and hence also the pressure were chosen to match the values at which we see good assembly in the previous section. To determine which phase is stable for any given set of parameters we started simulations from square, Λ_0, and Λ_1 phases. Example configurations are shown in Fig. S7.

Bidepletant

In this section we demonstrate the possibility of switchable phases by considering a system made up of superballs and two species of depletant. The big depletants are spheres with size ratio $q_1 = 0.35$ and the small depletants are spheres with size ratio $q_2 = 0.04$. Both depletants can overlap with each other but not with the superballs. The changes in size always occur at constant reservoir number density so that the average number of small depletants remains constant throughout the simulation. This is an average because the depletants are treated grand canonically and their numbers fluctuate.

Self-Assembly. In this ensemble the number of superballs is fixed at $N = 169$ and the box size is constant at $L_x = L_y = 30\sigma_c$ and $L_z = 1.02\sigma_c$. Both depletants are treated grand canonically with constant chemical potentials, μ_1 and μ_2. The simulations start with all of the superballs evenly distributed and the box filled with depletant. Although there is potentially a large parameter space, we have found that starting with $q_1 = 0.35$ and $q_2 = 0.04$ and at reservoir number density $n_1 = 24.9\sigma_c^{-3}$ and $n_2 = 596.8\sigma_c^{-3}$ provides the best results.

As shown in Fig. S8 under the starting conditions the superballs assemble into a square structure. Even though the amount of small depletant would not be strong enough to drive assembly on its own, with the help of the larger depletant to hold the particles together it is enough to direct the superballs into a square phase. At this point the size of the small depletant is changed from $q_2 = 0.04$ to $q_2 = 0.032$, holding the number density fixed, resulting in a canted lattice. When the small depletants are swollen back to $q_2 = 0.04$, the square phase is restored, demonstrating a mechanism that induces reversibly switchable phases.

We note that to see transitions in a computationally accessible timescale, the parameters must be chosen such that the interactions are not too strong. Due to the weaker and competing interactions, the bond angles that we see in the canted phase are slightly different from those in the close-packed Λ_1 phase.

Bulk Phase. This is a constant $NPT\mu_2$ ensemble. N is the number of superballs. The pressure is set by the depletant pressure in the reservoir, which is far higher than pressure from the superballs. Because the reservoir is an ideal gas, the reservoir pressure is the sum of the depletant number densities, $\beta P = n_1 + n_2$. The big depletants are too big to penetrate the crystal structure so although it contributes to the pressure, it is not explicitly simulated in this ensemble. As in the previous bulk section, as well as in volume-changing moves (L_x and L_y only), the box may also make shape-changing moves. This allows the Λ_1 phase to properly fit around the periodic boundaries.

The contribution to the pressure from the big depletant is fixed at $\sigma_c^3 \beta P_1 = 30$. The box is filled with small depletant with $q_2 = 0.04$ at $n_2^r = 596.8\sigma_c^{-3}$, so the total pressure is $\beta P = \beta(P_1 + P_2) = 626.8$. The number densities remain fixed so this pressure is the same in all results shown here.

Fig. S9 shows the switchable nature of the crystals. The superballs are started in a square configuration and then the box is filled with depletant at $q_2 = 0.04, n_2^r = 596.8\sigma_c^{-3}$, where the square phase is stable. The small depletant is then changed in size to $q_2 = 0.032$ and the system reliably changes into the canted phase. From this configuration the small depletant size is changed back to $q_2 = 0.04$, and the crystal changes back to the square (Movie S4).

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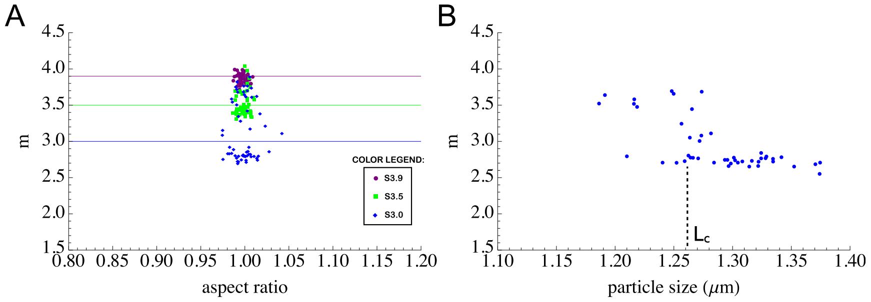


Fig. S1. (*A*) The points of this graph represent the shape parameters *m* of the silica superballs measured by fitting the shape of 80–100 particles. Different colors correspond to different samples as indicated in the legend. The average values are indicated with the horizontal lines interpolating the *y* axis in their corresponding mean values. (*B*) For sample S3.0 the shape parameter (*m*) of the particle is plotted against the particle size (*L*). A sharp transition is visible around a critical value $L_c = 1.26$ μm, which shows a rapid decay in shape polydispersity after the transition.

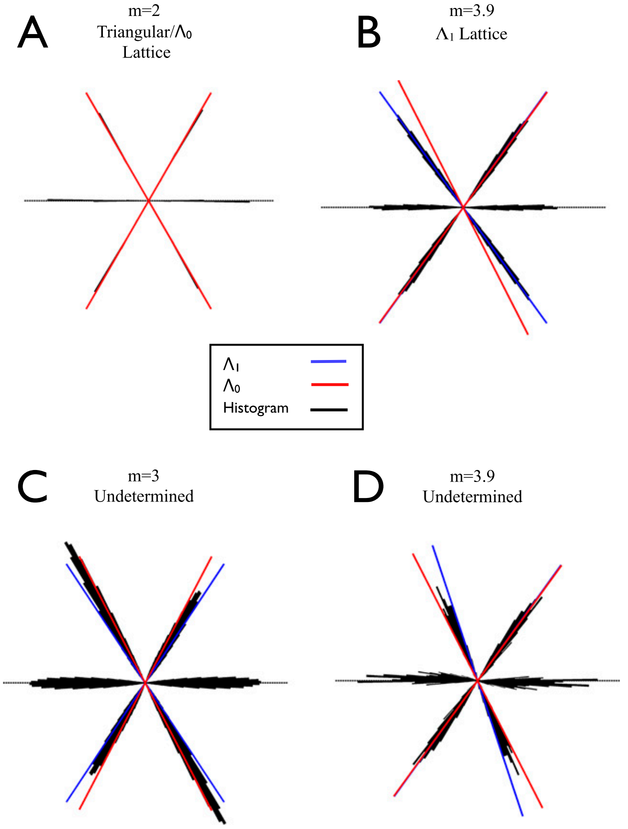


Fig. S2. Angular histograms of experimental data. (*A*) Angular histograms for spherical particles show sharp peaks indicating 60° bond angles between particles, as expected for a triangular lattice, which is consistent with both the Λ_0 and Λ_1 lattices for $m = 2$. (*B*) Example angular histogram from which a Λ_1 lattice is identified. *C* and *D* show examples of distributions in which a clear identification is not possible.

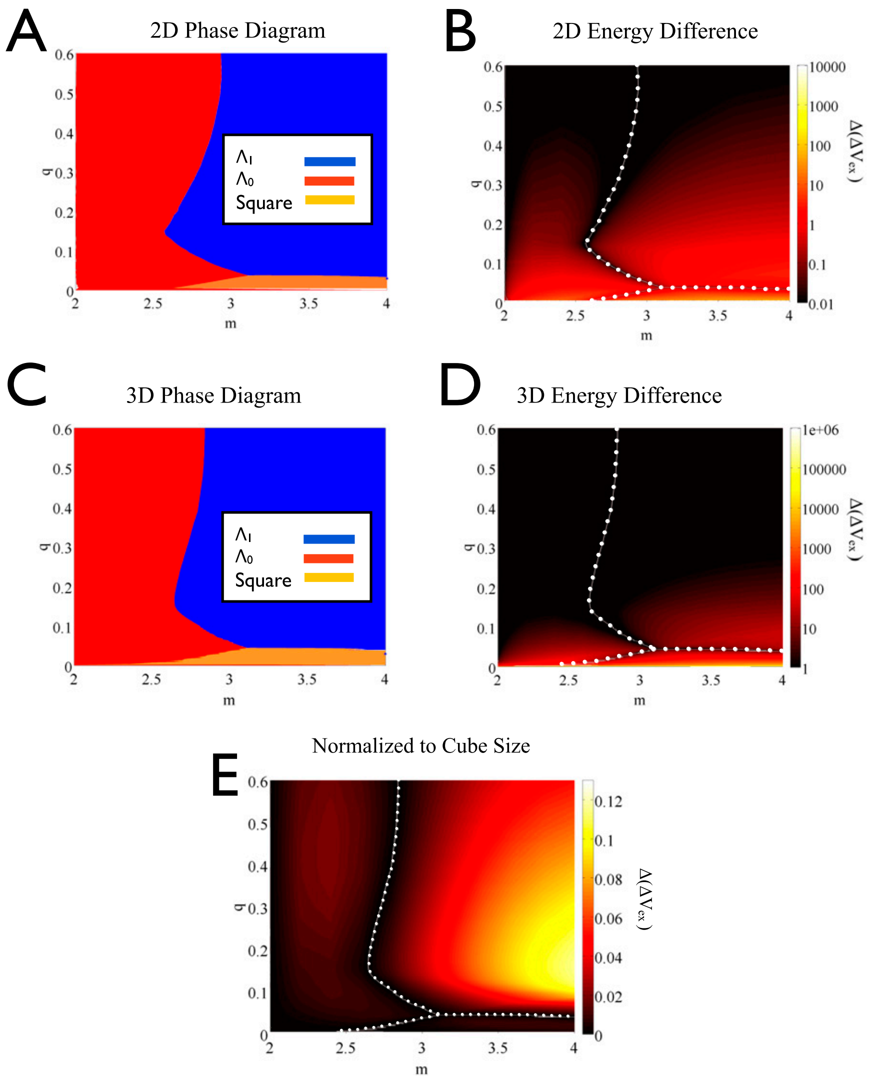


Fig. S3. Phase diagrams and energetic characterization of superball lattices. (*A*) The phase diagram of 2D superdisks is computed by computing ΔV_{ex} of each lattice type for each value of *m* and *q*. (*B*) The energetic benefit of choosing a particular lattice type for 2D superdisks is computed for each *m* and *q* by finding the difference in the energy of the two most energetically favorable lattices. (*C* and *D*) Phase diagram for 3D superballs arranged in 2D lattices. The structures of the diagrams are qualitatively similar to those of the 2D diagrams. (*E*) The energy difference between the two most favorable lattices computed using a constant number density of depletants.

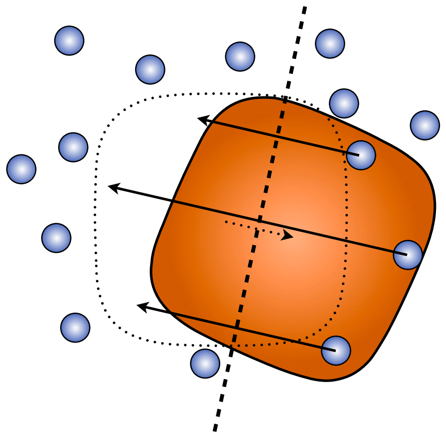


Fig. S4. Starting from the dotted outline the colloid particle is reflected in the plane (thick dashed line). As a result it overlaps with three depletant particles that are reflected in the same plane into the space left by the colloid.

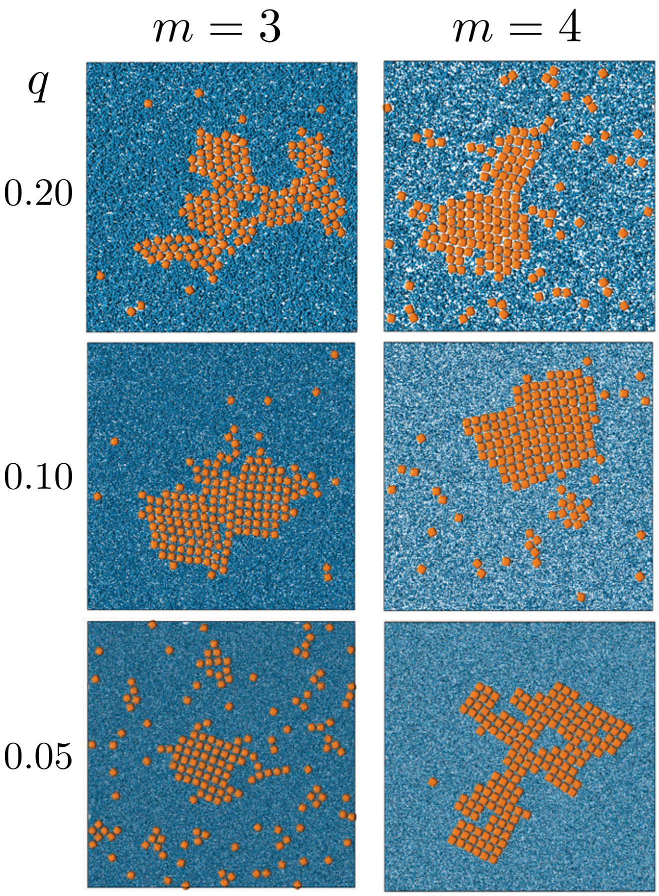


Fig. S5. Final configurations for the self-assembly simulation runs for varying size ratios *q* and superball shape parameter *m* as labeled.

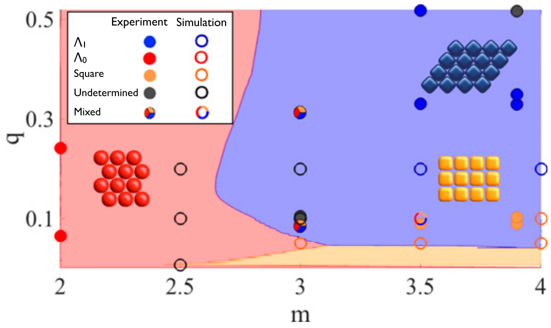


Fig. S6. Comparison of finite crystal self-assembly simulation results with experiment results.

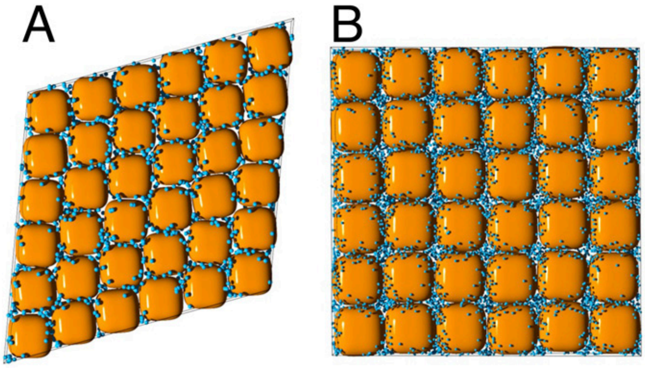


Fig. S7. (*A* and *B*) Floppy box *NPT* simulations showing the stable structures for superballs with shape parameter $m = 3.5$ (*A*) Λ_1 phase for size ratio $q = 0.1$ and (*B*) square phase for $q = 0.05$.

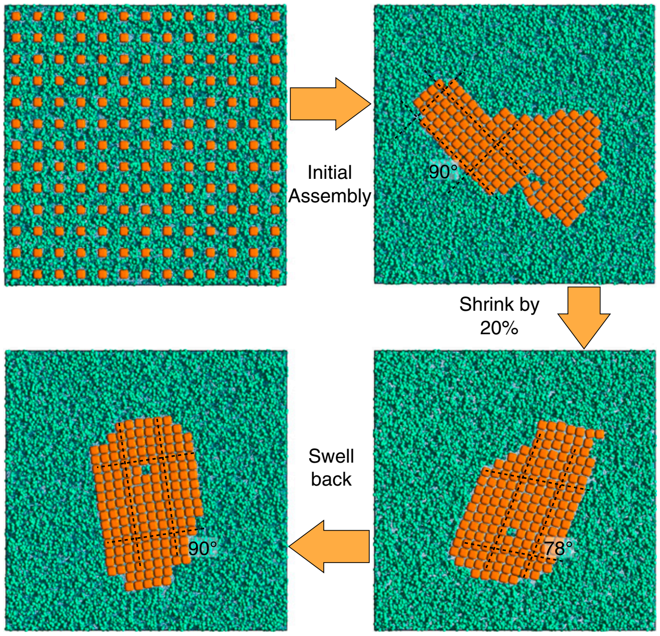


Fig. S8. After initial assembly into a square phase the small depletant is shrunk by 20% from $q_2 = 0.04$ to $q_2 = 0.032$, holding the densities of both depletant species and superballs fixed. The crystal rearranges to a canted phase. The depletant then goes back to $q_2 = 0.04$ and the square phase is recovered.

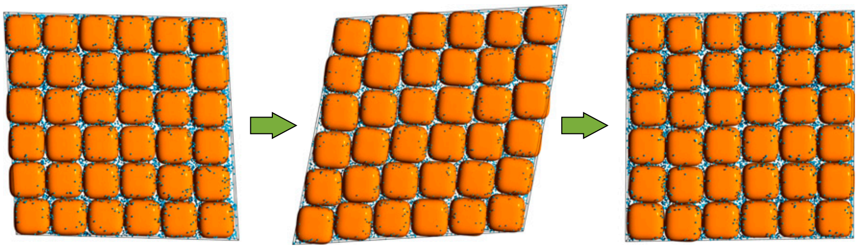
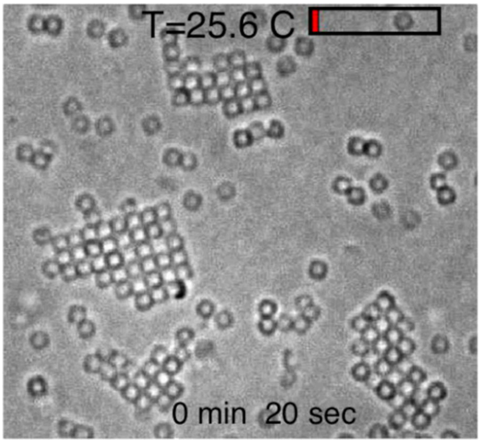
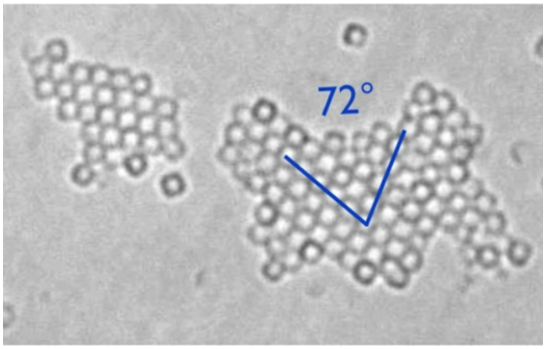


Fig. S9. Constant pressure simulations with a flexible "floppy" box. Starting from a square phase we cycle to a Λ_1 phase and back again by changing the small depletant size from $q_2 = 0.04 \rightarrow 0.032 \rightarrow 0.04$ at constant number density. The big depletants do not penetrate the crystal so are treated implicitly as a pressure term.



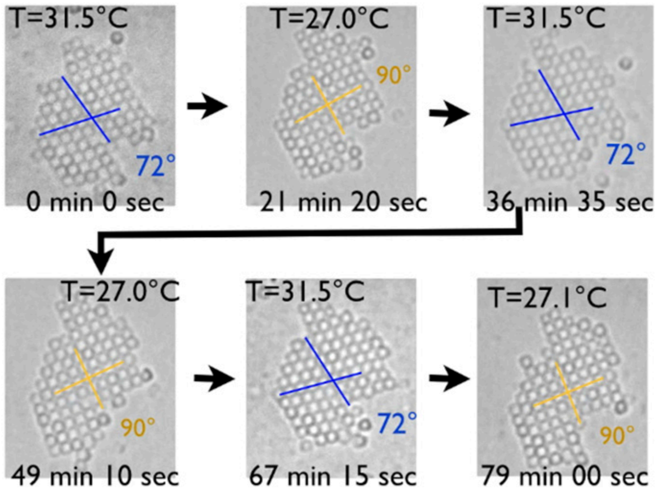
Movie S1. Silica superballs with $m = 3.9$ are dispersed with pNIPAM depletants and equilibrated at room temperature, where they form square crystallites. As the temperature is increased to 28.5 °C, the crystallites melt. Upon decreasing the temperature back to room temperature, the particles begin to reassemble.

Movie S1



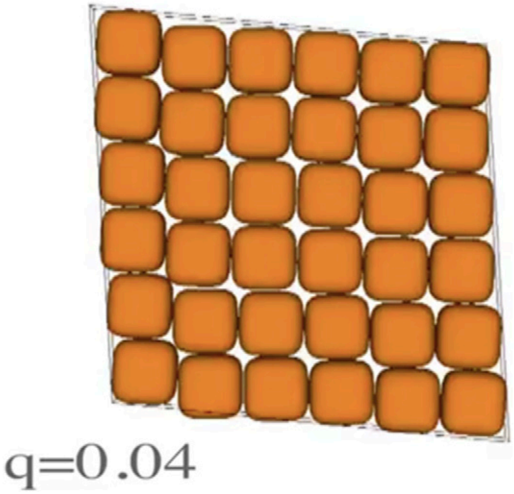
Movie S2. Silica superballs with $m = 3.9$ are dispersed in the presence of PEO depletants with molecular weight 8 M. In these conditions the superballs assemble into Λ_1 crystallites.

Movie S2



Movie S3. Silica superballs with $m = 3.9$ are dispersed in the presence of a mixture of PEO (molecular weight 8 M) and pNIPAM depletants. At 27 °C, the superballs assemble into square crystallites, as observed when the particles are dispersed with pNIPAM alone. As the temperature is increased we observe that the lattice shifts to a Λ_1 configuration as observed when the superballs are dispersed with PEO alone. This happens because at higher temperatures the interactions induced by the pNIPAM weaken whereas those induced by the PEO are fixed. By cycling the temperature, we are able to observe a reversible solid-to-solid phase transition over several iterations.

Movie S3



Movie S4. Periodic bulk crystal simulations are performed with superballs with a fluctuating simulation box. Superballs are dispersed with two species of depletants, one with size ratio $q_1 = 0.35$ and one with size ratio $q_2 = 0.04$. For these parameters, The square lattice configuration is stable. By decreasing the size ratio of the smaller species from $q_2 = 0.04$ to $q_2 = 0.032$, we observe a transition into a canted phase, as we observe when the superballs are dispersed only with depletants with a size ratio $q_1 = 0.35$. When the size of the smaller depletant is once again increased ($q_2 = 0.04$), the square phase is restored.

Movie S4