Crossover Behavior in the Packing and Assembly of Concave Hard Spheres

N. Khalid Ahmed,1 Greg van Anders,1 Elizabeth R. Chen,1,2 and Sharon C. Glotzer1,3

1Department of Chemical Engineering, University of Michigan, Ann Arbor, MI 48109-2136, USA
2School of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts 02138, USA
3Department of Materials Science and Engineering, University of Michigan, Ann Arbor, MI 48109-2136, USA

(Dated: January 14, 2015)

Particle shape plays an important role in assembly and packing. The combination of concave and convex surfaces in particular influence the way particles arrange, both entropically and in the limit of infinite pressure. We study recently synthesized spheroidal particles with up to six symmetric concavities (dimples) between the convex and concave extents of their shape. These particles exhibit a crossover in behavior during both packing and assembly arising from a competition between their convex and concave features. We identify the shape features that control this crossover as the total circumference to depth ratio of dimples in packing, and the individual dimple volume in assembly.

Introduction.— The role of colloid shape in self-assembly is of great interest [1–4] due to the complexity of structures assembled [5, 6]. Entropy drives the ordering of these systems through emergent directional entropic forces, causing the particles to assume local dense packing motifs that repeat throughout the system [4]. This has given rise to a new paradigm of entropically patchy particles obtained through different shape modifications [7, 8].

Here, we study the effect on packing and assembly of the most basic feature of particle shape: whether it is convex or concave. The convexity and concavity of a particle will directly affect its entropic patchiness. We specifically consider dimpled lock-and-key colloids [8, 9] that can be easily tuned between convex and concave shapes as shown in Fig. 1a. Dimpled lock-and-key colloids bind convex particle features to concave features by maximizing local packing density [10]. It was recently shown that optimizing local packing is a generic feature of entropy-driven colloidal systems [4]. We expect dimpled particles, by virtue of their concave features, to exhibit strong structural differences from their convex counterparts.

Concave particles with a single dimple have been studied in various contexts, including the assembly of spherical caps [11, 12], bowls [13, 14] and lenses [15, 16], as well as lock-and-key dynamics [9] and ferroelectric liquid crystals [17]. Dimpled particles with multiple dimples and various dimple configurations have been synthesized in a number of recent experiments [18–24].

Motivated by these experiments, we study families of multi-dimpled concave spheroidal particles (Fig. 1c) as an example of shapes that can be tuned between their convex (sphere) and concave limits via a single dimpling parameter. We demonstrate that both their packing and assembly behaviors are determined by a competition between the concave and convex features of the particles. We show that for these families, the putative densest packing is achieved at a certain critical ratio of the total dimple circumference to dimple depth. Below (above) the critical ratio, the packing is dominated by the convex (concave) features of the particle. Away from infinite pressure corresponding to densest packings, we show that the thermodynamically self-assembled crystal structure is determined instead by the volume of a single dimple relative to the particle size. We show that below (above) the critical dimple volume, the assembly is dominated by the convex (concave) features of the particle. By exploiting these crossovers, we establish simple geometric criteria for controlling particle geometry for shape-induced structural reconfigurations of a family of colloidal crystals.

Model and methods.— The particles, shown schematically in Fig. 1c and denoted by $P_x$, comprise a central sphere $P$ that is symmetrically dimpled by a subtractive construction involving $x$ valence spheres, all of the same radius as the central sphere. The valence sphere positions are chosen to be related by discrete symmetries, and are equidistant from the central sphere as shown in Fig. 1b. We study bivalent (P2), trivalent (P3), tetrahedrally tetravalent (P4t), square tetravalent (P4s), and hexavalent (P6) dimpled particles. We work in units of...
the sphere radii. To create a family of shapes for a given $x$, the distance $d$ between the central and valence spheres is varied from the maximum (valence spheres tangent to the central sphere) to the minimum (dimples are tangent to each other) amount.

Constructed as above, a dimple is formed by a pair of spherical caps bounded by the intersection of the central and valence spheres. The volume, surface area, and circumference of a dimple are thus given by

\[
\begin{align*}
V_d &= \frac{\pi}{12} (d + 4)(2 - d)^2 \\
S_d &= \pi (2 - d) \\
C_d &= \pi \sqrt{4 - d^2}
\end{align*}
\]

We parameterize the dimple geometry by linearly mapping $d^2$ to the "dimpling amount" $f$, where $f = 0$ ($f = 1$) when $d^2$ is maximum (minimum).

Monte Carlo simulations are performed in standard fashion, (see, e.g., [25]) to obtain both assemblies and putative densest packings. In both cases, we determine particle overlaps by implementing a geometric algorithm developed for dimpled particles [26] (see Supplemental Materials (SM) for details). To verify the putative densest packings, we perform analytic packing calculations for these particles to determine the unit cell of their densest packing structure where possible (see Supplemental Materials (SM) for details). To identify a crystal structure, each particle is replaced by a point at its centroid to give a configuration isostructural to that of an atomic crystal, an approach used in several previous works [4–6, 27, 28].

In certain cases (P3 and P4t) we are unable to assemble a thermodynamically stable structure from a homogeneous fluid at any density on the time scale of our simulations. In the case of P3, we set up the trivalent particles into the expected triangular lattice and observed melting transitions. In the case of P4t, we achieve assembly in the presence of a seed cluster of particles fixed in a diamond lattice, as formed for tetrahedrally patterned enthalpically patchy particles in Ref. [27].

Densest Packings.—Similar to previous work [29], we perform a continuous change in the shape of our particles. We compute putative densest packings for each of the five families of particles at 100 different dimpling amounts $f \in [0, 1]$ per family; see Fig. 2. In all cases, for small $f \approx 0$, particles pack most densely into FCC lattices, like hard spheres. For slightly larger values $f \leq f_{\text{DP}}^*$, all particle types pack like soft spheres [6] into the BCC structure, like hard spheres. For the critical dimpling amount $f_{\text{DP}}^*$, the convex features of the particles are completely encased within the dimples of neighboring particles. For $f \geq f_{\text{DP}}^*$, neighboring particles interlock within each other and the resulting structure formed is governed by the number and arrangement of dimples on individual particles. Bivalent particles (P2) pack into a parquet structure. Trivalent particles (P3) form triangular sheets.

![FIG. 2. Numerical calculations of the density $\phi$ of the densest obtained packing for dimpled particles as a function of dimpling amount $f$. The curves for different particles are shifted along the $y$-axis for clarity. Packing fraction is maximum at a critical dimpling amount $f = f_{\text{DP}}^*$ when the dominating features switch from convex to concave regions of the particles. (Left Insets) For small $f$, particles always switch from a thermodynamic preference for FCC packing to BCC packing, analogous to the expected transition from hard spheres to soft spheres. (Right Insets) For tetrahedral tetravalent and hexavalent particles, a second transition at larger $f$ is seen from diamond to FCC and sheared cubic to simple cubic respectively.](image-url)
Tetrahedrally tetravalent particles (P4t) pack into the diamond structure for a certain range of \( f \). Square tetravalent (P4s) and hexavalent (P6) particles pack into the cubic lattice, while the former exhibit a rotational parquet symmetry. A further increase in \( f \) beyond \( f^{*}_{DP} \) introduces larger voids between particles and a reduction in packing fraction. At sufficiently large values of \( f \), the trivalent (P3), tetrahedrally tetravalent (P4t) and hexavalent (P6) particle families pack less densely than spheres.

We find at least two different arrangements for each particle shape, dependent on the dimpling amount. The maximum packing fraction \( \phi_{M} \) changes either smoothly or abruptly according to the densest structures formed by continuously changing shape, as observed in previous works \([5, 29, 30]\). For bivalent (P2), trivalent (P3) and hexavalent (P6) particles, the packing fraction increases or decreases smoothly. Close inspection reveals this is because the two structures about the critical dimpling amount \( f^{*}_{DP} \) are similar in their coordination number and can be obtained by simple shear from each other. In the case of tetrahedrally tetravalent (P4t) and square tetravalent (P4s) particles, there is a sharp change in the densest packing fraction at \( f^{*}_{DP} \) indicating a complete rearrangement of the particles in their densest structure. This change corresponds to the change from FCC to diamond for tetrahedral tetravalent (P4t) particles. For square tetravalent (P4s) particles, the structure changes from FCC to simple cubic. Interestingly, however, we observe a sharp change in packing fraction due to the presence of rotational parquet symmetry in the simple cubic lattice, which cannot be obtained by a simple shear from the FCC structure.

For tetrahedrally tetravalent (P4t) particles at high dimpling amounts, \( f = 0.7374 \), we find another transition from diamond to FCC, shown in the first right inset of Fig. 2. At these large dimpling amounts, the densest packing structure arises from a competition between the parallel and anti-parallel alignment of the dimples. With increase in the size of the dimples, neighboring particles find more room to rotate while they are interlocked. This results in a denser packing that is achieved with the parallel alignment of the dimples, resulting in a transition from diamond, in which they exhibit anti-parallel alignment, to the FCC structure.

Similar to tetrahedrally tetravalent (P4t) particles, we find another transition for hexavalent (P6N) particles at \( f = 0.6510 \), shown in the second right inset of Fig. 2. The particles transition from a sheared cubic arrangement to a simple cubic arrangement. This transition is observed in hexavalent particles because of their ability to shear along the 110 lattice vector direction, while neighboring particles remain interlocked in the same configuration.

To understand the packing of multi-dimpled spheroidal particles, we determine the primary feature in the shape of these particles that affects their behavior. We investigate the value of \( f^{*}_{DP} \) compared to the total volume \( V_d \), surface area \( S_d \) and circumference \( C_d \) of all dimples on a single particle as \( d \) is varied. We normalize each of these three parameters by the volume, surface area and depth, respectively, of a single dimple. Further details of these calculations can be found in the Supplemental Materials (SM). We compute the total normalized dimple volume, surface area and circumference to depth ratio in each family of particle at \( f^{*}_{DP} \). We find that the total circumference to depth ratio \( C_d \) of the dimples is \( 1.2341 \pm 0.060 \) at \( f^{*}_{DP} \) across all five particle families; see Fig. 3. In contrast, no universal behavior was found for dimple volume or surface area; see SM. This scaling behavior is also understood from the geometry of the putative densest packings. At \( \phi_{M} \), all neighboring particles in a unit cell are completely encased within the dimples of a central particle. However, calculating the geometry of this interlocking is a non-trivial problem that cannot be easily generalized as it depends on the number of dimples and their geometry.

Self-Assembly.—We next investigate if there exists similar universal behavior in structures self-assembled away from infinite pressure.

Similar to the results we obtain for the putative densest packings, we find that the dimpled particles self-assemble like spheres into either BCC or FCC crystals at \( f \leq f^{*}_{SA} \). For \( f \geq f^{*}_{SA} \), self-assembly of the particles is controlled by their concave features and is dependent on the number and arrangement of the dimples as shown in Fig. 4. We find that bivalent particles (P2) self-assemble into the parquet lattice. In the case of trivalent particles (P3), we find triangular sheets to be thermodynamically favored but difficult to realize kinetically. Similarly, tetrahedrally tetravalent particles (P4t) are stable in a diamond structure, their densest packing structure, over a wide range of packing fractions on simulation time scales. However they require a seed to assemble diamond, as found in...
that for the class of particles we studied, the emergent valence or binding specificity is difficult. Here we have shown that assembly behavior is determined by the geometry of individual dimples. Moreover, our proposal in [4] that assembly is controlled not by global dense packing, but by local dense packing.

Local dense packing drives particle assembly through shape entropy maximization [4]. Because this causes particles to have emergent valence, precise, a priori, control over particle valence or binding specificity is difficult. Here we have shown that for the class of particles we studied, the emergent valence of particles depends on individual dimple volume. This result is sensible if particles “bind” at entropic patch sites through osmotic pressure, as suggested in [4]. However, our results also give a general heuristic for controlling particle features to alter assembly behavior. There have been recent advances in the synthesis of convex reconfigurable particles, [31–33]. We have shown that convex-concave reconfigurability in a building block can also give rise to different valencies. Given a new shape that can be tuned between an overall convex and concave shape, its behavior can be tuned between convex feature dominated and concave feature dominated assemblies.

Our heuristic summarizes how and when particle dimples affect valence. Particles with polyvalent dimples such as those studied here have been synthesized experimentally [18] and present a more complex instance of lock-and-key colloids [8–10] [34]. The lock-and-key mechanism gives rise to complex behaviors in biomolecular systems, and here we have demonstrated how to control its expression in colloidal systems using shape. By modifying the shape of dimpled particles, for e.g. by swelling or shrinking the particles, or controlling surface ligand adsorption [35] [36], we expect that crossover in particle shape from convex-dominated to concave-dominated behavior will be useful for bulk reconfiguration of materials.

We thank Oleg Gang and John Crocker for helpful discussions. We also thank Andrew Karas for help with visualizations of PMFT. The U.S. Army Research Office under Grant Award No. W911NF-10-1-0518 and the DOD/ASD(R&E) under Award No. N00244-09-1-0062 supported the assembly work. The Biomolecular Materials Program of the Materials Engineering and Science Division of Basic Energy Sciences at the U.S. Department of Energy under Grant No. DE-FG02-02ER46000 supported the packing studies and PMFT calculations. ERC acknowledges NSF MRPFR grant DMS-1204686. N.K.A. performed packing and self-assembly studies. G.v.A. calculated PMFTs. E.R.C. developed the overlap algorithm and helped in its implementation. N.K.A., G.v.A., and S.C.G. calculated PMFTs. E.R.C. developed the overlap algorithm and helped in its implementation. N.K.A., G.v.A., and S.C.G. calculated PMFTs. E.R.C. contributed the analytic packing curves. N.K.A., G.v.A., and S.C.G. wrote the paper.

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