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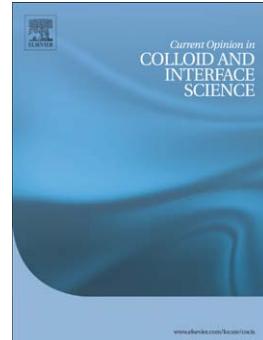
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# Clusters of Anisotropic Colloidal Particles: from Colloidal Molecules to Supracolloidal Structures

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## Abstract

Colloidal clusters have received considerable attention in recent years in the context of the fabrication of “colloidal molecules”, mimicking the symmetry of molecular structures, as well as for the self-assembly of finite supracolloidal structures, especially from anisotropic colloidal particles. Here we review recent studies on clusters of anisotropic colloidal particles, highlighting certain classes of supracolloidal structures that have emerged as recurrent themes in these studies. We emphasize the interplay of colloidal interactions, often arising from the presence of one or more anisotropy attributes, which drives the self-assembly into finite supracolloidal structures.

Keywords: colloidal clusters; colloidal molecules; anisotropic colloidal particles; colloidal self-assembly; hierarchical self-assembly; dynamic self-assembly

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## I. Introduction

In recent years, a large body of work has focused on colloidal clusters – finite-size systems of microparticles – as “colloidal molecules” have come to prominence in colloid science alongside the traditional picture, where colloidal particles are viewed as “big atoms” useful for studying various physical phenomena.<sup>1,2</sup> Colloidal molecules refer to small clusters of colloidal particles, which mimic the symmetry of molecular structures.<sup>2</sup> While colloidal molecules, as molecular analogues on a different length scale, have drawn attention, colloidal clusters are of fundamental and practical interest in their own right. Since colloidal particles are large enough to be amenable to direct real space imaging and yet small enough to sustain Brownian motion, colloidal clusters provide an attractive platform for investigating the structure, thermodynamics, and kinetics of finite-size systems on the mesoscale from a fundamental point of view.<sup>3</sup> Another salient feature of colloidal particles, distinct from atoms and molecules, is that their length scale is comparable to the wavelength of visible light. This feature makes colloidal self-assembly especially attractive for engineering optical properties. Although colloidal crystals have been at the center of attraction in this context,<sup>4,5</sup> colloidal clusters have also simulated interest for their exotic optical properties.<sup>6–8</sup> For example, colloidal clusters can be used as building blocks for isotropic optical metamaterials, known as metafluids, capable of exhibiting optical properties previously non-existent in nature.<sup>6,9,10</sup>

Colloidal clusters have also been at the focal point because of remarkable examples of self-assembly of anisotropic colloidal particles into finite supracolloidal structures. Recent advances in the ability to synthesize colloidal particles with a variety of shapes and rich surface chemistry in a controlled way have been the key to these research activities.<sup>11–15</sup> Unlike isotropic colloidal particles featuring in the traditional picture of big atoms and in the majority of self-assembled plasmonic colloidal clusters, these novel colloidal particles are empowered with highly directional interactions, commonly associated with molecular building blocks at a smaller length scale. Recent progress in fabricating “patchy particles”, which refer to nano- and micro-particles with their surfaces decorated with geometrically well-defined sticky spots,<sup>16</sup> have expanded the arsenal of anisotropic colloidal building blocks significantly.<sup>13,17–21</sup> Patchy particles offer directional interactions and have shown promise to stabilize, in particular, low-coordinated structures.<sup>22</sup> Another strategy, which involves functionalizing the colloidal surface by DNA strands to obtain directional interactions that are highly specific as well due to the binding specificity encoded in the DNA sequence, has also proved to be powerful.<sup>23–26</sup> Yet another approach, which exploits anisotropic shape of colloidal particles, has shown enormous potential for colloidal self-assembly.<sup>11,27–29</sup> Other variants of anisotropic colloidal building blocks also ex-

ist, for example, the so-called “inverse patchy colloids”.<sup>30,31</sup> New avenues to self-assembled soft materials exploiting such a variety of anisotropic colloidal building blocks have thus opened up. Colloidal self-assembly is enormously promising as a bottom-up means of structure fabrication because of the scope for tuning the interparticle interactions.

This review is organized around certain classes of finite supracolloidal structures, which have appeared as recurrent themes in studies of colloidal clusters formed predominantly by anisotropic colloidal particles, as opposed to focusing on specific types of anisotropic colloidal building blocks. Such an organization lays a platform for us to highlight the critical role of the intriguing interplay of colloidal interactions, often involving more than one anisotropy attribute,<sup>11</sup> in driving colloidal self-assembly. In this review we restrict ourselves to colloidal particles with size larger than a few tens of nanometers, where nonadditivity of various interparticle interactions is not important.<sup>32</sup> We finally conclude with an outlook on new lines of inquiry relating to colloidal clusters, which will, in our opinion, push the frontiers of the field of colloidal self-assembly. A variety of colloidal crystals have been predicted by extensive numerical simulations of anisotropic colloidal building blocks, and a few of them have been realized so far in experimental work.<sup>33,34</sup> These studies are, however, beyond the scope of this review. Also, we will not cover here the field of so-called active colloids,<sup>35</sup> which has grown rapidly in recent years in its own right, where clustering is a phenomenon of interest.

## II. Colloidal molecules: mimicking molecular structures

In this section we provide a brief historical account, describing how the concept of “colloidal molecules” has evolved since its introduction and thus making reference also to clusters of isotropic colloidal particles for the sake of completeness. In one of the early studies of colloidal clusters, Pine and coworkers demonstrated a route to small colloidal clusters by evaporating oil droplets suspended in water, with equal-sized microspheres adsorbed to the surface of the oil droplets.<sup>36</sup> The packing of  $N = 2 - 15$  microspheres, driven by capillary forces, resulted in a variety of polyhedra, including some with fivefold rotational symmetry. Many of these polyhedra were distinct from the polytetrahedral structures typically identified as the global minima on the potential energy surface for small clusters bound by longer-ranged isotropic potentials.<sup>37</sup> The study reported that the packing of the microspheres in this case was governed by the minimization of the second moment of the mass distribution,<sup>36</sup> which influenced the shape and symmetry of these clusters. The term “colloidal molecules” was coined to refer to these small colloidal clusters mimicking molecular geometry.<sup>2</sup>

A colloidal suspension where depletion attraction promotes aggregation and screened electro-

static repulsion prevents coagulation has gained considerable attention in the context of cluster formation.<sup>38–42</sup> Manoharan and coworkers mapped the free energy landscape in experiments for small colloidal clusters where both depletion attraction and screened electrostatic repulsion are short ranged.<sup>41</sup> In the presence of short-ranged interactions, the energy contribution to the stability is essentially governed by the number of nearest neighbor contacts. The experiments revealed that of the clusters with equal numbers of nearest neighbor contacts, highly symmetric clusters were relatively disfavored (see Figure 1A) – a result interpreted theoretically by symmetry considerations, which take into account the entropy cost for highly symmetric clusters.<sup>41</sup> Wales presented the disconnectivity graph representation of the potential energy landscape as well the free energy landscape for small colloidal clusters, using a short-ranged Morse potential to model the depletion interaction and normal mode analysis to obtain free energies within the harmonic approximation (Figure 1B).<sup>43</sup> The occupation probabilities calculated at a reduced temperature were in agreement with those reported by Meng *et al.* within a few percent for the Morse range parameter  $\rho = 30$ .<sup>41,43</sup> These small colloidal clusters bound by relatively weak interparticle interactions at equilibrium, when conceived as “colloidal molecules”, present a picture where the particles are viewed as atoms, the attractive interactions between them as bonds, and the different structures observed at equilibrium as isomers.<sup>44–46</sup>

In line with this picture, Malins *et al.* considered the yield of clusters of different structures as a function of the strength of the interactions in a Brownian dynamics simulation study.<sup>40</sup> They employed the traditional one-component description to study small clusters of ( $N = 3 - 7, 10, 13$ ) colloidal particles in the presence of a short-ranged attraction and a weak long-ranged electrostatic repulsion. As the strength of the attractive interaction was increased, the average bond lifetime approached the simulation run time, making the system nonergodic on that timescale. For  $N \geq 7$ , a lower yield of the structures that maximize the number of nearest-neighbor contacts was observed in the nonergodic regime, where geometric frustration arising from metastable structures was argued to play a significant role and result in kinetic trapping. Colloidal clusters thus also serve as a useful test bed to investigate the statistical mechanics of finite systems.<sup>42,47–49</sup>

Recent progress in the synthesis of colloidal molecules suggests that they themselves can serve as building blocks with anisotropy attributes for colloidal superstructures.<sup>19,50–54</sup> Kraft *et al.* reported on the synthesis of colloidal molecules with well-controlled shape and tunable patchiness, utilizing a variation of the seeded polymerization technique (see Figure 1C).<sup>19</sup> This method exploits the assembly of cross-linked polystyrene spheres with a liquid protrusion by coalescence of the liquid protrusions. Subsequently, control over the synthesis of colloidal molecules with well-defined bond angles was achieved by adjusting the size of the liquid protrusion.<sup>50</sup> The au-

thors of the latter study concluded that the unique shape was due to a polymerization-induced aggregation of the seeds inside the liquid droplets.

Malins *et al.* suggested more sophisticated means beyond the spherically symmetric microspheres, such as patchy particles, for fabrication of complex colloidal molecules in good yields.<sup>40</sup> In a recent study, patchy colloidal particles with chemically distinct surface patches imitating hybridized atomic orbitals were obtained from the so-called ‘minimal-moment’ clusters with reproducible symmetries.<sup>25</sup> The patches were functionalized with DNA having single-stranded sticky ends to realize directionality as well as specificity in the interparticle interactions. Such interactions were found to drive the self-assembly of the colloidal particles into “colloidal molecules” with triangular, tetrahedral and other bonding symmetries (see Figure 1D).<sup>25</sup>

### III. Micellar analogues

Janus colloidal particles, named after the two-faced Roman god, can be viewed as a special type of patchy colloidal particles with different surface chemistry on their opposing hemispheres.<sup>55</sup> Amphiphilic Janus colloidal particles, hydrophobic on one hemisphere and charged on the other, have received attention for their ability to form micellar structures. Such Janus particles, albeit rigid for all practical purposes, mimic molecular amphiphiles, such as surfactants, on the mesoscopic scale. In an early study with amphiphilic Janus particles, Granick and coworkers observed the formation of extended worm-like rings via link-up of small compact clusters, whose structures were analogous to the micellar shapes, as the electrostatic screening was enhanced in an aqueous medium by increasing the salt concentration (Figure 2A).<sup>56</sup>

More recently, experimental fabrication of patchy colloidal particles with one patch offered a model system to study self-assembly into clusters that resemble surfactant micelles.<sup>57</sup> In this study, Kraft *et al.* showed curved, smooth patches on rough colloidal particles to be exclusively attractive due to their different overlap volumes. The patchy particles in this case resembled dumbbells, which had one spherical lobe with a smooth surface and the other spherical lobe with a rough surface. The self-assembly of these particles resulted in finite clusters reminiscent of micelles (Figure 2B). The cluster size distribution simulated starting from a homogeneous state was found to be in good agreement with those observed in experiments.<sup>57</sup>

Drawing inspiration from the experimental study by Hong *et al.*,<sup>56</sup> a simple model representing these Janus particles has been investigated by Sciortino and co-workers in periodic systems,<sup>58,59</sup> for which a cluster phase was observed. The model, introduced by Kern and

Frenkel,<sup>60</sup> represents Janus particles in terms of hard-core particles with two hemispheres that are attractive and repulsive. A square-well potential describes an attractive patch-patch interaction whenever the attractive hemispheres on two particles face each other. For a relatively large attraction range, a cluster phase of micelles formed at low temperatures and the phase diagram included a colloid-poor (gas) and colloid-rich (liquid) demixing region, which was increasingly suppressed upon cooling due to the formation of micelles in the gas phase.<sup>58</sup> When the phase behavior of model colloidal dumbbells described by two identical tangent hard spheres, with the first one surrounded by an attractive square-well interaction, was studied, it was observed that a larger hard-sphere site promoted the formation of clusters, whereas a gas-liquid phase separation took place in the case of a smaller hard-sphere site.<sup>61</sup>

#### IV. Supracolloidal chirality

A common thread running through a number of studies in recent years has been the design and control of emergent supracolloidal chirality.<sup>62–67</sup> The term ‘chirality’ refers to handedness and is a geometric attribute associated with non-superimposable mirror images. Homochirality of biological molecules underpins many spectacular examples of the structure-function relationship in living matter. Zerrouki *et al.* employed asymmetric colloidal silica dumbbells, linked by a paramagnetic ferrofluid belt at the waist, in the presence of an applied magnetic field to realize two competing length scales for interactions, seemingly present in DNA, as a route to chiral colloidal clusters.<sup>62</sup> In the presence of a magnetic field, a linear chain was observed with symmetric dumbbells, while the asymmetry of the dumbbell, *i.e.* the difference in size between its two spherical lobes, forced the chain to coil when this size ratio was between 2 and 3 (Figure 3A).<sup>62</sup> Drawing motivation from this experimental work, Chakrabarti *et al.* devised a general strategy for the programmed assembly of helical ground state structures with different achiral building blocks, underpinning the physics of emergent chirality in the cases considered in their computational study.<sup>63</sup> This study demonstrated how chirality could emerge from an interplay between two competing length scales for anisotropic interactions, realized, perhaps in the simplest form, with soft oblate ellipsoids of revolution.<sup>63</sup> Using a rare-event simulation technique, the fastest pathway for the reversal of handedness was characterized for a helix assembled from asymmetric dipolar dumbbells in the presence of an external field.<sup>64</sup> The mechanism for switching of handedness involved a boundary between two segments of opposite handedness, which was called a defect, propagating along the helical structure from one end to the other through a sequence of hopping events supported by highly cooperative rearrangements.<sup>64</sup> A more recent computational study by Wales and coworkers demonstrated control over the pitch length of a

helical superstructure, obtained via directed self-assembly of charge-stabilized colloidal magnetic dumbbells in the presence of an applied magnetic field. The study shows that the pitch length can be controlled considerably by varying the salt concentration of the medium, thus modulating the electrostatic screening (Figure 3B).<sup>67</sup>

In their experiments, Granick and coworkers exploited the salt concentration as a control parameter to induce the self-assembly of Janus colloidal particles having hydrophobic attractions on one hemisphere and electrostatic repulsions on the other, and elucidated kinetic pathways for self-assembly into supracolloidal architectures and their isomerization.<sup>65</sup> In particular, they reported the formation of the Bernal spirals,<sup>68</sup> also known as triple helices which are three-stranded helices composed of a chain of face-sharing tetrahedra, as kinetically favored structures (Figure 3C).<sup>65</sup> The self-assembly pathway was found to involve the formation of kinetically favored capped trigonal bipyramidal clusters, which fused together to form the supracolloidal triple helix. The Bernal spiral is a chiral architecture (see Figure 3C); interestingly, the experiments observed a spontaneous switching of handedness occurring occasionally. The pathway for chirality switching was observed to involve an intermediate structure in which one particle had seven nearest neighbors.<sup>65</sup>

In a subsequent computational study by Morgan *et al.*,<sup>66</sup> a minimalist design rule was derived for thermodynamically favored Bernal spirals using patchy particles. These colloidal building blocks involved two different types of attractive surface sites, described as complementary patches and antipatches, such that a patch interacted only with antipatches and vice versa. A tailored spatial arrangement for three pairs of patches and antipatches, deduced from the geometry of the Bernal spiral, was shown to produce thermodynamically favored Bernal spirals. By systematic removal of patches, the designer patchy colloidal particles with only one patch-antipatch pair offset by about 10° from the directly opposite spatial arrangement were then shown to support Bernal spirals as the ground state structures.<sup>66</sup> This minimal design rule presents a realistic target for state-of-the-art experimental fabrication.

## V. Hollow spherical structures

Hollow spherical structures at different length scales have many practical applications, especially in drug delivery, predominantly because of their ability to encapsulate guests and deliver cargoes,<sup>69</sup> and thus serve as attractive targets also for colloidal self-assembly.<sup>70–75</sup> In a seminal early work, microcapsules were fabricated by the self-assembly of colloidal particles onto the interface of emulsion droplets.<sup>70</sup> Several studies of targeted self-assembly into hollow spherical structures in the absence of a template have drawn motivation from fascinating examples

of viral capsid assembly,<sup>71–73,75</sup> which results in a remarkable structural hierarchy via protein subunits.<sup>76</sup> Early models of patchy particles were used as a minimal representation of globular proteins for numerical studies of protein crystallization.<sup>60,77</sup> Self-assembly into a range of platonic solids has been explored with such models to achieve the control and fidelity of virus capsid assembly in synthetic systems by Doye, Louise and coworkers.<sup>71,72</sup> Figure 4A shows the global minima identified for clusters of  $N = 12, 24, 36$  patchy particles, each decorated with five patches, illustrating the propensity to form hollow icosahedra. This study found an optimal patch width to be a crucial parameter to strike a balance between structural specificity and kinetic accessibility.<sup>71</sup> It is relevant to note that a recent study has investigated dense packings of up to  $N = 60$  polyhedral particles in spherical confinement.<sup>78</sup> The interplay between shape anisotropy of particles and isotropic three-dimensional confinement resulted in a wide variety of symmetries and structures, demonstrating the effects of spherical confinement. For many  $N$  values, icosahedra and dodecahedra form clusters, which surprisingly include layers of optimal spherical codes.<sup>79,80</sup>

In a computational study Morphew and Chakrabarti have recently demonstrated hierarchical self-assembly of charge-stabilized colloidal magnetic particles into reconfigurable hollow spheroidal polyhedra via a biomimetic design route.<sup>73</sup> In a remarkable display of two-level structural hierarchy, the colloidal building blocks formed uniform triangular subunits at an intermediate level, and the assembly of these planar trimers at the next level resulted in the formation of a number of spheroidal polyhedra with emergent faces depending upon the system size (see Figure 4B).<sup>73</sup> The ground state structures for size-selected clusters were found to be topologically equivalent to the snub cube and the snub dodecahedron, which are chiral despite having high degree of rotational symmetry. In this study, the designer building blocks included a permanent point-dipole shifted away from the center, closely resembling the micron-sized colloidal magnetic particles, synthesized by Sacanna *et al.*<sup>81</sup> The synthesis produced charge-stabilized colloidal magnetic particles with a single-domain hematite cube inclusion underneath the surface of an organosilica polymer sphere. When the electrostatic screening length was reduced by increasing the salt concentration of the medium, the particles were found to form planar trimers through an interplay of magnetic, steric, and electrostatic interactions.<sup>81</sup> The computational study shows that these supracolloidal polyhedra open up in response to an external magnetic field - a feature especially sought-after for a variety of applications as cages that can encapsulate guests and release them on demand. It is relevant to note here that magnetic particles with off-centered dipoles have drawn special interest in computer simulation studies in recent years,<sup>73,75,82–85</sup> in connection with the synthesis of a variety of exotic colloidal magnetic particles.<sup>81,86–88</sup>

Evers *et al.* recently reported a fascinating realization of hollow microcapsules via self-assembly of snowman-shaped colloidal particles, which combined shape anisotropy, attractive interaction and deformability.<sup>74</sup> The particles consisted of deformable core with a hydrophobic polystyrene-rich interior and a hydrophilic poly(acrylic acid)-rich outer layer onto which a rigid protrusion was grown by swelling with additional styrene. The presence of hydrophobic polystyrene groups also in the outer layer imparted mutual attraction to these particles. Evers *et al.* demonstrated that all three attributes were necessary for the colloidal building blocks they synthesized to self-assemble into microcapsules, which they observed using both scanning electron microscopy and optical microscopy (see Figure 4C).<sup>74</sup>

## VI. Tubular structures

A variety of colloidal self-assembly routes have recently shown to lead to finite tubular structures.<sup>75,89,90</sup> By applying a precessing magnetic field, where the precession angle was used as the control parameter, Yan *et al.* demonstrated the self-organisation of magnetic Janus particles into microtubes (see Figure 5A).<sup>89</sup> In this study, the colloidal particles were observed to rotate and oscillate continuously, but their motion was synchronized. In this case, the formation of the microtubes, which can be viewed as staggered stacks of regular polygons, followed a nucleation-and-growth scheme.<sup>89</sup> Interestingly, a recent computational study reported on hierarchical self-assembly of charge-stabilized colloidal magnetic particles into tubular structures, which also resulted from stacking of square-planar subunits in the anti-prismatic arrangement, as shown in Figure 5B.<sup>75</sup> The designer colloidal building blocks included a permanent magnetic dipole, located away from the center and directed perpendicular to the radial shift. By employing a rare-event simulation technique,<sup>91</sup> this computational study demonstrated a growth mechanism for the tubular structure via sequential attachment of the square-planar subunits as they formed.<sup>75</sup>

In yet another route, Crassous *et al.* demonstrated the self-assembly of colloidal particles with a prolate ellipsoidal shape into regular tubular structures when subjected to an alternating electric field (see Figure 5C).<sup>90</sup> Their experimental state diagram shows that tubular structures were formed for moderate values of the aspect ratio and relatively large values for the electric field strength.<sup>90</sup> The tubes were found to have a highly regular structure with a circular cross-section, single-particle wall and a periodic arrangement of the aligned particles. The study identified the interplay between the shape anisotropy and the polarization effects to be the key factor for the hollow tubes with curved surfaces to emerge via self-assembly.

## VII. Structural hierarchy

Hierarchical self-assembly of colloidal building blocks offers a route to structural hierarchy starting from simpler microparticles via structured aggregates,<sup>92</sup> such as triangles,<sup>73,75</sup> square-planar units,<sup>75</sup> tetrahedra,<sup>93</sup> or octahedra.<sup>93</sup> These colloidal clusters can be viewed as secondary building blocks for the next level of assembly, where the self-assembly pathway for multi-level structural hierarchy is itself hierarchical.<sup>75,94</sup> Programming even a two-level hierarchical self-assembly scheme faces the challenge of achieving self-limited assembly at the intermediate level to produce uniform secondary building blocks.<sup>95</sup>

The proof-of-principle study by Chen *et al.* shows the potential of colloidal clusters, formed via the self-assembly of so-called triblock colloidal particles, to be the building blocks for the next level of assembly (see Figure 6A).<sup>93</sup> The triblock Janus colloidal particles were produced using the glancing angle deposition technique, which deposited thin films of titanium and gold onto the sulphate polystyrene spherical core, and the reaction of the metal films thereafter with *n*-octadecanethiol. The colloidal particles thus exhibited two hydrophobic regions at either pole separated by a charged belt in the middle.<sup>93</sup> The synthesis could control the patch width of the two patches on the poles, which were previously shown to be a crucial factor controlling the kinetic accessibility of target structures in a computational study.<sup>71</sup> These colloidal particles were shown to undergo staged assembly triggered by stepwise change of the ionic strength of the medium, where the patch width proved to be important. At an intermediate salt concentration, small clusters, such as tetrahedra, trigonal bipyramids and octahedra, were observed to form via the hydrophobic interactions of the larger patches.<sup>93</sup> The second stage of assembly was then induced by increasing the salt concentration. At a high salt concentration, the small clusters formed initially interacted through the newly activated smaller patches to show the potential for unprecedented porous networks.<sup>93</sup> However, the study recognized the limitations due to the distribution of sizes that the secondary building blocks exhibited.

In recent work Crocker and co-workers demonstrated the potential for realizing structural hierarchy via a variety of colloidal clusters with distinct symmetries formed using colloidal crystal templates and reprogrammable DNA interactions.<sup>96,97</sup> They employed a templating approach with a closed-packed “host” lattice of DNA-functionalized microspheres containing “impurity” species at substitutional or interstitial defect sites. The colloidal crystal includes DNA bridges between the two species formed by enzymatic ligation. Upon melting the colloidal crystal, colloidal clusters consisting of a single impurity particle surrounded by host particles were produced. By adjusting the size ratio of the two types of spheres and the timing of the ligation, colloidal clusters having the symmetry of tetrahedra, octahedra, cuboctahedra,

triangular orthobicupola, and icosahedra, were produced from single type of the host lattice as the template. These colloidal clusters exhibited multiple binding sites for DNA-mediated directional interactions, which could drive the next stage of self-assembly (see Figure 6B).<sup>97</sup> In fact, a more recent computational study by Zanjani *et al.* demonstrated a self-assembly scheme for pre-assembled cubic, tetrahedral, and octahedral clusters into superstructures in which the clusters are connected to each other indirectly via “bond spheres”.<sup>98</sup>

In a computer simulation study, Grunwald *et al.* showed the assembly of finite clusters of well-defined structure and composition from a mixture of spherical particles with short-range isotropic interactions by controlling only their sizes and a small number of binding affinities.<sup>99</sup> These finite clusters, referred to as “metaparticles”, exhibited emergent patchiness (see Figure 6C). In order to study the next stage of assembly of these metaparticles exploiting their patchiness, the metaparticles were treated as rigid bodies and were shown to assemble into a variety of complex superstructures, including filamentous networks, ordered sheets, and highly porous crystals.<sup>99</sup>

## VIII. Conclusion

In this review, we have focused on clusters formed by anisotropic colloidal particles, describing recent progress in the synthesis of colloidal molecules, which have become a prominent feature in colloid science alongside the traditional picture of colloidal particles as big atoms, and the self-assembly of finite supracolloidal structures. The colloidal particles with directional interactions have proved to be promising building blocks for supracolloidal structures, which could be fabricated bottom-up via self-assembly. We have highlighted examples of self-assembly into a variety of finite supracolloidal structures, which have emerged through an interplay of colloidal interactions, often due to the presence of more than one anisotropy attribute. The examples included here are by no means exhaustive, but serve, we believe, to highlight certain classes of finite supracolloidal structures appearing as recurrent themes in studies of colloidal clusters. There are also recent studies,<sup>100–105</sup> which notably have advanced the field of colloidal clusters but fall beyond the scope of this review given its focus on anisotropic colloidal particles.

It is, however, important to emphasise the structural diversity that self-assembled colloidal clusters demonstrate. These structures show a wide spectrum of size-sensitivity. While the morphology of tubular or helical structures shows less sensitivity to the size of the clusters, hollow spherical structures are often formed only for size-selected clusters commensurate with closed-shell architectures. It is relevant to note that the formation of self-limited clusters with uniform size is of topical interest for both fundamental and practical applications.<sup>10,106</sup> A recent

study presented a generic, particle-based model, which predicted the formation of self-limited assemblies due to the renormalization of the repulsion between particles “on-the-fly” as the particles aggregate.<sup>106</sup>

In the context of targeted colloidal self-assembly, a major challenge is to be able to manipulate the interactions between the colloidal building blocks such that the target structure is not only thermodynamically favorable, but also kinetically accessible on the experimental time scale. Reversible association or contact formation allows for facile annealing of defects, and hence removal of kinetic traps which arise from metastable structures. Such reversibility is, however, often achieved at the expense of weak thermodynamic driving forces. Thus there often exist competing thermodynamic and kinetic criteria for optimal design rules for targeted self-assembly. In the presence of colloidal building blocks with directional interactions, which strongly favor certain contacts, the task of finding the optimal design rules is even more formidable.

Hierarchical self-assembly of anisotropic colloidal particles, despite being at an early stage of exploration, has already shown great promise.<sup>34,73,75,93</sup> Targeted structural hierarchy exploiting this scheme poses a multiscale design problem, which faces a grand challenge from the requirement of bridging multiple hierarchies of length- and time-scales associated with the structure and dynamics, respectively, along the self-assembly pathway. On the other hand, dynamic self-assembly, which requires continuous energy input for emergence and sustenance of ordered structure or pattern and thus refers to a non-equilibrium phenomenon,<sup>107,108</sup> has proven challenging to understand and engineer. Dynamic self-assembly is of special interest as it closely mimics functional organizations in living systems. The conceptual framework of dynamic self-assembly is still not well developed. The development of this framework has also been impeded by the paucity of the experimental systems. However, the scenario is changing with recent studies on colloidal clusters, for example, those involving magnetic Janus particles in a time-varying magnetic field.<sup>89</sup> We envisage that research activities in coming years on these two strands, in particular, will push the frontiers of colloidal self-assembly.

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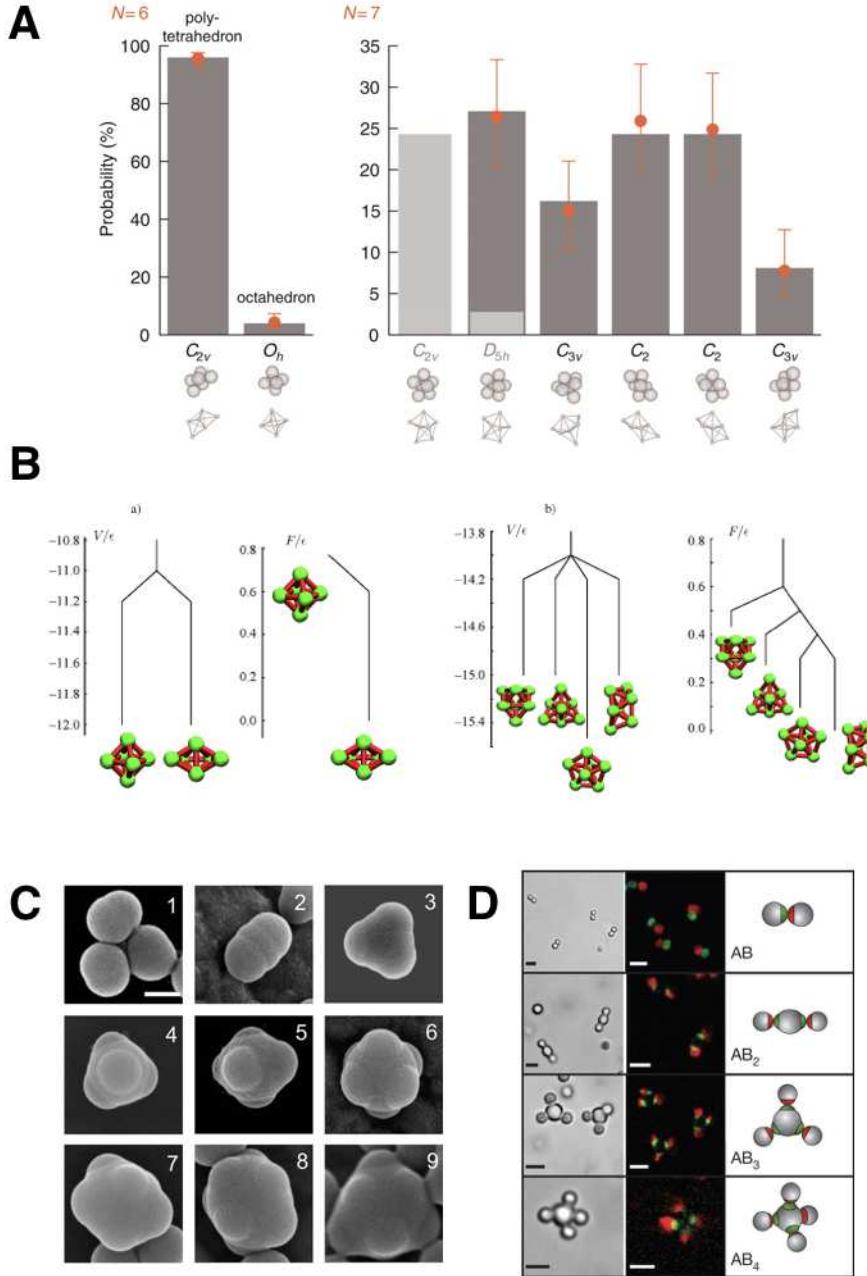
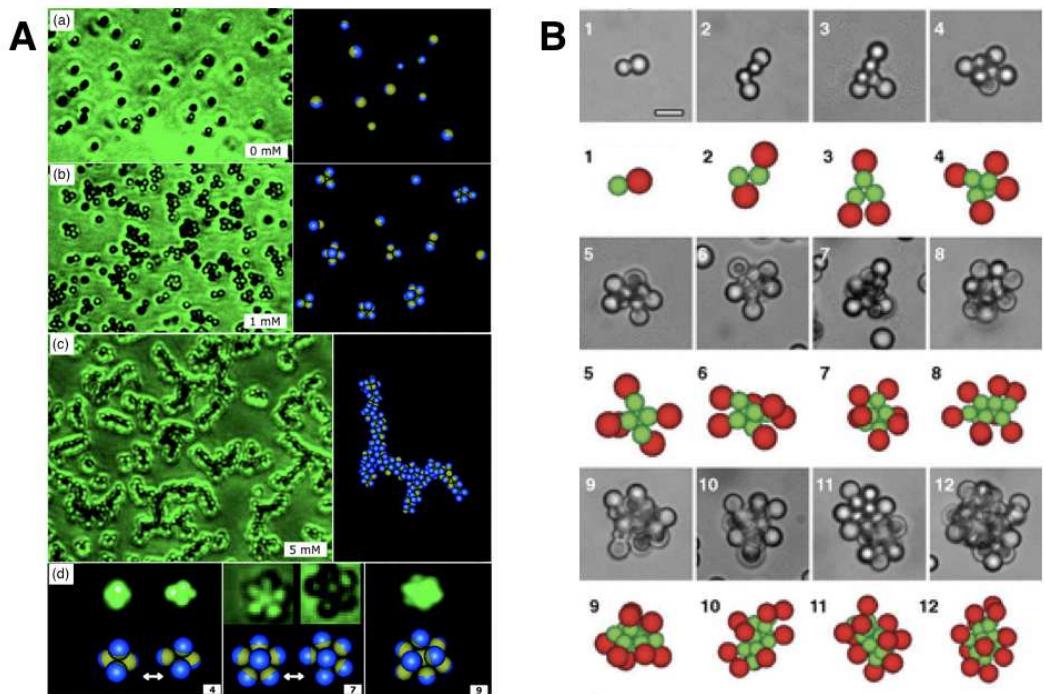


FIG. 1. **(A)** Comparison of probabilities for different structures as observed in experiments (orange dots) and as predicted by theoretical calculations (grey bars), reported in Ref. 41, for clusters of size  $N = 6$  and 7. From Ref. 41. Reprinted with permission from AAAS. **(B)** Potential ( $V$ ) and free energy ( $F$ ), calculated at the reduced temperature of 0.25, disconnectivity graphs for colloidal clusters, bound by the Morse potential with the range parameter  $\rho = 30$  of size  $N = 6$  and 7. From Ref. 43, reproduced with permission from John Wiley and Sons. **(C)** Scanning electron micrographs of colloidal molecules for  $N = 1$  to  $N = 9$  created by merging liquid protrusions as reported in Ref. 19. Reprinted with permission from Ref. 19. Copyright (2009) American Chemical Society. **(D)** Colloidal molecules self-assembled from patchy particles, as shown in bright-field (left panels), confocal fluorescent (middle panels), and schematic images (right panels) in Ref. 25. Reprinted by permission from Macmillan Publishers Ltd: Nature (Ref. 25), copyright (2012).



**FIG. 2. (A)** Cluster of various sizes and shapes formed via the self-assembly of amphiphilic Janus colloidal particles at different salt concentrations. The images with green background represent epifluorescence experiments and those with black background are from Monte Carlo simulations, showing cluster formation as the salt concentration increased from (a) to (c). The panel (d) highlights that the structures dynamically interconvert between different shapes as observed both in experiments and simulations. Adapted with permission from Ref. 56. Copyright (2008) American Chemical Society. **(B)** Typical structures observed for one-patch colloidal particles in experiments (upper rows with grey background) and simulations (lower rows with white background), showing the self-assembly into finite structures resembling micelles; in experiments and simulations, the smaller attractive sides with a smooth surface are located at the interior of the clusters. Adapted from Ref. 57.

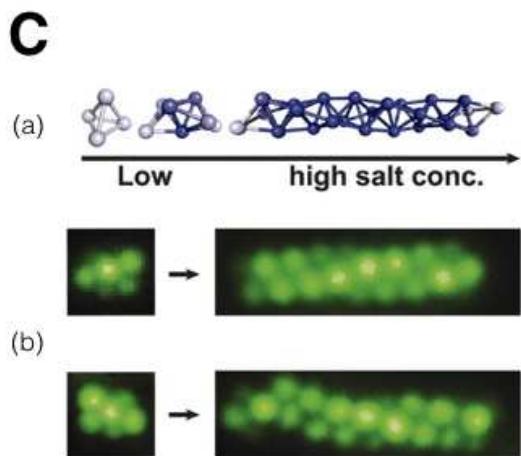
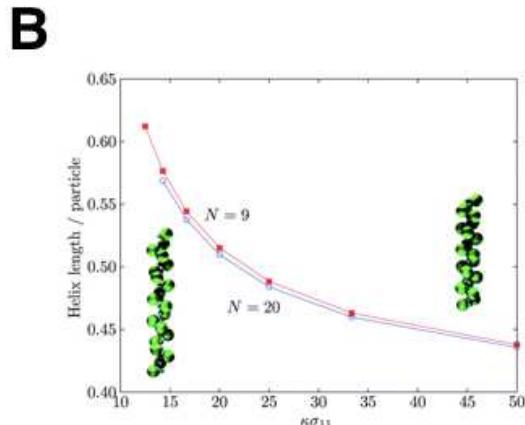
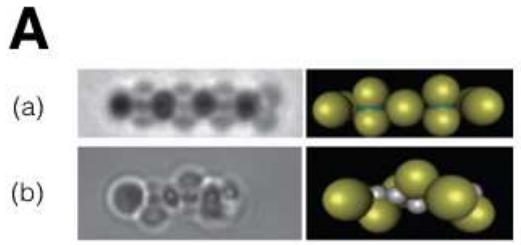


FIG. 3. **(A)** Optical microscopy images and their corresponding schematic representations, showing emergent helicity through the interplay between steric and magnetic interactions, experimentally realized by magnetic dumbbells in the presence of an external magnetic field: (a) chain formed by symmetric dumbbells (b) a helical structure formed by asymmetric dumbbells. Reprinted by permission from Macmillan Publishers Ltd: Nature (Ref. 62), copyright (2008). **(B)** A plot showing the helix pitch length as the inverse Debye screening length was varied for finite supracolloidal helices, obtained via directed self-assembly of charge-stabilized colloidal magnetic dumbbells in the presence of an applied magnetic field, for two different cluster sizes. Reproduced from Ref. 67 with permission from The Royal Society of Chemistry. **(C)** A geometrical representation of (a) the growth of triple helix and (b) fluorescence images of the chiral structures (both right- and left-handed) as observed in experiments with spherical Janus colloidal particles. Triple helices are formed at higher salt concentrations. From Ref. 65. Reprinted with permission from AAAS.

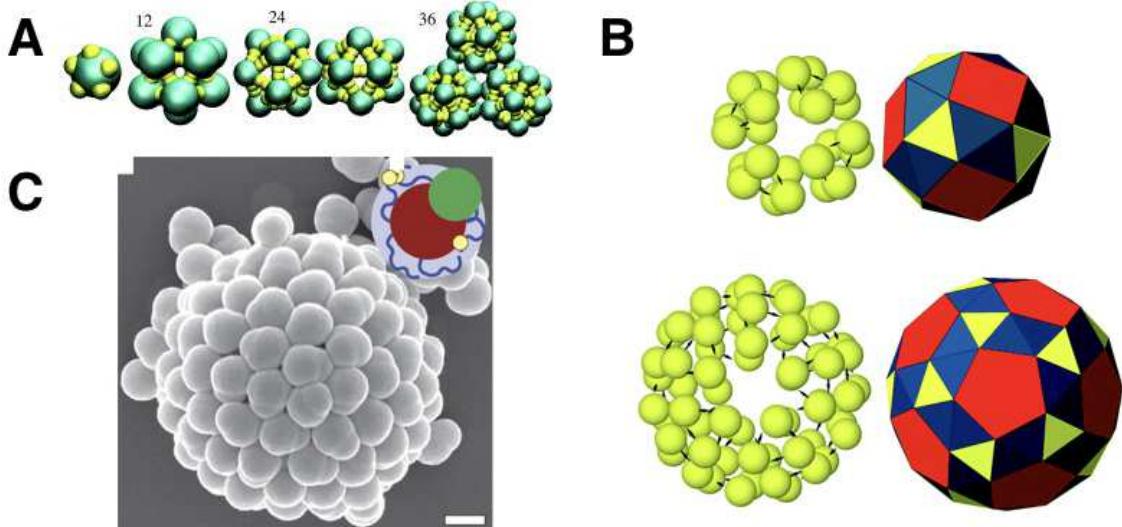
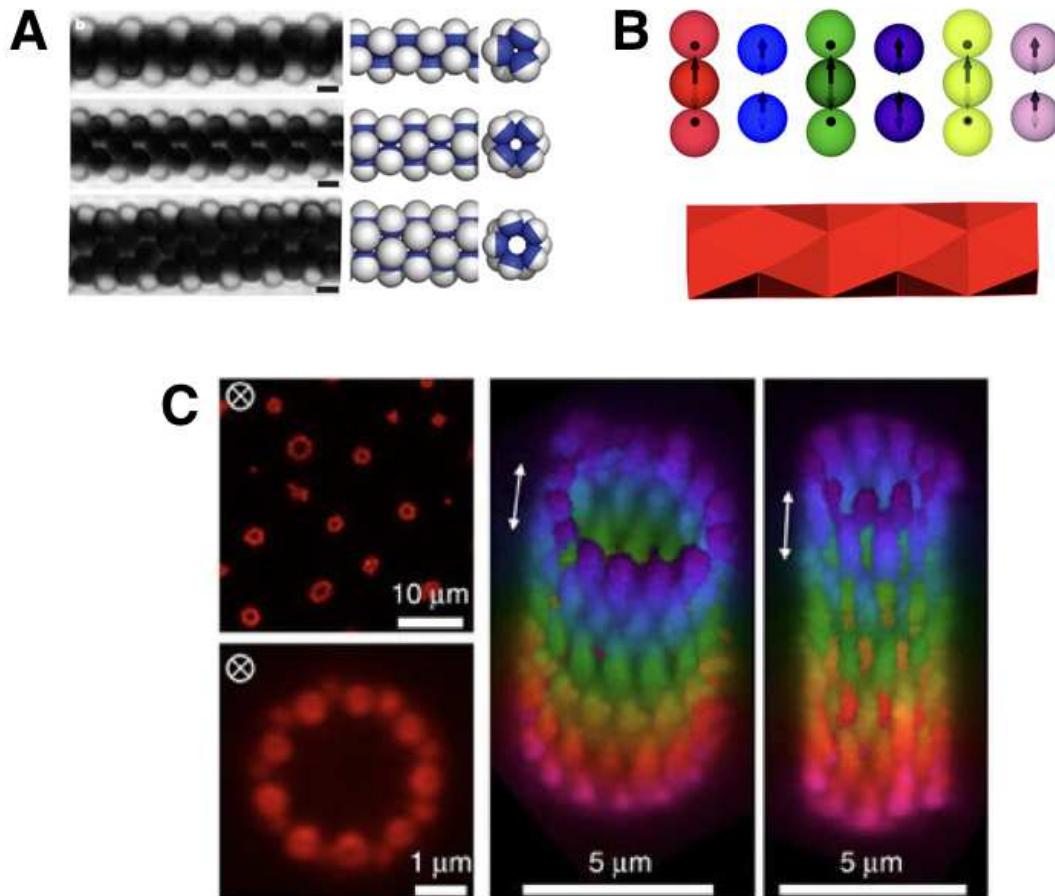


FIG. 4. (A) A five-patch colloidal particle and the global minima for clusters of  $N = 12$ ,  $24$  and  $36$  such particles, as identified in Ref. 71, showing the formation of hollow icosahedra. Reprinted from Ref. 71, with the permission of AIP Publishing. (B) The ground state structures and their polyhedral representations for  $N = 24$  and  $N = 48$  charge-stabilized colloidal magnetic particles, illustrating hollow spheroidal structures that are topologically equivalent to the snub cube and snub dodecahedron, respectively. Reproduced from Ref. 73 with permission from The Royal Society of Chemistry. (C) The scanning electron microscopy (SEM) image of microcapsules formed via self-assembly of deformable, anisotropic, mutually attractive colloidal particles. A schematic representation of the colloidal building block, consisting of a core (red) with hydrophilic (blue) and hydrophobic (yellow) moieties and a rigid protrusion (green). Reprinted by permission from Macmillan Publishers Ltd: Nature (Ref. 74), copyright (2008).



**FIG. 5. (A)** Microtubes formed by self-organization of magnetic Janus particles in the presence of a precessing magnetic field: (left) observed images and (right) corresponding models (side and end views) of microtubes parallel to the precession axis. Reprinted by permission from Macmillan Publishers Ltd: Nature (Ref. 89), copyright (2012). **(B)** (top) The tubular structure identified as the global minimum structure for  $N = 24$  charge-stabilized colloidal magnetic particles in Ref. 75. The structure is color coded to distinguish between identical square planar units self-assembled at the intermediate level. (bottom) A polyhedral representation for the tubular structure showing the stacking of square-planar subunits in the anti-prismatic arrangement. Reproduced from Ref. 75 with permission from The Royal Society of Chemistry. **(C)** 2D images and 3D reconstructions of tubular structures formed via self-assembly of colloidal particles with a prolate ellipsoidal shape when subjected to an alternating electric field. Reprinted from Ref. 90 under a Creative Commons Attribution 4.0 International License.

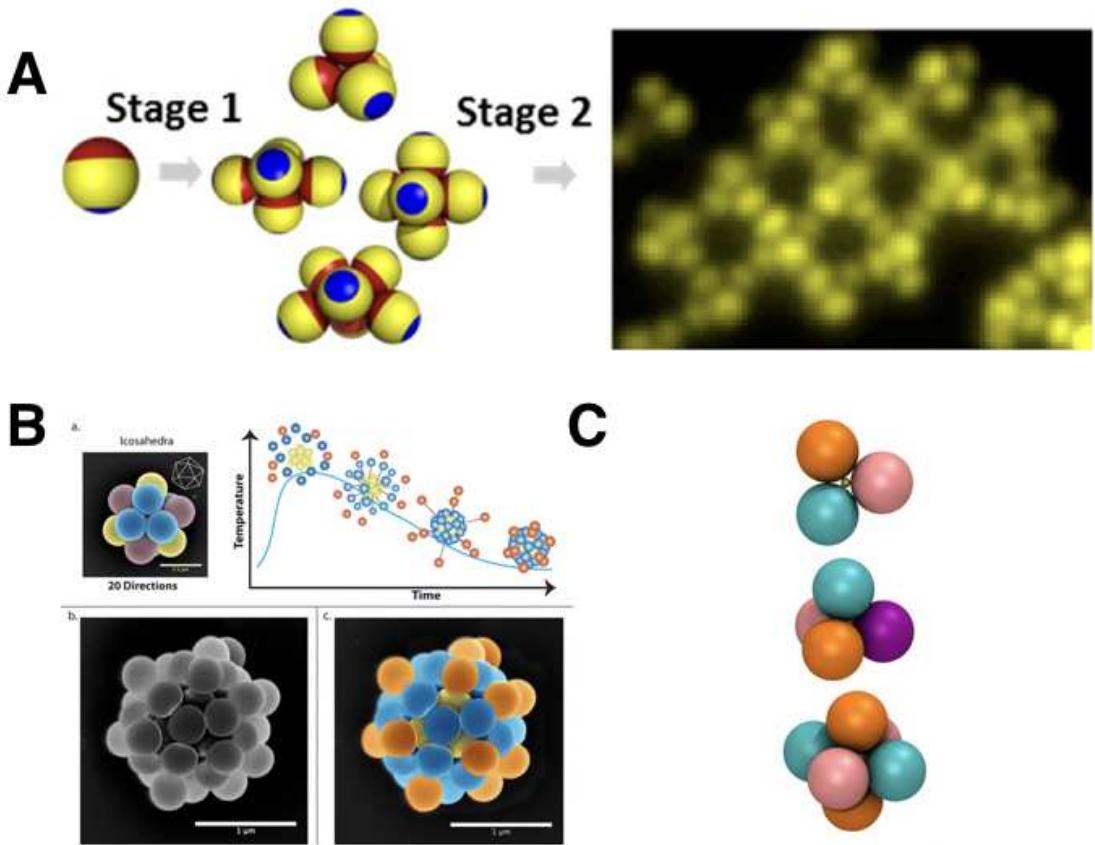


FIG. 6. **(A)** A schematic representation of small colloidal clusters formed by triblock particles and an illustrative network structure. The two patches on the poles are of different patch widths and are distinguished by color coding. Reprinted with permission from Ref. 93. Copyright (2012) American Chemical Society. **(B)** The SEM visualization of an icosahedral cluster (a) exhibiting directional bonding (b) when a system of pure icosahedra was annealed with an excess of complementary spheres Reprinted with permission from Ref. 97. Copyright (2015) American Chemical Society. **(C)** Three example metaparticles that can be obtained via self-assembly with high yield through appropriate choices of attraction strengths and glue particle size. Reprinted from Ref. 99 under a Creative Commons Attribution 4.0 International License.

## Graphical abstract

