

Toward Design Rules of Directional Janus Colloidal Assembly

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Abstract

Burgeoning interest in supracolloidal assembly has reached the point at which the field can seek so-called intelligent design rather than solely rely on evolution. Emphasizing Janus and triblock particles, this review presents a progress report on formulating design rules for the assembly of interesting structures. We discuss how to design building blocks, bearing in mind that patchy particles embody not just geometric shape but also chemical shape, that chemical shape determines particle–particle interactions, and that the assembly process can be designed to proceed in hierarchical stages. Remarks are included about the potential of kinetic and nonequilibrium control, as well as the potential for the augmented use of soft building blocks. Whereas the reverse design problem, in which arbitrarily selected structures can be designed from the bottom up, still stands as a grand challenge, the field has reached the point of understanding necessary, although not always sufficient, conditions.

INTRODUCTION

Starting from “dead” building blocks, it is a scientist’s dream to design materials whose self-assembling, responsive attributes rival those of living creatures. This dream has spawned a large industry of scientific endeavor, originating in the supramolecular chemistry of small molecules (1) but now encompassing the assembly of copolymers, proteins, DNA, and colloidal particles. This review focuses on the latter. Researchers in this field focus on various applications, including self-healing materials (2, 3), artificial muscles (4, 5) and other biomimetic structures (6), and the creation of periodic structures for applications such as photonics (7). We also note that for the dream of emulating life to go beyond rhetoric, the invention of self-assembled structures that self-replicate and self-correct is required (8).

The assembly of colloid-sized particles differs fundamentally from that of atoms, molecules, and nanoparticles, as the range of their particle–particle interactions is generally small relative to the particle size, whereas this is not so for those other objects. Thus, with colloidal particles (larger than the diffraction limit but still small enough to be moved around by Brownian motion), one can approach distinctively different conceptual problems. Moreover, their size range can be attractive to experimentalists, as such particles can be tracked individually, in real space and real time, with modern optical microscopy (9) when the experiment is designed appropriately. Hence, pointed questions of physical behavior can be posed, especially as synthetic advances now allow one to synthesize particles in large quantities, with spherical particles standing as the hydrogen atom of this field (10). For the reasons described above, this review is not concerned directly with nanoparticles, but their assembly has been studied as well (11).

We write this review during a period governed by the question of relevance. A large motivation for scientific activity in this area is to advance the field beyond the now-classical study of suspensions (12, 13). Crystalline structures analogous to those formed by atoms have been produced with potentially useful optical properties. Because the wavelength of visible light is comparable to the size of the building blocks (14–16), crystals of such particles might conduct, and of course forbid, the transport of light. Photonic crystals have been developed based on this idea (16–18). More exotic crystals have been assembled using oppositely charged particle mixtures (19). In a larger sense, these are examples of assembly not from covalent bonds as in the case of molecules, but rather from weak interactions as in the case of supramolecular chemistry (1). Extending this approach, it is evident that colloidal clusters and assemblies could in principle be designed to manipulate matter and perform functions on larger scales than is possible with molecular-sized building blocks, perhaps using selective coordination (20). Regarding reconfigurability, mutability, and responsiveness, these large building blocks are easier to design and control than smaller building blocks (21), although liquid crystals are a remarkable exception (22, 23).

An anisotropic colloid with two sides is now widely known as a Janus particle: The name, popularized by de Gennes (24) after it was earlier introduced by experimentalists in his research group (25), alludes to the Roman god with two faces. Focusing on Janus particles, this review is a modest first attempt to formulate design rules for nontrivial self-assembly. The notion of Janus particles has been extended to multiblock particles with more than two patches, made possible using modern particle-coating techniques (26–28). Indeed, some degree of anisotropy in the building block is needed to achieve nontrivial structure; when building blocks are isotropic, their assembly tends to be mundane, for example, simple dense packing into hexagonal or cubic lattices (9). Molecular assemblies often achieve anisotropy via dipole–dipole interactions, of which hydrogen bonding is a special type, with consequences as profound as protein folding (29) when combined with hydrophobic–hydrophilic sequences. Even electrostatic interactions between

particles can become directional, provided that surface charge is distributed nonuniformly and the screening length is sufficiently small (of the order of a few nanometers) (30).

We seek to identify common threads in this still-evolving field, emphasizing physical principles, and do not review the proliferating synthesis methods that actually concern many present-day chemists in the field (31–34). We discuss three aspects of the directional assembly of colloids—the selection of particle shape (35–41), particle interaction (28, 37, 42–50), and hierarchical control (51–53)—recognizing that successful design also relies on integrating these factors, which are not fully independent. Although mainly concerned with thermodynamically stable assemblies (48, 50), we also contemplate the possibility of kinetic and nonequilibrium control of the assembly process, mentioning hierarchical assembly (51, 52) and external field control (54–57). Directing the discussion toward the vision of functional (adaptable and reconfigurable) assembled structures, we take the perspective that the most interesting building blocks are those simple enough to be created experimentally.

SHAPE DESIGN

The primary constraint on packing behavior and particle–particle interaction is the shape of the building block. Beyond obvious considerations of geometric shape (examples are noted below), chemical shape (i.e., anisotropic surface chemistry) matters.

Patch Design

The coordination number (i.e., the maximum number of nearest neighbors) of colloidal spheres can be designed via attractive surface patches. Obviously, this mechanism differs fundamentally from covalent bonds resulting from quantum-mechanical hybridization in organic chemistry of molecules (58), yet there is a common phenomenology (59, 60).

Isotropic spheres adopt close-packed conformations, corresponding to a coordination number of 12. This can be reduced by endowing particles with a patchy chemical makeup (48–50) or alternatively a lock-and-key mechanism to provide attraction at specific points (45). The coordination number of chemically patchy particles depends on the area, number, and positions of the patches. Each patch can be seen as a coordination site, and the shape and area of each site limit its coordination. For example, particles with two small point patches, one at each pole, will assemble into chains (61), and particles with four symmetric patches around a sphere could conceivably assemble into the diamond crystal structure that is desirable for photonic applications (59). However, the favored structure is not always directly predictable by intuition, especially when particles include multiple, asymmetrically distributed patches, or when there is more than one type of interaction. In those cases, computer simulations can be helpful. Simulations have been used for so-called inverse design to target specific structures (62) and to explore parameters not accessible in experiments (63).

Selective decoration of spherical particles using deposited metal coatings has created symmetric and asymmetric multiple (up to three) patches (49). This technique has also been applied to shapes other than spheres, including rods and spheroids (see **Figure 1a**). Such patches can be readily functionalized with biotin, avidin, DNA (64), hydrophobic chains (48–50), and other functional groups (28). To introduce additional patches on one particle, investigators have used various techniques, for example, seeded emulsion (**Figure 1b**). Although this technique still suffers from difficulty producing samples that are monodisperse in the number of patches (59), patches produced via this approach enjoy an attractive scope for functionalization, as they can be functionalized either in an independent step before being integrated into a single particle to achieve

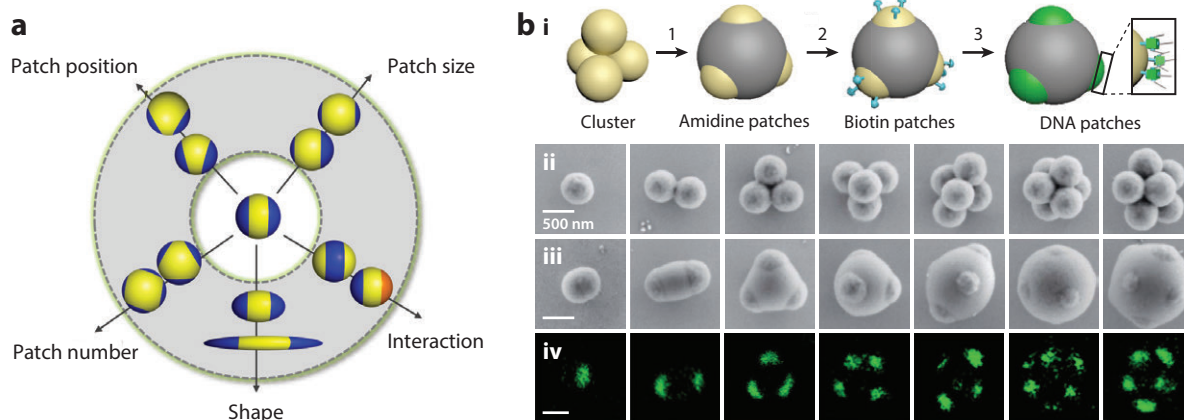


Figure 1

(a) Schematic illustration of various patch parameters to control colloid self-assembly using DNA patches. Panel *a* adapted with permission from Reference 60. (b) Synthesis of DNA-functionalized patchy particles with different numbers of patches. (i) Four symmetrically arranged DNA-functionalized patches, which are produced on spherical particles by taking a cluster of isotropic particles and decorating them with amidine patches, to which first biotin and then DNA are attached. (ii) Electron micrographs of amidinated colloidal clusters. (iii) Electron micrographs of amidinated patchy particles after encapsulation to protect all elements of the cluster except the outermost spots, which subsequently are functionalized. (iv) Confocal fluorescent images of the resulting patchy particles. The fluorescence is emitted from dye-labeled streptavidin that links DNA with the amidine patches. Panel *b* adapted with permission from Reference 59.

different functionality on each patch or after integration to achieve the same functionality on each patch (38).

A design concern is that, if too many identical patches are introduced, they tend to collectively produce a quasi-isotropic net interaction. This can occur, in particular, if the patches are arranged symmetrically. Thus, paradoxically, the more patches a particle possesses, the less anisotropically it may behave in interactions with its neighbors. The selection of patch interactions (**Figure 1a**) is discussed in the next section.

Geometric Shape

Apart from the limitation that experimental production in monodisperse form may be challenging in some cases (or even impossible in other cases), the variety of imaginable geometrical shapes is endless. Although classical colloid science deals exhaustively with spherical colloids, particles of other shapes have been developed, including rods, spheroids, and polyhedra (38–40, 65, 66). Shape anisotropy alters not only the possible packings but also the entropy of the system; as an example of how this matters, maximization of entropy explains the liquid-crystal phase of rod-shaped molecules and particles (67, 68). Compared to spheres, rods possess an additional orientational degree of freedom and shape-dependent interactions that can alter the structure of assemblies (68–70) and other suspension properties (68). The aspect ratio, characterizing the degree to which elongated shapes deviate from a sphere, is an important design parameter to consider (71).

Faceted particles are different, as they tend to align their facets to maximize entropy (41, 72–74) and, in some cases, to maximize specific facet–facet attraction. Micrometer-sized, monodisperse polyhedra have been developed recently (40), thus extending to colloidal length scales from the metal-based nanocrystals known earlier. **Figure 2** displays examples based on metal-organic

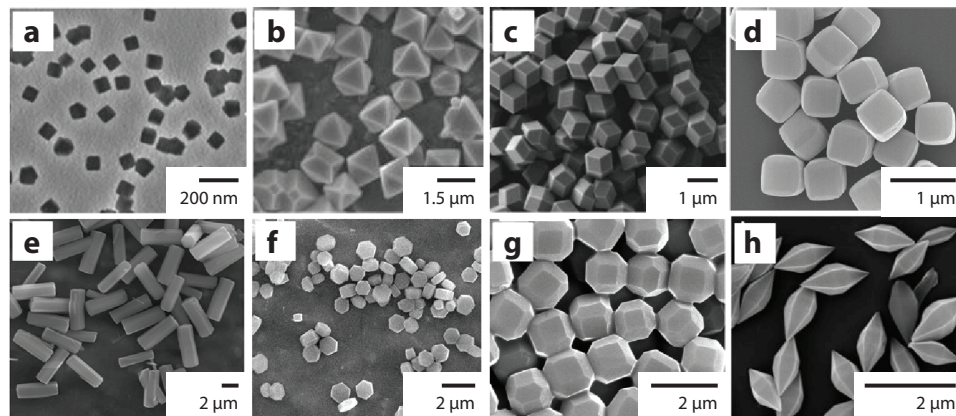


Figure 2

Examples of monodisperse colloid-sized polyhedra from colloidal metal-organic frameworks: (a) cubes, (b) octahedra, (c) rhombic dodecahedra, (d) truncated cubes, (e) hexagonal rods, (f) hexagonal discs, (g) truncated rhombic dodecahedra, and (h) bipyramidal hexagonal prisms. Figure adapted with permission from Reference 40.

framework materials. Although only simple ordered structures have been reported to date (40), one can anticipate more discoveries as experiments begin to catch up with predictions from theories and computer simulations (36, 41). It is noteworthy that specific facet-to-facet attraction, through simple capillary or van der Waals attraction (66), and polymer-mediated depletion interaction (76), appears to be significant in experiments (40, 66, 76) and computer simulation (76).

Particles with small rounded protrusions from spherical cores have also been studied (45–47). This motif can be used as a template for chemical functionalization to produce patches (**Figure 1b**), such that each protrusion becomes a functional patch (59). Selectively dissolving protrusions from parent composite particles can produce lock-and-key colloids consisting of colloids with complementary shapes (47). The original concept of lock-and-key colloids was demonstrated by a different fabrication method, however (45). Directional bonding between particles of complementary shape can then be achieved with high fidelity and efficiency under the action of the depletion attraction (45, 47). Other examples of directional bonding using particles of these shapes include multivalent colloids (59), chiral colloidal clusters (77), magnetic click assembly (55), and sticky dimpled particles (37). Still other methods to fabricate particles with arbitrary shapes rely on lithography (78) and so-called PRINT techniques (79), but to date, the resulting shapes are mostly planar.

At the time of this writing, rapid advances in three-dimensional (3D) printing techniques are likely to lead to the facile design and fabrication of arbitrary-shaped colloidal particles, what one might call colloidal Lego pieces. However, whereas great efforts have already gone into the synthesis of interesting geometrical shapes, there remains significant potential to more closely investigate the assembly that can be anticipated for many of these shapes. Currently, there is insufficient understanding of which nonspherical “Lego” shapes are desirable to produce a stipulated assembly. To appreciate the difficulty of this problem, it is instructive to consider the deep problem of how virus capsids assemble; for a long time, virus capsids have been understood to assemble from definite shapes of protein aggregates (80), but the overarching physical rules predicting structures from these multicomponent mixtures are still imperfectly understood.

INTERACTION DESIGN

In this section, we refer to interaction as a separate subject, while recognizing that shapes (discussed in the previous section) also influence interactions. In the absence of external driving forces, particle–particle interactions must be weak enough to permit a spontaneous thermal search for the free-energy minimum (50) without the system becoming trapped in a metastable state (81). Much is known from classical colloid science about the interplay between van der Waals attraction and screened electrostatic (double-layer) repulsion to produce the so-called DLVO interaction profile (82), and this carries over when considering Janus colloids when the range of interaction is small compared to the particle size (60). Other short-range attractions include hydrophobic (37) and specific guest–host ones (28). If we go beyond the classical emphasis on suspensions of monodisperse colloids, there appears to be untapped potential to design large-scale structures of binary and multicomponent systems (43, 83, 84). As an example, simulations recently predicted the hierarchical assembly of a colloidal system by fine-tuning the isotropic interactions between constituent spherical particles of different sizes (85), and there are many ways to generalize concepts of this sort. Beyond this, there is increasing experimental interest in magnetic attraction, which is longer ranged (55, 77). For dynamic assembly out of equilibrium, hydrodynamic interactions may also come into play, which are long ranged as well (86). However, nonequilibrium self-assembly is governed not necessarily by principles of minimization of energy, but rather by principles that remain only partially developed (56).

Concept of Maximum Coordination Number from Short-Range Attractions

Weak, short-range attraction has been used experimentally to form colloidal clusters (**Figure 3**). Janus spheres that are weakly attractive on one hemisphere are able to form colloidal clusters and helices, including triple helices known as Boerdijk–Coxeter helices (50). Patchy spheres that are weakly attractive at regions near their north and south poles, triblock Janus particles, are able to form the 2D analog of a diamond crystal, the so-called Kagome lattice (48). Although hydrophobic interactions were used in these studies, other short-range attractions should produce the same effects. Notably, the structures of both colloidal clusters and the Kagome lattice are stabilized by rotational entropy (75). Thus, a design consideration is that particles do not have to fit together too perfectly; a little wiggle room, the allowance of small rotations around the points of attraction, adds entropic stabilization.

Another design consideration is the balance between long-range repulsion (typically electrostatic) and short-range attraction. When Janus spheres with a charged and a hydrophobic hemisphere are placed in deionized water, the electrostatic repulsion can be so long ranged that particles are precluded from assembling, and only the addition of salt screens the long-range repulsion sufficiently to allow the short-range attraction to be effective (48, 50). The strength of hydrophobic attraction involved in these studies at moderate salt concentrations is believed to be around $5 k_B T$ per particle (50), low enough to allow the assembled structure to cure defects via thermal excitations. However, at higher salt concentrations, the aggregation could become irreversible (60).

Janus particles with one attractive hemisphere have a coordination number of six, as seen in the colloidal Boerdijk–Coxeter helices (50). When the size of the attractive domain on a Janus particle is less than a hemisphere, the coordination number can be decreased to four in 3D systems (three in quasi-2D systems). This makes it possible to obtain near-monodisperse tetrahedra and trimers (60).

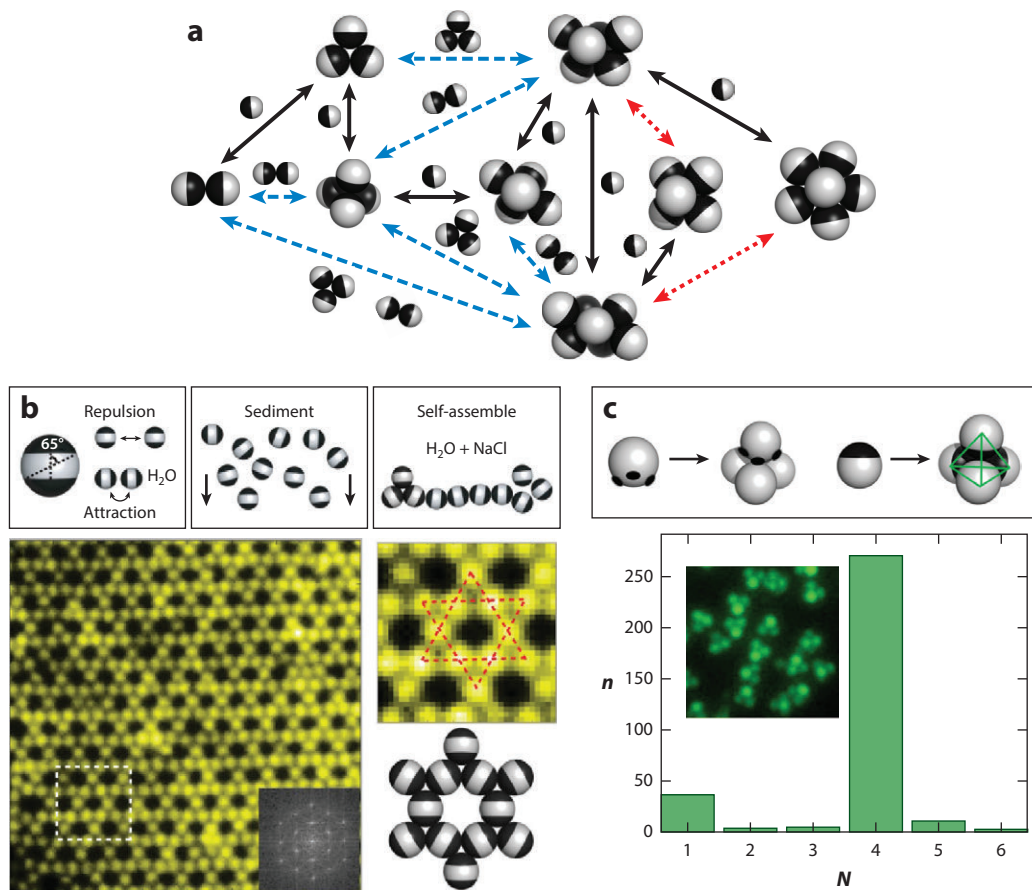


Figure 3

Examples of assembly from the short-range attraction of patchy colloids. (a) Network of reaction pathways of Janus particles. Isomers with $N = 6$ and $N = 7$ elemental spheres are highlighted in boxes. Panel a adapted with permission from Reference 50. (b) Assembly of a Kagome lattice from triblock Janus particles. Panel b adapted with permission from Reference 48. (c) Assembly of tetrahedra from small-patch Janus particles, where the attractive patches generate a coordination number of four. Panel c adapted with permission from Reference 60.

Electrostatic Interactions

Another design parameter is the number of components in the mixture, especially when dealing with charged colloids. To balance opportunity with complexity, many studies focus on binary systems. For example, by mixing two types of oppositely charged particles and tuning the strength and range of the electrostatic interactions, one can obtain colloidal and nanoscale crystals with structures reminiscent of various atomic ionic crystals (43). But unlike atomic and nanoscale systems (87, 88), in which the requirement of charge neutrality determines the stoichiometry, part of the charges can reside in the electrolyte in colloidal systems (43). Nonetheless, the right balance of charge, size ratio, and screening length can produce superlattices in both nanoscale and colloidal binary systems. Depending on the size and charge ratio, various crystal phases, including CsCl, NaCl, and other structures, have been formed (43) (**Figure 4a**). One particular opportunity provided by binary systems is that it is possible to use one type of particle as a sacrificial support and

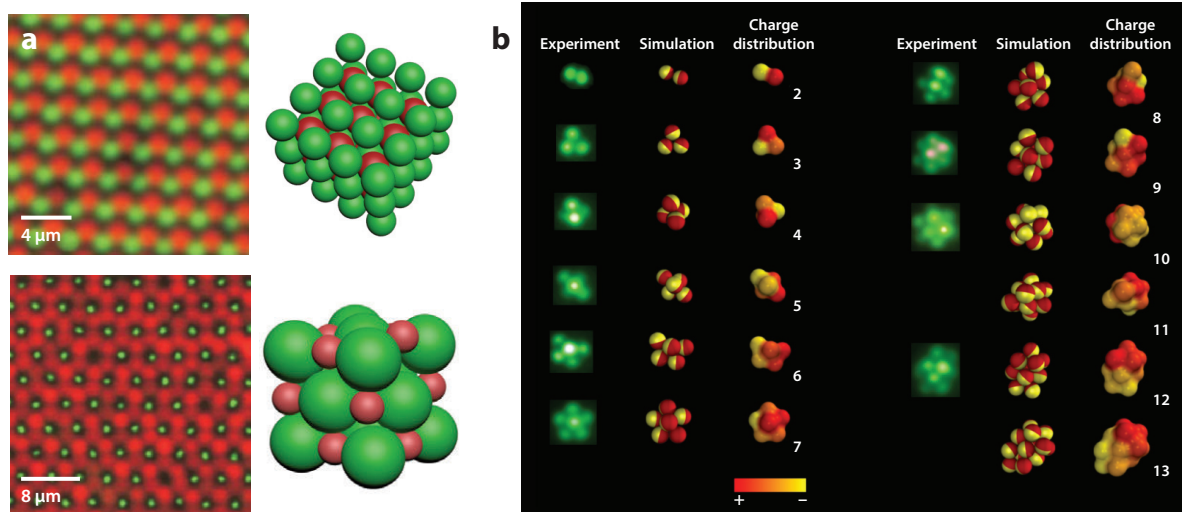


Figure 4

Structures from electrostatic self-assembly. (a) Binary mixtures of oppositely charged particles: a CsCl crystal with a scale bar of 4 μm and an NaCl crystal with a scale bar of 8 μm . Panel a adapted with permission from Reference 43. (b) Monodisperse bipolar Janus particles, electrically neutral but with hemispheres carrying opposite charge. Shown is a comparison of experimental optical microscopy fluorescence images with Monte Carlo computer simulations, with good agreement. Panel b adapted with permission from Reference 30.

obtain otherwise inaccessible open lattices, although an additional stabilization step then becomes necessary (89). Such use of sacrificial templates can be exploited to create new structures.

Particles that are net neutral but have hemispheres of opposite charge also attract, but not quite as a mathematical dipole, as the charge is distributed over a large area (30). In a suitable range of ionic strength, such that the screening length is much smaller than the particle size, the structures differ from the chain and ring structures expected for point dipoles (90). Instead, the assembled structures are mainly clusters, but the reduced symmetry of these electrostatic Janus particles causes the cluster structures to differ from the dense packing observed for homogenous particles (91) (**Figure 4b**). Real-time imaging has shown that after particles assemble into clusters, those clusters merge. Such bipolar functionality could also generalize to other shapes and to particles with more than two patches. Moreover, it is intriguing to note that, based on experiments, asymmetric charge distribution has been proposed as an explanation for the aggregation of certain proteins (92). It is tantalizing to speculate that this idea could be used for the inverse design of structures based on particles with asymmetric surface charge distribution, but this ambition remains to be realized.

Electric and Magnetic Responses at Rest and in External Fields

How does hydrogen bonding between molecules generalize, as a concept, to the colloidal domain? This section concerns directional bonding that results from anisotropic electric and magnetic interactions. Although almost all colloidal particles become polarized in response to electric fields, only certain materials respond to magnetic fields. It is noteworthy that even in the absence of an external electric field, directional assembly can result from the polarization of dielectric particles owing to the dielectric mismatch between particles and solvent (83). Although assembly originating in anisotropic charge is convenient to model as a dipolar interaction, in practice that charge is

usually distributed over a volume. Therefore, the mathematically convenient dipole approximation is just an idealization of reality. A challenge in designing specific structures is the many-body nature of polarization, which causes the induced moments to change under the influence of the assembly.

Going beyond the dipole approximation, anisotropic particles in electric fields have been approximated mathematically as multipolar (54). Assembly is then governed by the interactions between induced dipoles and multipoles. Various chain-like structures have been observed, aligning themselves with the electric field (93, 94). Less trivially, it is found that 2D colloidal superlattices can form perpendicular to an electric field, including square and honeycomb lattices. This occurs using two types of colloids such that particles with parallel dipoles are repulsive, whereas antiparallel dipoles attract, and we note that the magnitude and even the sign of the dipole moment of a colloidal particle in an aqueous suspension can depend on the frequency of an alternating electric field (95). There appears to be good potential, using particles with anisotropic polarizability, to produce new 3D structures, as the approach allows interaction energies to be easily tuned from a few $k_B T$ to thousands of $k_B T$, depending on the strength of the electric field (96).

This approach offers great capacity for external control. The strong dipoles induced by electromagnetic fields allow interactions between colloids to be manipulated, often instantaneously (97, 98), with fewer requirements regarding shape or surface functionalization than are needed for thermally driven assembly (99, 100). Moreover, external electromagnetic fields can easily be turned on and off, or applied with programmed patterns, allowing colloidal assembly to be programmed as well (101), both in time and in space. A simple example of this would be the ability to switch between two crystal structures. Actuation is another example. Electric fields have been used to melt crystals (43) and to assemble colloidal chains (100). Most such structures disassemble when the electric field is turned off, unless additional action is taken to permanently fix the structures (e.g., by chemical cross-linking).

Magnetic interactions offer different opportunities because the magnitude and direction of the magnetic moment induced by an applied static magnetic field depend on the material and temperature and may persist without a field (102). Furthermore, even permanent magnets can be demagnetized by a sufficiently strong magnetic field and reprogrammed (103). This rewritable feature, which already underpins magnetic storage devices in the electronics industry, may open up new future approaches toward reconfigurable colloidal assembly (104).

How can Janus particles be designed to be magnetically responsive? Two popular approaches are ferromagnetic coating (105) and magnetic nanoparticles embedded in larger particles (77). Magnetic dipoles then align with each other. Based on this, colloidal zigzag chains and clusters (**Figure 5**) have been reported (55, 77). As an approach to disassemble structures, repulsion between parallel dipoles can be useful, provided that the embedded dipoles are perpendicular to the magnetic field causing sufficiently strong repulsion between them (55). There exists significant potential to capitalize on this by producing Janus magnetic particles with various types of magnetic response (paramagnetic, ferromagnetic, antiferromagnetic, superparamagnetic). It is easy to imagine colloidal particles that are magnetically anisotropic, for example, by making Janus particles that are half ferromagnetic and half antiferromagnetic, or even more complicated configurations.

The particular case of ferromagnetic particles (permanent dipoles) offers intrinsic directional bonding in the absence of an external magnetic field and also when an external magnetic field is applied (55, 106). Energetically optimal structures are few; closed-loop structures with the topology of knots and links have been predicted (90). Various dipolar ferromagnetic nanoparticles have been synthesized and studied for their assembly behavior (107–109), and colloidal particles doped or decorated with magnetic patches have been studied for their potential capacity for directional assembly (55, 77, 105). When 2D colloidal layers are confined to be perpendicular to a

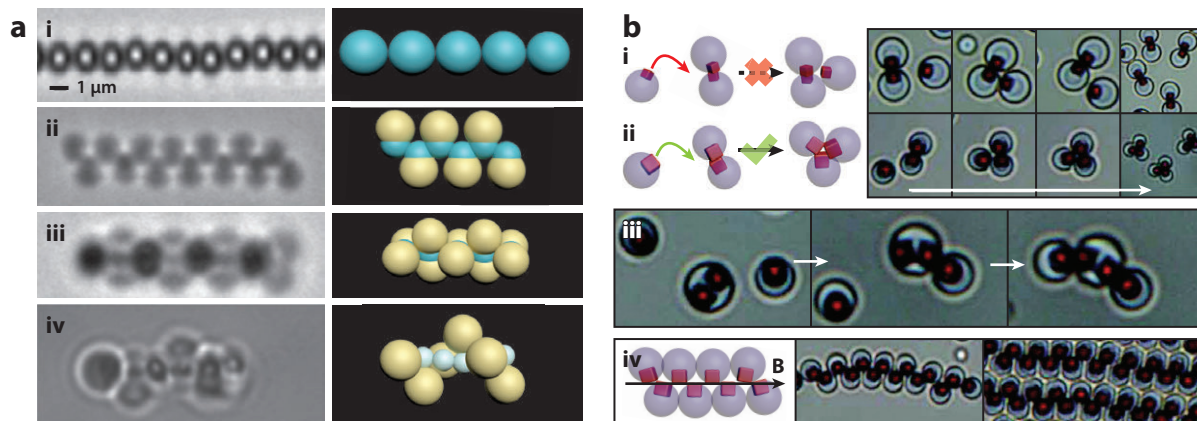


Figure 5

Magnetic-based assembly. (a) Magnetic assembly of colloidal particles based on the shape of building blocks. (i) Spherical ferromagnetic particles self-assemble into linear chains. (ii) Janus particles with magnetic caps self-assemble by ordering alternately up and down along the chain direction. (iii) To satisfy both steric and magnetic constraints, symmetric dumbbells rotate by 90° relative to their neighbors along the chain and field direction. (iv) Asymmetric dumbbells self-assemble into helices. Panel a adapted with permission from Reference 77. (b) Magnetic-click colloidal assembly of monodisperse clusters, colloidal molecules, and linear chains. (i,ii) Particles with one magnetic patch selectively form dimers (with small patches) or trimers (with large patches). (iii) In the time sequence shown, a colloidal molecule assembles from directional magnetic bonds between one divalent and two monovalent particles. (iv) An external magnetic field force clusters to rearrange into long linear structures or, at high particle volume fraction, into layers. Panel b adapted with permission from Reference 55.

magnetic field, various structures, including close-packed hexagonal, square, chain-like, and stripe labyrinthine, have been observed (110).

DNA-Mediated Attractions

The exploitation of DNA to encode colloidal assembly is under active development, and the high potential of this approach is evident. Materials can be assembled with high fidelity (111, 112), and DNA functionalization brings the attractive freedom to design interactions, including their strength, range, selectivity, and temperature dependence (113). The first studies involved nanoparticles (114–116), which more recently have been extrapolated to larger, colloidal particles (113, 117). The idea is simple in principle: to design complementary single-stranded (ss)DNA molecules that couple exclusively to each other. To implement this, one can connect two particles that are each functionalized with ssDNA using sequences with complementary base pairs (59). It is also possible to link particles via ssDNA linkers that are designed to have complementary base pairs with ssDNA strands on both particles (42). Both approaches can be employed to assemble colloidal particles into desired structures, although the interparticle potential will be tuned differently. The first method can be used to probe the existence of certain DNA sequences via, for example, a change in color of the suspension due to colloidal aggregation (118). Measurements show that an interaction energy on the scale of several $k_B T$ can produce the aggregation of polystyrene particles with ssDNA linkers (Figure 6) (42). This approach lends itself well to multicomponent systems; examples include binary nanoparticle crystals (114), DNA patchy particles (64), and multivalent patchy particles (Figure 6) (59). The design of DNA for these purposes involves two relatively independent considerations: first, to control the range of interactions via inert spacers whose length and rigidity might be varied and, second, to produce attraction via the sticky ends (113).

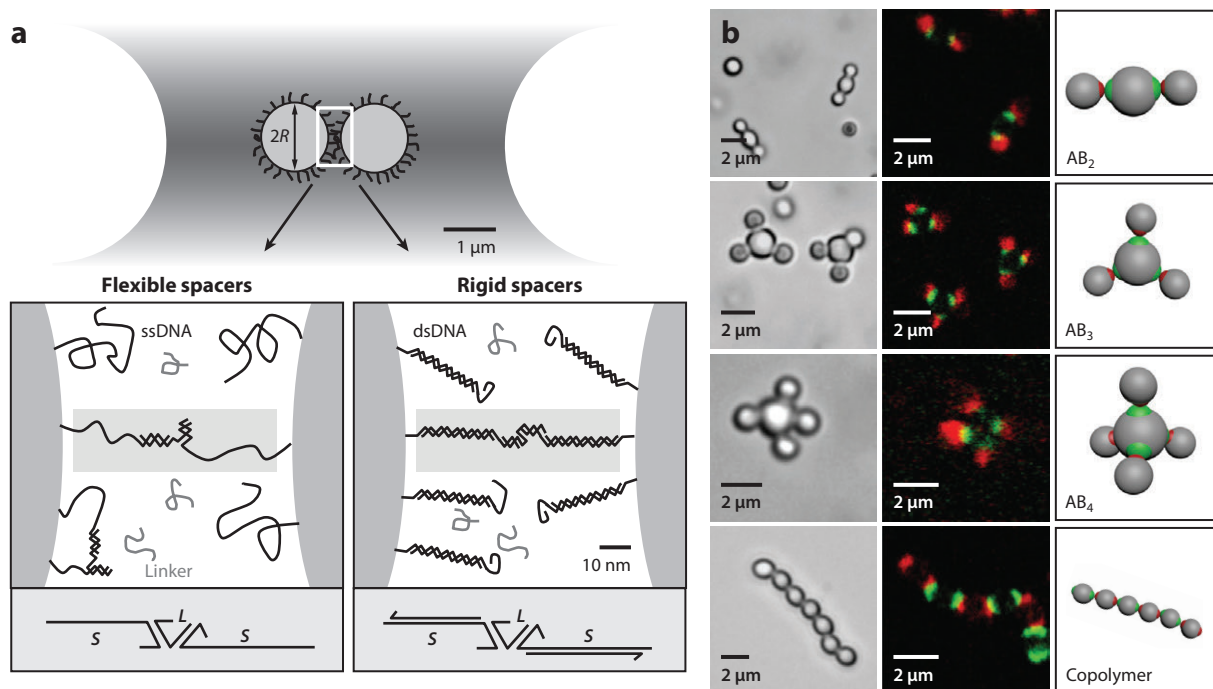


Figure 6

Examples of DNA-mediated assembly. (a) Two microspheres trapped in the focal plane of a line optical tweezer and placed close together so that complementary DNA sequences can associate. Also shown are microsphere surfaces chemically grafted with single-stranded DNA with flexible (*bottom left*) and rigid (*bottom right*) spacers. Panel a adapted with permission from Reference 42. (b) Colloidal molecules self-assembled from patchy DNA-functionalized particles, showing optical microscopy bright-field images (*left panels*), confocal images with fluorescence labeling (*middle panels*), and schematic illustrations (*right panels*). Panel b adapted with permission from Reference 59.

For these complex systems, the devil is in the details. First, DNA is naturally negatively charged, resulting in electrostatic repulsion; second, DNA is a chain molecule, so steric repulsion can prevent particles from approaching closely, depending on the length and stiffness of the DNA; third, the interaction of multiple DNA linkers can yield metastable states, even though DNA hybridization is reversible at elevated temperatures. Thus, DNA functionalization of particles requires careful design, with considerations that include not only the DNA base pair sequence, but also the grafting density. Although temperature is the experimental parameter that is most explored (112), the interactions also depend on ionic strength, pH, and solvent polarity (113). The effectiveness of special DNA structures such as palindromic ssDNA, together with programmed temperature changes, has been demonstrated to achieve self-protection; palindromic ssDNA strands are designed to disable further interparticle bonding by forming intraparticle hairpin structures (112). These complications help to explain why the great promise of DNA-mediated interactions is so difficult to implement.

Good progress is being made in understanding how to exploit the kinetics of assembly with hierarchical assembly approaches, so ubiquitous in biological systems yet still rare in manmade materials (51, 53). Another target of opportunity is that these ideas can encode colloids, as DNA is a natural information carrier, opening the door to the design of smart materials with capabilities such as self-replication (111) and polymorphous response to complicated environments, similar to

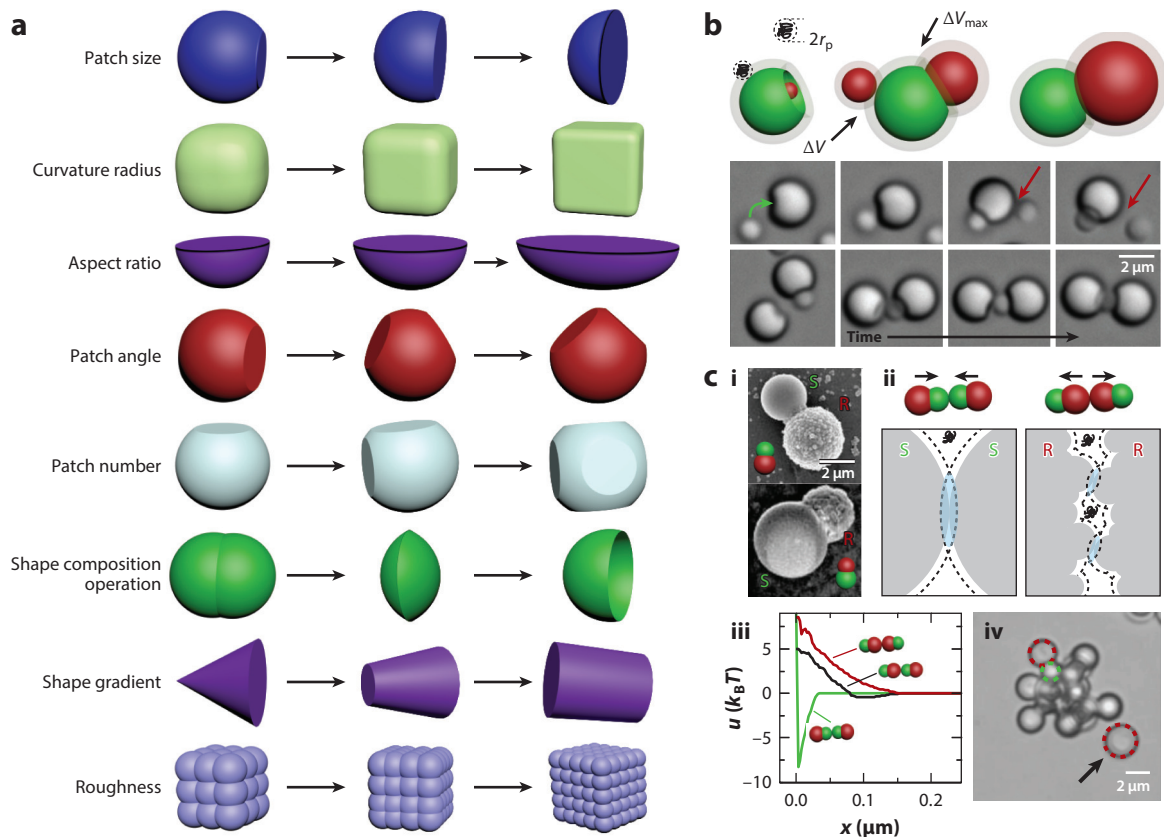


Figure 7

Examples of entropy-based attraction, the so-called depletion interaction. (a) Illustration of the concept that entropic patches can result from an anisotropic geometrical shape. This involves (from *top to bottom*) the patch size, curvature radius, aspect ratio, patch angle, number of patches, shape composition operation, shape gradient, and roughness. Panel *a* adapted with permission from Reference 41. (b) Illustration of the concept of depletion attraction as exploited for the assembly of lock-and-key particles, including snapshots from a movie showing the depletion-driven self-assembly of lock-and-key particles. Panel *b* adapted with permission from Reference 45. (c) Depletion attraction of patchy particles with designed roughness. (i) Dimers of one smooth sphere joined to a sphere whose surface is rough on the scale of polymers that act as a depletant. (ii) The colloidal particles are surrounded by a region that is inaccessible to the depletant. (iii) Depletion potentials between surfaces of various roughness obtained from simulations. (iv) One rough sphere (indicated by the *black arrow*) is left out of the colloidal micelles formed by the particles with one attractive patch. Panel *c* adapted with permission from Reference 46.

a biologically active molecule. There has been notable recent relevant theoretical and experimental progress (119–121).

Entropic Attractions

A powerful idea to render particle–particle interactions directional is to exploit shape anisotropy (41), which gives rise to directional entropic forces that have been studied systematically in computer simulations (**Figure 7a**). Entropic effects can induce order in several ways: on the one hand, through depletion interactions and, on the other hand, through entropy gain due to packing, as in hard-sphere crystallization. Depletion attractions arise when large colloidal particles in solution in

the presence of small particles (depletants), such as nonabsorbing polymers (46) or small particles (44), aggregate to enhance the entropy of the system (122). The range and strength of this interaction are tunable (44, 46). Because the depletion attraction is ultimately a packing problem as well, anisotropic particle shapes are required for depletion attraction to be used for the directional assembly of particles.

So far, this idea has been implemented experimentally by designing particles with regions of different surface roughness (46) and by using shape-complementary particles, the so-called lock-and-key approach (45). For the first approach, dumbbell-shaped particles were used with one smooth lobe and one rough lobe. Because smooth surfaces have a larger overlap volume than rough surfaces, the smooth patches are more strongly attractive to each other than to rough patches, provided that the depletant is smaller than the scale of roughness. Janus dumbbells with a smaller smooth patch organize into clusters, their smooth sides pointing inward. Moreover, the elongated shape endows particles with the freedom to rotate inside a cluster, allowing iso-energetic structures and the capacity to correct energetically unfavorable configurations (46). The larger, rough sides of the particles are located on the outside of the clusters, analogous to the hydrophilic head groups of surfactant micelles (**Figure 7c**). In the alternative lock-and-key approach to achieve directional bonding (45), cavities on the lock particles match the shapes of the key particles. The coordination number of the lock-and-key particles, specified by the number and arrangement of cavities and protrusions, offers a possible avenue to design 3D structures (47), provided that monodisperse building blocks with the needed arrangements of cavities can be produced synthetically.

HIERARCHICAL DESIGN

The exploitation of hierarchical assembly is in an early stage for colloids (51, 53), yet its high potential is evident when one surveys what is already known regarding the organization of biological molecules (123), synthetic polymers (124), DNA architecture (125), and nanocrystals (126). Given this, it is remarkable that so much of the current colloidal self-assembly strategy is predicated on specifying the particle–particle interactions from the outset rather than reconfiguring them on the fly (21). For hierarchical assembly, at least two types of interactions must be encoded in the initial building blocks, but all except one of them must be protected so that the first-stage assembly can proceed independently. The inverse design of building blocks for hierarchical assembly has been explored theoretically (52).

As an illustration, let us consider tetrahedra formed via hydrophobic attractions (60); they could in principle undergo higher-level assembly if they were decorated with DNA sticky ends, although the authors of that study did not do so. Alternatively, one can manipulate the interaction strength at different stages of hierarchical assembly. For example, clusters may form owing to hydrophobic attraction between Janus particles, and once the pH is changed to reduce charge on the outer hemispheres, van der Waals attraction can cause clusters to attract each other (51). Another example is a triblock Janus particle with two hydrophobic domains of different size. The size difference leads to different responsive windows of salt concentration, so that hierarchical structures are assembled (**Figure 8**) (53). There is insufficient theoretical understanding, however, of how different interactions influence each other.

In a different approach, multicomponent systems appear to hold promise, as isotropic small particles can bind isotropic larger particles in various structures, either via many-body effects (83) or via selective binding affinities (85). In the latter approach, stable metastructures could assemble first through strong interactions, followed by higher-level assembly through weaker interactions. Whereas these approaches sidestep the need to begin with synthesizing patchy particles, the feasibility of controlling the assembly kinetics remains to be explored.

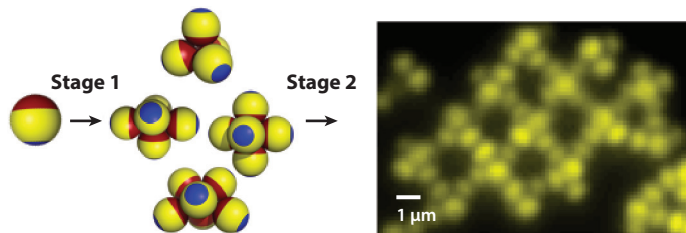


Figure 8

Example of hierarchical assembly based on the sequential introduction of different interactions. Shown are triblock Janus particles with one large and one small attractive patch. Attractions between the larger patches are already effective at low salt concentrations, but attractions between the smaller patches take effect only at higher salt concentrations. Figure adapted with permission from Reference 53.

CHALLENGES AND PROMISES

The excitement of this field lies in the promise to develop new types of materials, with new functions that perhaps cannot yet be fully imagined. A grand goal is to combine the uniqueness of colloidal-sized building blocks with the control and selectivity that, traditionally, are associated only with molecular self-assembly. Whereas traditional colloid science considers colloids whose states of association are just dispersed, crystalline, or gel, directional bonding points the way toward fundamentally new possibilities. Even though the reverse design problem has not been solved, above we have considered some design rules that can assist in that endeavor.

As no magic bullet can solve all problems, we now consider limitations. Efficiency is a great problem when seeking to implement self-assembly; to be realistically applicable beyond academic proofs of concept and in useful technological settings, defect tolerance should be low. This field does not know enough yet about how to control the efficiency of thermal self-assembly. It also does not know enough about the stability of the resulting structures; although intriguing structures have been fabricated from weak thermal interactions, methods to freeze them in place, to render the products robust, are at an early stage of development. Taking an even longer view, it is not only the final structure that matters. The extraordinary functionality of living matter involves self-correction and self-replication (127), but how to achieve this is at an early stage of development. Finally, we mention a pragmatic consideration: In some situations, the use of directional building blocks is simply not needed. There exists the alternative approach of achieving directional bonding by using isotropic building blocks with control over the assembly kinetics (117, 119, 128). This too can produce colloidal chains and labyrinths, by tuning the strength and range of short-range attraction and long-range repulsion (128).

The defects that are intrinsic to thermally driven assembly provide motivation to direct assembly out of equilibrium. Energy can be injected into colloidal systems by the application of electromagnetic fields, by the addition of chemical fuels that allow the conversion of chemical energy to kinetic energy, and even by other fields, resulting in self-propelled motion and the emerging field of active matter (129, 130). Then additional interactions become relevant; for example, hydrodynamic interactions can cause colloidal particles to move collectively and form patterns without conventional equilibrium bonding (101), and this may compete with thermal interactions (131).

Looking beyond this, it is clear that nonequilibrium assembly demands new ways of thinking about self-assembly. Particle interactions can be modulated by magnetic fields (56, 132). For example, in a precessing magnetic field at the magic angle, superparamagnetic spherical colloids experience a time-averaged isotropic pair attraction whose form is analogous to van der Waals

attraction, except with the advantage that many-body polarization interactions between the particles induce an ordered self-healing membrane (132). The synchronized self-assembly of Janus particles has similarly been realized by their rotation in a precessing magnetic field, resulting in organization into rotating tubes because of the synchronized motion of the particles (56). These experiments again demonstrate that dynamic effects could be important in colloidal assembly, but at the time of this writing, the examples are limited.

A large limitation of all work covered in this review is that the examples are mainly clusters and 2D structures. This technical problem is surmountable, when there is reason enough to make the effort, as it originates in the density mismatch between colloids and the medium in which they are suspended. A more fundamental limitation is that the colloid shapes used are static and nondeformable. Softer particles, such as microgel particles (133), droplets (134), vesicles (135), and block copolymer micelles (136), can potentially offer different but interesting opportunities for the assembly of colloid-sized objects. One can expect the equilibrium phase behavior and rheology to be greatly enriched by different packing, different excluded-volume behavior, and malleable shape (137), with nontrivial consequences even in the context of magnetic response, as elastic deformations can produce the misalignment of magnetic dipoles, for example (138). More fundamentally, soft particles are more sensitive to external stimuli (139), and this attribute could be essential to produce responsive materials. A simple example is that if the size of a particle can adjust on the fly, then crystal parameters can be tuned for different application purposes.

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