ANNUAL REVIEWS Further
Click here for quick links to Annual Reviews content online, including:
• Other articles in this volume
• Top cited articles
• Top downloaded articles
• Our comprehensive search

Toward Design Rules of Directional Janus Colloidal Assembly

Jie Zhang,[1] Erik Luijten,[4] and Steve Granick[1,2,3,5]

Departments of [1]Materials Science and Engineering, [2]Physics, and [3]Chemistry, University of Illinois, Urbana, Illinois 61801; email: sgranick@uiuc.edu

[4]Departments of Materials Science and Engineering, Engineering Sciences and Applied Mathematics, and Physics and Astronomy, Northwestern University, Evanston, Illinois 60208

[5]Center for Soft and Living Matter and UNIST, Ulsan 689-798, South Korea

Annu. Rev. Phys. Chem. 2015. 66:581–600

First published online as a Review in Advance on February 4, 2015

The *Annual Review of Physical Chemistry* is online at physchem.annualreviews.org

This article's doi: 10.1146/annurev-physchem-040214-121241

Copyright © 2015 by Annual Reviews. All rights reserved

Keywords

patchy particle, hierarchical assembly, anisotropic interactions

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.

Annu. Rev. Phys. Chem. 2015.66:581-600. Downloaded from www.annualreviews.org
Access provided by Ulsan National Institute of Science and Technology on 08/01/18. For personal use only.

Annu. Rev. Phys. Chem. 2015.66:581-600. Downloaded from www.annualreviews.org
Access provided by Ulsan National Institute of Science and Technology on 08/01/18. For personal use only.

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 suprachemistry (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.

Annu. Rev. Phys. Chem. 2015.66:581-600. Downloaded from www.annualreviews.org
Access provided by Ulsan National Institute of Science and Technology on 08/01/18. For personal use only.

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 1*a***). 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 1*b***). 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

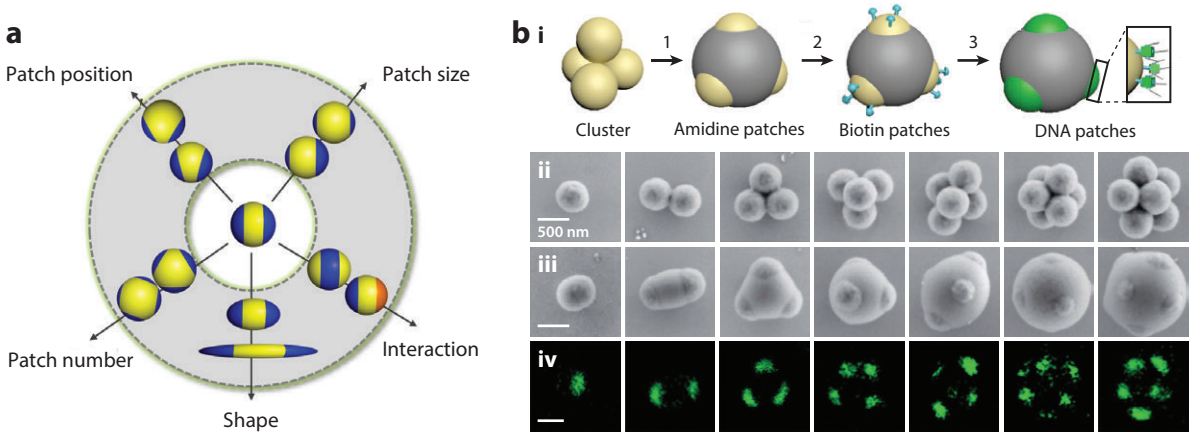


Figure 1

(*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 1*a***) 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

Annu. Rev. Phys. Chem. 2015.66:581-600. Downloaded from www.annualreviews.org
Access provided by Ulsan National Institute of Science and Technology on 08/01/18. For personal use only.

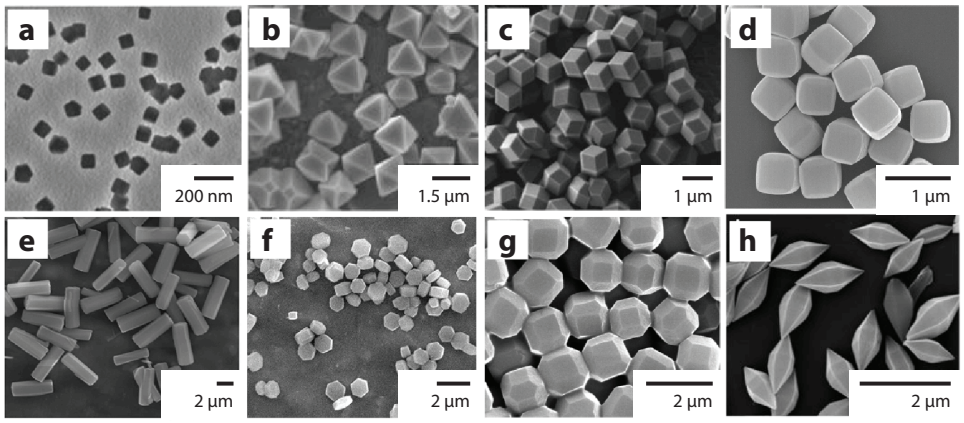


Figure 2

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 1*b***), 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.

Annu. Rev. Phys. Chem. 2015.66:581-600. Downloaded from www.annualreviews.org
Access provided by Ulsan National Institute of Science and Technology on 08/01/18. For personal use only.

Annu. Rev. Phys. Chem. 2015.66:581-600. Downloaded from www.annualreviews.org
Access provided by Ulsan National Institute of Science and Technology on 08/01/18. For personal use only.

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).

Annu. Rev. Phys. Chem. 2015.66:581-600. Downloaded from www.annualreviews.org
Access provided by Ulsan National Institute of Science and Technology on 08/01/18. For personal use only.

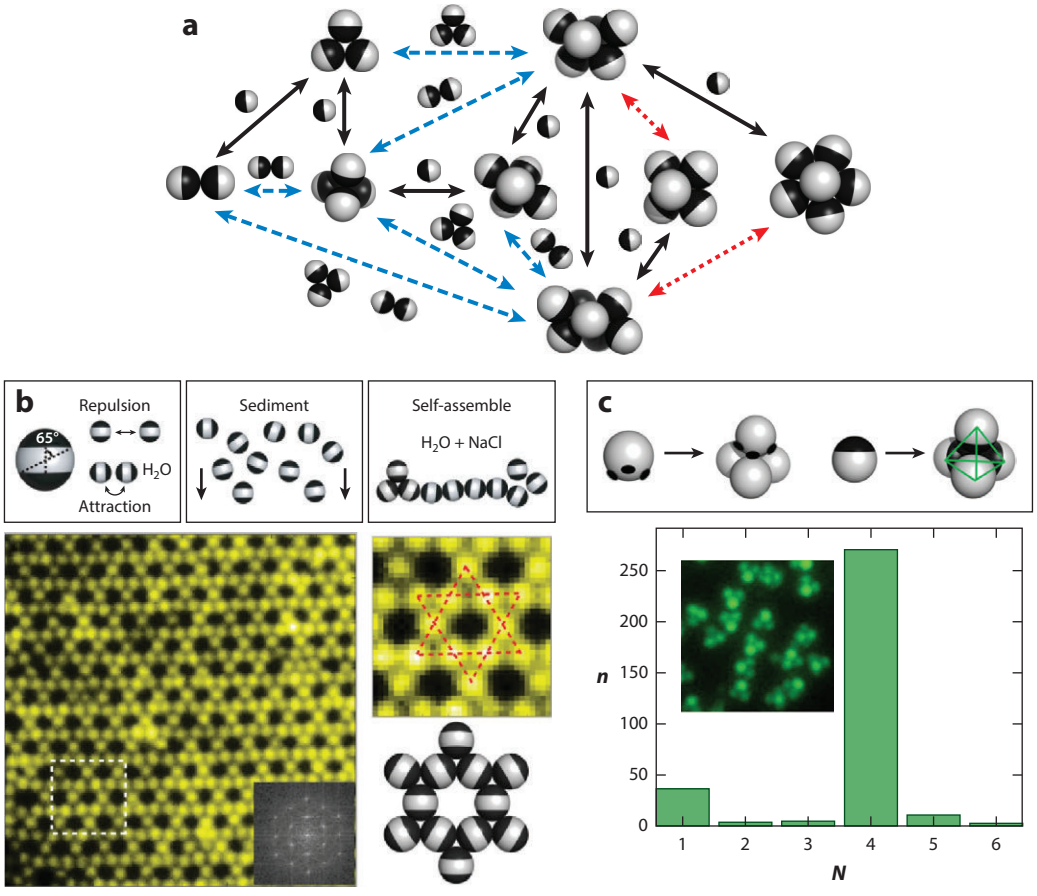


Figure 3

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 4*a***). One particular opportunity provided by binary systems is that it is possible to use one type of particle as a sacrificial support and

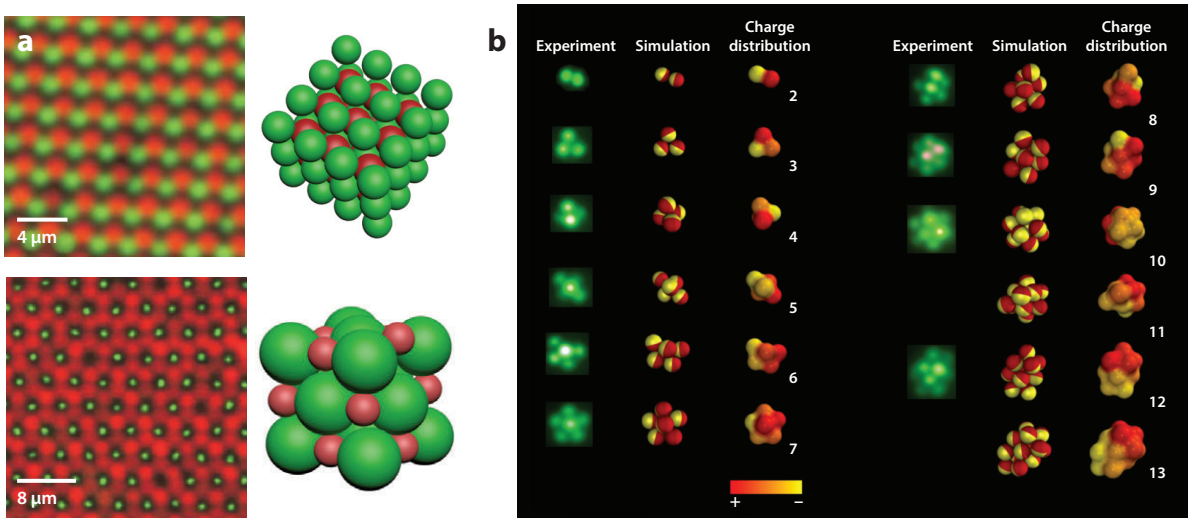


Figure 4

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 4*b***). 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

Annu. Rev. Phys. Chem. 2015.66:581-600. Downloaded from www.annualreviews.org
Access provided by Ulsan National Institute of Science and Technology on 08/01/18. For personal use only.

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_BT to thousands of k_BT, 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

Annu. Rev. Phys. Chem. 2015.66:581-600. Downloaded from www.annualreviews.org
Access provided by Ulsan National Institute of Science and Technology on 08/01/18. For personal use only.

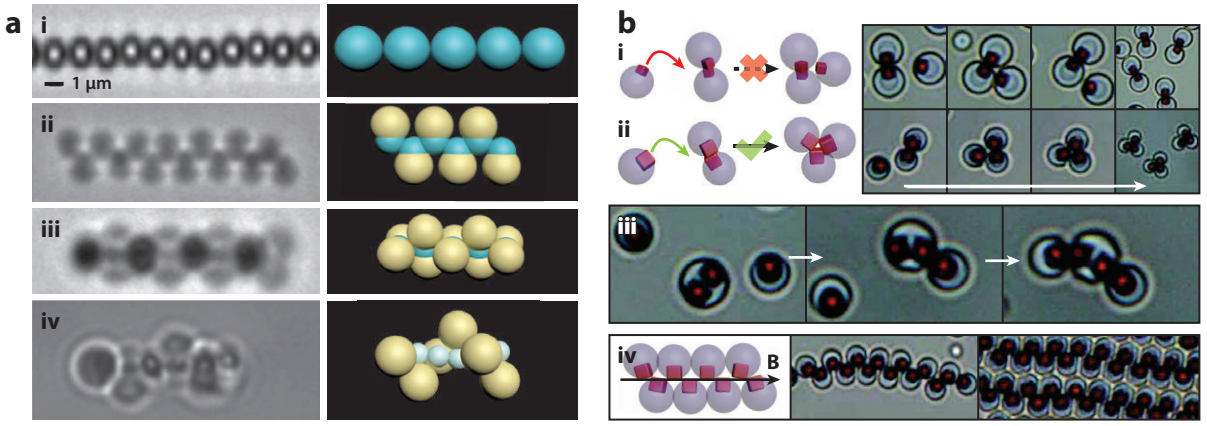


Figure 5

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 alternatingly 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_BT 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).

Annu. Rev. Phys. Chem. 2015.66:581-600. Downloaded from www.annualreviews.org
Access provided by Ulsan National Institute of Science and Technology on 08/01/18. For personal use only.

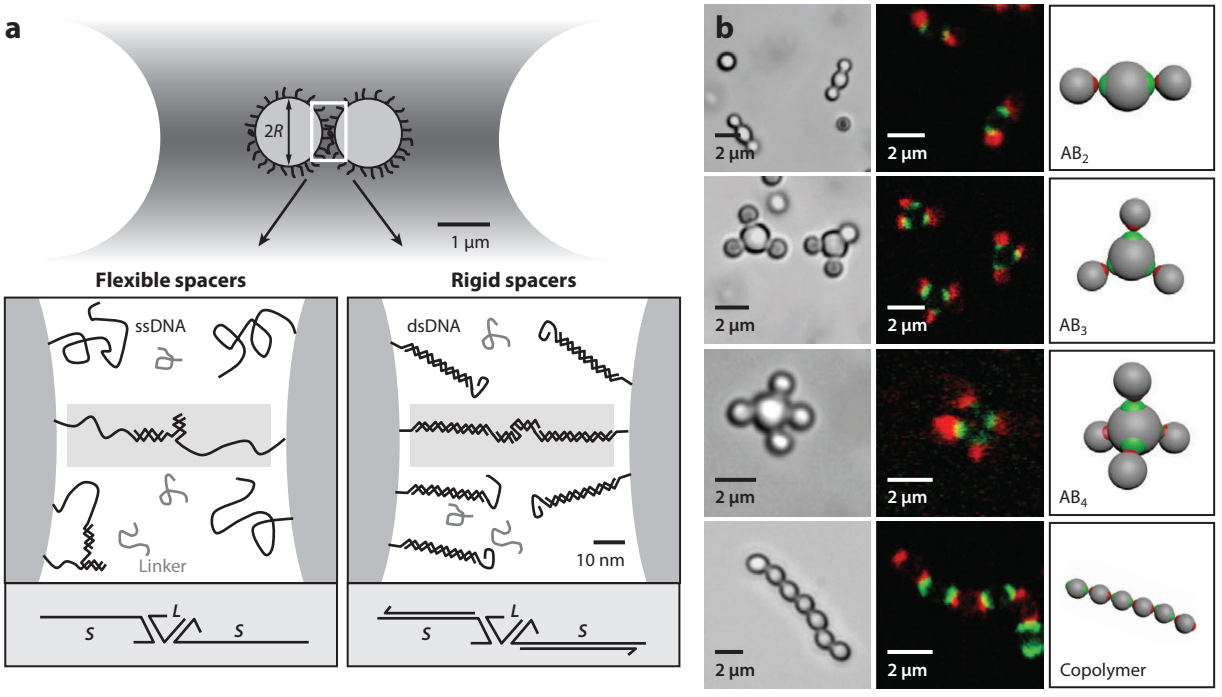


Figure 6

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

Annu. Rev. Phys. Chem. 2015.66:581-600. Downloaded from www.annualreviews.org
Access provided by Ulsan National Institute of Science and Technology on 08/01/18. For personal use only.

Annu. Rev. Phys. Chem. 2015.66:581-600. Downloaded from www.annualreviews.org
Access provided by Ulsan National Institute of Science and Technology on 08/01/18. For personal use only.

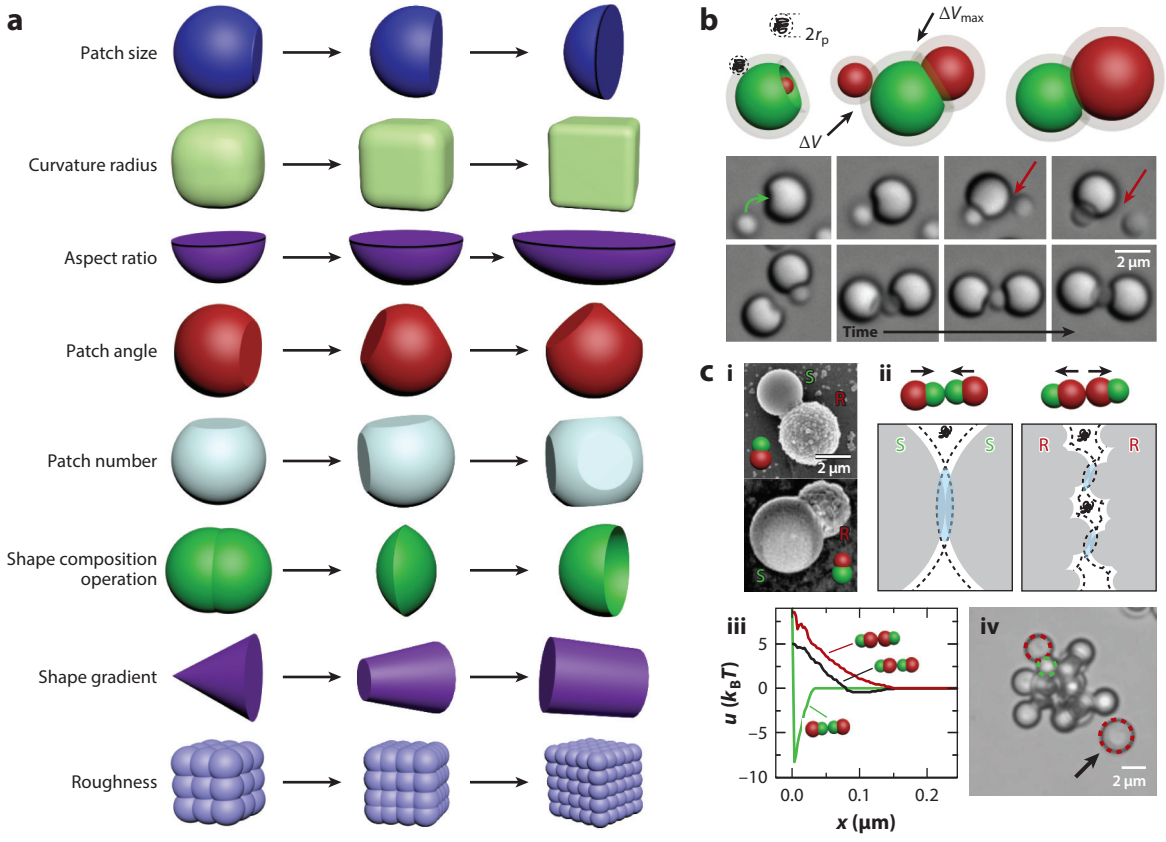


Figure 7

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 7*a***). 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 7*c***). 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.

Annu. Rev. Phys. Chem. 2015.66:581-600. Downloaded from www.annualreviews.org
Access provided by Ulsan National Institute of Science and Technology on 08/01/18. For personal use only.

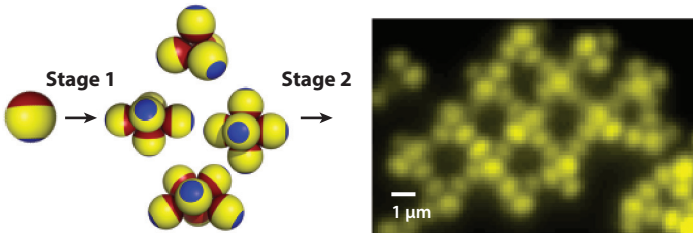


Figure 8

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

Annu. Rev. Phys. Chem. 2015.66:581-600. Downloaded from www.annualreviews.org
Access provided by Ulsan National Institute of Science and Technology on 08/01/18. For personal use only.

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.

Annu. Rev. Phys. Chem. 2015.66:581-600. Downloaded from www.annualreviews.org
Access provided by Ulsan National Institute of Science and Technology on 08/01/18. For personal use only.

DISCLOSURE STATEMENT

The authors are not aware of any affiliations, memberships, funding, or financial holdings that might be perceived as affecting the objectivity of this review.

ACKNOWLEDGMENTS

This work was supported at the University of Illinois by the US Department of Energy, Division of Materials Science, under award DE-FG02-07ER46471 through the Frederick Seitz Materials Research Laboratory. At Northwestern University, it was supported by the National Science Foundation under awards DMR-1310211 and DMR-1121262 at the Materials Research Center. At the IBS Center for Soft and Living Matter, it was supported by the Institute for Basic Science, project code IBS-R020-D1.

LITERATURE CITED

1. Lehn JM. 1993. Supramolecular chemistry. *Science* 260:1762–63
2. Chen XX, Dam MA, Ono K, Mal A, Shen HB, et al. 2002. A thermally re-mendable cross-linked polymeric material. *Science* 295:1698–702
3. White SR, Sottos NR, Geubelle PH, Moore JS, Kessler MR, et al. 2002. Autonomic healing of polymer composites. *Nature* 409:794–97
4. Lima MD, Li N, de Andrade MJ, Fang SL, Oh J, et al. 2012. Electrically, chemically, and photonically powered torsional and tensile actuation of hybrid carbon nanotube yarn muscles. *Science* 338:928–32
5. Stoyanov H, Kollosche M, Risse S, Wache R, Kofod G. 2013. Soft conductive elastomer materials for stretchable electronics and voltage controlled artificial muscles. *Adv. Mater.* 25:578–83
6. Kushner AM, Guan ZB. 2011. Modular design in natural and biomimetic soft materials. *Angew. Chem. Int. Ed. Engl.* 50:9026–57
7. Colvin VL. 2001. From opals to optics: colloidal photonic crystals. *MRS Bull.* 26:637–41

Annu. Rev. Phys. Chem. 2015.66:581-600. Downloaded from www.annualreviews.org
Access provided by Ulsan National Institute of Science and Technology on 08/01/18. For personal use only.

8. Wang T, Sha RJ, Dreyfus R, Leunissen ME, Maass C, et al. 2011. Self-replication of information-bearing nanoscale patterns. *Nature* 478:225–28
9. Yethiraj A, van Blaaderen A. 2003. A colloidal model system with an interaction tunable from hard sphere to soft and dipolar. *Nature* 421:513–17
10. Stober W, Fink A, Bohn E. 1968. Controlled growth of monodisperse silica spheres in the micron size range. *J. Colloid Interface Sci.* 26:62–69
11. Mandal T, Dasgupta C, Maiti PK. 2013. Engineering gold nanoparticle interaction by PAMAM dendrimer. *J. Phys. Chem. C* 117:13627–36
12. Hiltner PA, Papir YS, Krieger IM. 1971. Diffraction of light by nonaqueous ordered suspensions. *J. Phys. Chem.* 75:1881–86
13. Hiltner PA, Krieger IM. 1969. Diffraction of light by ordered suspensions. *J. Phys. Chem.* 73:2386–89
14. Jones JB, Segnit ER, Sanders JV. 1964. Structure of opal. *Nature* 204:990–91
15. Masuda Y, Itoh T, Itoh M, Koumoto K. 2004. Self-assembly patterning of colloidal crystals constructed from opal structure or NaCl structure. *Langmuir* 20:5588–92
16. Pavarini E, Andreani LC, Soci C, Galli M, Marabelli F, Comoretto D. 2005. Band structure and optical properties of opal photonic crystals. *Phys. Rev. B* 72:045102
17. Yethiraj A, Thijssen JHJ, Wouterse A, van Blaaderen A. 2004. Large-area electric-field-induced colloidal single crystals for photonic applications. *Adv. Mater.* 16:596–600
18. van Blaaderen A, Velikov KP, Hoogenboom JP, Vossen DLJ, Yethiraj A, et al. 2001. Manipulating colloidal crystallization for photonic applications: from self-organization to do-it-yourself organization. In *Photonic Crystals and Light Localization in the 21st Century*, ed. CM Soukoulis, pp. 239–51. New York: Springer
19. Klasin AM, Fialkowski M, Paszewski M, Smoukov S, Bishop KJM, et al. 2006. Electrostatic self-assembly of binary nanoparticle crystals with a diamond-like lattice. *Science* 312:420–24
20. Oh M, Mirkin CA. 2005. Chemically tailorable colloidal particles from infinite coordination polymers. *Nature* 438:651–54
21. Yu C, Zhang J, Granick S. 2014. Selective Janus particle assembly at tipping points of thermally-switched wetting. *Angew. Chem. Int. Ed. Engl.* 53:4364–37
22. Gray GW, Harrison KJ, Nash JA. 1973. New family of nematic liquid crystals for displays. *Electron. Lett.* 9:130–31
23. Madsen LA, Dingemans TJ, Nakata M, Samulski ET. 2004. Thermotropic biaxial nematic liquid crystals. *Phys. Rev. Lett.* 92:145505
24. de Gennes PG. 1992. Soft matter (Nobel Lecture). *Angew. Chem. Int. Ed. Engl.* 31:842–45
25. Casagrande C, Fabre P, Raphaël E, Veyssié M. 1989. "Janus beads": realization and behaviour at water/oil interfaces. *Europhys. Lett.* 9:251–55
26. He ZP, Kretzschmar I. 2013. Template-assisted GLAD: approach to single and multipatch patchy particles with controlled patch shape. *Langmuir* 29:15755–61
27. Pawar AB, Kretzschmar I. 2009. Multifunctional patchy particles by glancing angle deposition. *Langmuir* 25:9057–63
28. Ling XY, Phang IY, Acikgoz C, Yilmaz MD, Hempenius MA, et al. 2009. Janus particles with controllable patchiness and their chemical functionalization and supramolecular assembly. *Angew. Chem. Int. Ed. Engl.* 48:7677–82
29. Bennaim A. 1991. The role of hydrogen bonds in protein folding and protein association. *J. Phys. Chem.* 95:1437–44
30. Hong L, Cacciuto A, Luijten E, Granick S. 2006. Clusters of charged Janus spheres. *Nano Lett.* 6:2510–14
31. Perro A, Reculusa S, Ravaine S, Bourgeat-Lami E, Duguet E. 2005. Design and synthesis of Janus micro- and nanoparticles. *J. Mater. Chem.* 15:3745–60
32. Walther A, Müller AHE. 2008. Janus particles. *Soft Matter* 4:663–68
33. Wurm F, Kilbinger AF. 2009. Polymeric Janus particles. *Angew. Chem. Int. Ed. Engl.* 48:8412–21
34. Du J, O'Reilly RK. 2011. Anisotropic particles with patchy, multicompartment and Janus architectures: preparation and application. *Chem. Soc. Rev.* 40:2402–16
35. Kraft DJ, Vlug WS, van Kats CM, van Blaaderen A, Imhof A, Kegel WK. 2009. Self-assembly of colloids with liquid protrusions. *J. Am. Chem. Soc.* 131:1182–86

Annu. Rev. Phys. Chem. 2015.66:581-600. Downloaded from www.annualreviews.org
Access provided by Ulsan National Institute of Science and Technology on 08/01/18. For personal use only.

36. Damasceno PF, Engel M, Glotzer SC. 2012. Predictive self-assembly of polyhedra into complex structures. *Science* 337:453–57
37. Kim SH, Hollingsworth AD, Sacanna S, Chang SJ, Lee G, et al. 2012. Synthesis and assembly of colloidal particles with sticky dimples. *J. Am. Chem. Soc.* 134:16115–18
38. Sacanna S, Korpics M, Rodriguez K, Colon-Melendez L, Kim SH, et al. 2013. Shaping colloids for self-assembly. *Nat. Commun.* 4:1688
39. Sacanna S, Pine DJ, Yi G-R. 2013. Engineering shape: the novel geometries of colloidal self-assembly. *Soft Matter* 9:8096–106
40. Sindoro M, Yanai N, Jee AY, Granick S. 2014. Colloidal-sized metal-organic frameworks: synthesis and applications. *Acc. Chem. Res.* 47:459–69
41. van Anders G, Ahmed NK, Smith R, Engel M, Glotzer SC. 2014. Entropically patchy particles: engineering valence through shape entropy. *ACS Nano* 8:931–40
42. Biancaniello P, Kim A, Crocker J. 2005. Colloidal interactions and self-assembly using DNA hybridization. *Phys. Rev. Lett.* 94:058302
43. Leunissen ME, Christova CG, Hynninen AP, Royall CP, Campbell AI, et al. 2005. Ionic colloidal crystals of oppositely charged particles. *Nature* 437:235–40
44. Meng G, Arkus N, Brenner MP, Manoharan VN. 2010. The free-energy landscape of clusters of attractive hard spheres. *Science* 327:560–63
45. Sacanna S, Irvine WT, Chaikin PM, Pine DJ. 2010. Lock and key colloids. *Nature* 464:575–78
46. Kraft DJ, Ni R, Smallenburg F, Hermes M, Yoon K, et al. 2012. Surface roughness directed self-assembly of patchy particles into colloidal micelles. *Proc. Natl. Acad. Sci. USA* 109:10787–92
47. Wang Y, Wang Y, Zheng X, Yi GR, Sacanna S, et al. 2014. Three-dimensional lock and key colloids. *J. Am. Chem. Soc.* 136:6866–69
48. Chen Q, Bae SC, Granick S. 2011. Directed self-assembly of a colloidal kagome lattice. *Nature* 469:381–84
49. Chen Q, Diesel E, Whitmer JK, Bae SC, Luijten E, Granick S. 2011. Triblock colloids for directed self-assembly. *J. Am. Chem. Soc.* 133:7725–27
50. Chen Q, Whitmer JK, Jiang S, Bae SC, Luijten E, Granick S. 2011. Supracolloidal reaction kinetics of Janus spheres. *Science* 331:199–202
51. Onoe H, Matsumoto K, Shimoyama I. 2007. Three-dimensional sequential self-assembly of microscale objects. *Small* 3:1383–89
52. Tkachenko AV. 2011. Theory of programmable hierarchic self-assembly. *Phys. Rev. Lett.* 106:255501
53. Chen Q, Bae SC, Granick S. 2012. Staged self-assembly of colloidal metastructures. *J. Am. Chem. Soc.* 134:11080–83
54. Velev OD, Bhatt KH. 2006. On-chip micromanipulation and assembly of colloidal particles by electric fields. *Soft Matter* 2:738–50
55. Sacanna S, Rossi L, Pine DJ. 2012. Magnetic click colloidal assembly. *J. Am. Chem. Soc.* 134:6112–15
56. Yan J, Bloom M, Bae SC, Luijten E, Granick S. 2012. Linking synchronization to self-assembly using magnetic Janus colloids. *Nature* 491:578–81
57. Demirors AF, Pillai PP, Kowalczyk B, Grzybowski BA. 2013. Colloidal assembly directed by virtual magnetic moulds. *Nature* 503:99–103
58. Pauling L. 1931. The nature of the chemical bond. II. The one-electron bond and the three-electron bond. *J. Am. Chem. Soc.* 53:3225–37
59. Wang Y, Wang Y, Breed DR, Manoharan VN, Feng L, et al. 2012. Colloids with valence and specific directional bonding. *Nature* 491:51–55
60. Chen Q, Yan J, Zhang J, Bae SC, Granick S. 2012. Janus and multiblock colloidal particles. *Langmuir* 28:13555–61
61. Jiang S, Granick S. 2009. A simple method to produce trivalent colloidal particles. *Langmuir* 25:8915–18
62. Vissers T, Preisler Z, Smallenburg F, Dijkstra M, Sciortino F. 2013. Predicting crystals of Janus colloids. *J. Chem. Phys.* 138:164505
63. Romano F, Sciortino F. 2012. Patterning symmetry in the rational design of colloidal crystals. *Nat. Commun.* 3:975

Annu. Rev. Phys. Chem. 2015.66:581-600. Downloaded from www.annualreviews.org
Access provided by Ulsan National Institute of Science and Technology on 08/01/18. For personal use only.

64. Feng L, Dreyfus R, Sha R, Seeman NC, Chaikin PM. 2013. DNA patchy particles. *Adv. Mater.* 25:2779–83
65. Kraft DJ, Groenewold J, Kegel WK. 2009. Colloidal molecules with well-controlled bond angles. *Soft Matter* 5:3823–26
66. Yanai N, Granick S. 2012. Directional self-assembly of a colloidal metal-organic framework. *Angew. Chem. Int. Ed. Engl.* 51:5638–41
67. Onsager L. 1949. The effects of shape on the interaction of colloidal particles. *Ann. N. Y. Acad. Sci.* 51:627–59
68. Kuijk A, Byelov DV, Petukhov AV, van Blaaderen A, Imhof A. 2012. Phase behavior of colloidal silica rods. *Faraday Discuss.* 159:181–99
69. Shah AA, Schultz B, Kohlstedt KL, Glotzer SC, Solomon MJ. 2013. Synthesis, assembly, and image analysis of spheroidal patchy particles. *Langmuir* 29:4688–96
70. Mukhija D, Solomon MJ. 2011. Nematic order in suspensions of colloidal rods by application of a centrifugal field. *Soft Matter* 7:540–45
71. Dugyala VR, Daware SV, Basavaraj MG. 2013. Shape anisotropic colloids: synthesis, packing behavior, evaporation driven assembly, and their application in emulsion stabilization. *Soft Matter* 9:6711–25
72. Ye XC, Millan JA, Engel M, Chen J, Diroll BT, et al. 2013. Shape alloys of nanorods and nanospheres from self-assembly. *Nano Lett.* 13:4980–88
73. Nguyen TD, Jankowski E, Glotzer SC. 2011. Self-assembly and reconfigurability of shape-shifting particles. *ACS Nano* 5:8892–903
74. Keys AS, Iacovella CR, Glotzer SC. 2011. Characterizing structure through shape matching and applications to self-assembly. *Annu. Rev. Condens. Matter Phys.* 2:263–85
75. Mao XM, Chen Q, Granick S. 2013. Entropy favours open colloidal lattices. *Nat. Mater.* 12:217–22
76. Henzie J, Grünwald M, Widmer-Cooper A, Geissler PL, Yang P. 2012. Self-assembly of uniform polyhedral silver nanocrystals into densest packings and exotic superlattices. *Nat. Mater.* 11:131–37
77. Zerrouki D, Baudry J, Pine D, Chaikin P, Bibette J. 2008. Chiral colloidal clusters. *Nature* 455:380–82
78. Helgeson ME, Chapin SC, Doyle PS. 2011. Hydrogel microparticles from lithographic processes: novel materials for fundamental and applied colloid science. *Curr. Opin. Colloid Interface Sci.* 16:106–17
79. Rolland JP, Maynor BW, Euliss LE, Exner AE, Denison GM, DeSimone JM. 2005. Direct fabrication and harvesting of monodisperse, shape-specific nanobiomaterials. *J. Am. Chem. Soc.* 127:10096–100
80. Caspar DLD, Klug A. 1962. Physical principles in construction of regular viruses. *Cold Spring Harb. Symp. Quant. Biol.* 27:1–24
81. Hagan MF, Elrad OM, Jack RL. 2011. Mechanisms of kinetic trapping in self-assembly and phase transformation. *J. Chem. Phys.* 135:104115
82. Verwey EJW. 1947. Theory of the stability of lyophobic colloids. *J. Phys. Colloid Chem.* 51:631–36
83. Barros K, Luijten E. 2014. Dielectric effects in the self-assembly of binary colloidal aggregates. *Phys. Rev. Lett.* 113:017801
84. Sinkovits DW, Luijten E. 2012. Nanoparticle-controlled aggregation of colloidal tetrapods. *Nano Lett.* 12:1743–48
85. Grünwald M, Geissler PL. 2014. Patterns without patches: hierarchical self-assembly of complex structures from simple building blocks. *ACS Nano* 8:5891–97
86. Whitmer JK, Luijten E. 2011. Influence of hydrodynamics on cluster formation in colloid-polymer mixtures. *J. Phys. Chem. B* 115:7294–300
87. Shevchenko EV, Talapin DV, Kotov NA, O'Brien S, Murray CB. 2006. Structural diversity in binary nanoparticle superlattices. *Nature* 439:55–59
88. Redl FX, Cho KS, Murray CB, O'Brien S. 2003. Three-dimensional binary superlattices of magnetic nanocrystals and semiconductor quantum dots. *Nature* 423:968–71
89. Velikov KP, Christova CG, Dullens RP, van Blaaderen A. 2002. Layer-by-layer growth of binary colloidal crystals. *Science* 296:106–9
90. Miller MA, Wales DJ. 2005. Novel structural motifs in clusters of dipolar spheres: knots, links, and coils. *J. Phys. Chem. B* 109:23109–12
91. Sloane NJA, Hardin RH, Duff TDS, Conway JH. 1995. Minimal-energy clusters of hard spheres. *Discrete Comput. Geom.* 14:237–59

92. Stradner A, Sedgwick H, Cardinaux F, Poon WCK, Egelhaaf SU, Schurtenberger P. 2004. Equilibrium cluster formation in concentrated protein solutions and colloids. *Nature* 432:492–95
93. Gangwal S, Pawar A, Kretzschmar I, Velev OD. 2010. Programmed assembly of metallodielectric patchy particles in external AC electric fields. *Soft Matter* 6:1413–18
94. Gangwal S, Cayre OJ, Velev OD. 2008. Dielectrophoretic assembly of metallodielectric Janus particles in AC electric fields. *Langmuir* 24:13312–20
95. Ristenpart WD, Aksay IA, Saville DA. 2003. Electrically guided assembly of planar superlattices in binary colloidal suspensions. *Phys. Rev. Lett.* 90:128303
96. Hu Y, Glass JL, Griffith AE, Fraden S. 1994. Observation and simulation of electrohydrodynamic instabilities in aqueous colloidal suspensions. *J. Chem. Phys.* 100:4674–82
97. Liu B, Besseling TH, Hermes M, Demirors AF, Imhof A, van Blaaderen A. 2014. Switching plastic crystals of colloidal rods with electric fields. *Nat. Commun.* 5:3092
98. van Blaaderen A, Dijkstra M, van Roij R, Imhof A, Kamp M, et al. 2013. Manipulating the self assembly of colloids in electric fields. *Eur. Phys. J. Spec. Top.* 222:2895–909
99. Leunissen ME, Vutukuri HR, van Blaaderen A. 2009. Directing colloidal self-assembly with biaxial electric fields. *Adv. Mater.* 21:3116–20
100. Smallenburg F, Vutukuri HR, Imhof A, van Blaaderen A, Dijkstra M. 2012. Self-assembly of colloidal particles into strings in a homogeneous external electric or magnetic field. *J. Phys. Condens. Matter* 24:464113
101. Bricard A, Caussin JB, Desreumaux N, Dauchot O, Bartolo D. 2013. Emergence of macroscopic directed motion in populations of motile colloids. *Nature* 503:95–98
102. Kretzschmar I, Song JH. 2011. Surface-anisotropic spherical colloids in geometric and field confinement. *Curr. Opin. Colloid Interface Sci.* 16:84–95
103. Osborn JA. 1945. Demagnetizing factors of the general ellipsoid. *Phys. Rev.* 67:351–57
104. Yu CQ, Zhang J, Granick S. 2014. Directed colloidal assembly printing with magnets. *Nat. Mater.* 13:8–9
105. Smoukov SK, Gangwal S, Marquez M, Velev OD. 2009. Reconfigurable responsive structures assembled from magnetic Janus particles. *Soft Matter* 5:1285–92
106. Wang M, He L, Yin Y. 2013. Magnetic field guided colloidal assembly. *Mater. Today* 16:110–16
107. Bizdoaca EL, Spasova M, Farle M, Hilgendorff M, Caruso F. 2002. Magnetically directed self-assembly of submicron spheres with a Fe_3O_4 nanoparticle shell. *J. Magn. Magn. Mater.* 240:44–46
108. Anders S, Toney MF, Thomson T, Thiele JU, Terris BD, et al. 2003. X-ray studies of magnetic nanoparticle assemblies. *J. Appl. Phys.* 93:7343–45
109. Keng PY, Shim I, Korth BD, Douglas JF, Pyun J. 2007. Synthesis and self-assembly of polymer-coated ferromagnetic nanoparticles. *ACS Nano* 1:279–92
110. Osterman N, Babič D, Poberaj I, Dobnikar J, Ziherl P. 2007. Observation of condensed phases of quasiplanar core-softened colloids. *Phys. Rev. Lett.* 99:248301
111. Wang T, Sha R, Dreyfus R, Leunissen ME, Maass C, et al. 2011. Self-replication of information-bearing nanoscale patterns. *Nature* 478:225–28
112. Leunissen ME, Dreyfus R, Sha R, Wang T, Seeman NC, et al. 2009. Towards self-replicating materials of DNA-functionalized colloids. *Soft Matter* 5:2422–30
113. Geerts N, Eiser E. 2010. DNA-functionalized colloids: physical properties and applications. *Soft Matter* 6:4647–60
114. Maye MM, Kumara MT, Nykypanchuk D, Sherman WB, Gang O. 2010. Switching binary states of nanoparticle superlattices and dimer clusters by DNA strands. *Nat. Nanotechnol.* 5:116–20
115. Alivisatos AP, Johnsson KP, Peng XG, Wilson TE, Loweth CJ, et al. 1996. Organization of 'nanocrystal molecules' using DNA. *Nature* 382:609–11
116. Mirkin CA, Letsinger RL, Mucic RC, Storhoff JJ. 1996. A DNA-based method for rationally assembling nanoparticles into macroscopic materials. *Nature* 382:607–9
117. Leunissen ME, Dreyfus R, Cheong FC, Grier DG, Sha R, et al. 2009. Switchable self-protected attractions in DNA-functionalized colloids. *Nat. Mater.* 9:590–95
118. Rosi NL, Mirkin CA. 2005. Nanostructures in biodiagnostics. *Chem. Rev.* 105:1547–62

Annu. Rev. Phys. Chem. 2015.66:581-600. Downloaded from www.annualreviews.org
Access provided by Ulsan National Institute of Science and Technology on 08/01/18. For personal use only.

119. Wu K-T, Feng L, Sha R, Dreyfus R, Grosberg AY, et al. 2013. Kinetics of DNA-coated sticky particles. *Phys. Rev. E* 88:022304
120. Prigodich AE, Lee OS, Daniel WL, Seferos DS, Schatz GC, Mirkin CA. 2010. Tailoring DNA structure to increase target hybridization kinetics on surfaces. *J. Am. Chem. Soc.* 132:10638–41
121. Dreyfus R, Leunissen ME, Sha R, Tkachenko A, Seeman NC, et al. 2010. Aggregation-disaggregation transition of DNA-coated colloids: experiments and theory. *Phys. Rev. E* 81:041404
122. Asakura S, Oosawa F. 1954. On interaction between two bodies immersed in a solution of macromolecules. *J. Chem. Phys.* 22:1255–56
123. Alakent B, Camurdan MC, Doruker P. 2005. Hierarchical structure of the energy landscape of proteins revisited by time series analysis. II. Investigation of explicit solvent effects. *J. Chem. Phys.* 123:144911
124. Sai H, Tan KW, Hur K, Asenath-Smith E, Hovden R, et al. 2013. Hierarchical porous polymer scaffolds from block copolymers. *Science* 341:530–34
125. Liang HJ, Harries D, Wong GCL. 2005. Polymorphism of DNA-anionic liposome complexes reveals hierarchy of ion-mediated interactions. *Proc. Natl. Acad. Sci. USA* 102:11173–78
126. Rauda IE, Buonsanti R, Saldarriaga-Lopez LC, Benjauthrit K, Schelhas LT, et al. 2012. General method for the synthesis of hierarchical nanocrystal-based mesoporous materials. *ACS Nano* 6:6386–99
127. Anglana M, Apiou F, Bensimon A, Debatisse M. 2003. Dynamics of DNA replication in mammalian somatic cells: Nucleotide pool modulates origin choice and interorigin spacing. *Cell* 114:385–94
128. Haw MD. 2010. Growth kinetics of colloidal chains and labyrinths. *Phys. Rev. E* 81:031402
129. Wang S, Wu N. 2014. Selecting the swimming mechanisms of colloidal particles: bubble propulsion versus self-diffusiophoresis. *Langmuir* 30:3477–86
130. Ebbens SJ, Howse JR. 2010. In pursuit of propulsion at the nanoscale. *Soft Matter* 6:726–38
131. Schwarz-Linek J, Valeriani C, Cacciuto A, Cates ME, Marenduzzo D, et al. 2012. Phase separation and rotor self-assembly in active particle suspensions. *Proc. Natl. Acad. Sci. USA* 109:4052–57
132. Osterman N, Poberaj I, Dobnikar J, Frenkel D, Ziherl P, Babić D. 2009. Field-induced self-assembly of suspended colloidal membranes. *Phys. Rev. Lett.* 103:2228301
133. Sierra-Martin B, Fernandez-Nieves A. 2012. Phase and non-equilibrium behaviour of microgel suspensions as a function of particle stiffness. *Soft Matter* 8:4141–50
134. Weaver JVM, Rannard SP, Cooper AI. 2009. Polymer-mediated hierarchical and reversible emulsion droplet assembly. *Angew. Chem. Int. Ed. Engl.* 48:2131–34
135. Shillcock JC. 2012. Spontaneous vesicle self-assembly: a mesoscopic view of membrane dynamics. *Langmuir* 28:541–47
136. Groschel AH, Walther A, Lobling TI, Schacher FH, Schmalz H, Muller AHE. 2013. Guided hierarchical co-assembly of soft patchy nanoparticles. *Nature* 503:247–51
137. Koumakis N, Pamvouxoglou A, Poulos AS, Petekidis G. 2012. Direct comparison of the rheology of model hard and soft particle glasses. *Soft Matter* 8:4271–84
138. Dagallier C, Cardinaux F, Dietsch H, Scheffold F. 2012. Magnetic orientation of soft particles in a jammed solid. *Soft Matter* 8:4067–71
139. Fameau AL, Lam S, Velev OD. 2013. Multi-stimuli responsive foams combining particles and self-assembling fatty acids. *Chem. Sci.* 4:3874–81

Annu. Rev. Phys. Chem. 2015.66:581-600. Downloaded from www.annualreviews.org
Access provided by Ulsan National Institute of Science and Technology on 08/01/18. For personal use only.

Annual Review of
Physical Chemistry
Volume 66, 2015

Contents

Molecules in Motion: Chemical Reaction and Allied Dynamics in Solution and Elsewhere
James T. Hynes 1

Crystal Structure and Prediction
Tejender S. Thakur, Ritesh Dubey, and Gautam R. Desiraju 21

Reaction Dynamics in Astrochemistry: Low-Temperature Pathways to Polycyclic Aromatic Hydrocarbons in the Interstellar Medium
Ralf I. Kaiser, Dorian S.N. Parker, and Alexander M. Mebel 43

Coherence in Energy Transfer and Photosynthesis
Aurélia Chenu and Gregory D. Scholes 69

Ultrafast Dynamics of Electrons in Ammonia
Peter Vöhringer 97

Dynamics of Bimolecular Reactions in Solution
Andrew J. Orr-Ewing 119

The Statistical Mechanics of Dynamic Pathways to Self-Assembly
Stephen Whitelam and Robert L. Jack 143

Reaction Dynamics at Liquid Interfaces
Ilan Benjamin 165

Quantitative Sum-Frequency Generation Vibrational Spectroscopy of Molecular Surfaces and Interfaces: Lineshape, Polarization, and Orientation
Hong-Fei Wang, Luis Velarde, Wei Gan, and Li Fu 189

Mechanisms of Virus Assembly
Jason D. Perlmutter and Michael F. Hagan 217

Cold and Controlled Molecular Beams: Production and Applications
Justin Jankunas and Andreas Osterwalder 241

Spintronics and Chirality: Spin Selectivity in Electron Transport Through Chiral Molecules
Ron Naaman and David H. Waldeck 263

Annu. Rev. Phys. Chem. 2015.66:581-600. Downloaded from www.annualreviews.org
Access provided by Ulsan National Institute of Science and Technology on 08/01/18. For personal use only.

DFT: A Theory Full of Holes?
Aurora Pribram-Jones, David A. Gross, and Kieron Burke 283

Theoretical Description of Structural and Electronic Properties of Organic Photovoltaic Materials
Andriy Zhugayevych and Sergei Tretiak 305

Advanced Physical Chemistry of Carbon Nanotubes
Jun Li and Gaind P. Pandey 331

Site-Specific Infrared Probes of Proteins
Jianqiang Ma, Ileana M. Pazos, Wenkai Zhang, Robert M. Culik, and Feng Gai 357

Biomolecular Damage Induced by Ionizing Radiation: The Direct and Indirect Effects of Low-Energy Electrons on DNA
Elahe Alizadeh, Thomas M. Orlando, and Léon Sanche 379

The Dynamics of Molecular Interactions and Chemical Reactions at Metal Surfaces: Testing the Foundations of Theory
Kai Golibrzuch, Nils Bartels, Daniel J. Auerbach, and Alec M. Wodtke 399

Molecular Force Spectroscopy on Cells
Baoyu Liu, Wei Chen, and Cheng Zhu 427

Mass Spectrometry of Protein Complexes: From Origins to Applications
Shahid Mehmood, Timothy M. Allison, and Carol V. Robinson 453

Low-Temperature Kinetics and Dynamics with Coulomb Crystals
Brianna R. Heazlewood and Timothy P. Softley 475

Early Events of DNA Photodamage
Wolfgang J. Schreier, Peter Gilch, and Wolfgang Zinth 497

Physical Chemistry of Nanomedicine: Understanding the Complex Behaviors of Nanoparticles in Vivo
Lucas A. Lane, Ximei Qian, Andrew M. Smith, and Shuming Nie 521

Time-Domain Ab Initio Modeling of Photoinduced Dynamics at Nanoscale Interfaces
Linjun Wang, Run Long, and Oleg V. Prezhdo 549

Toward Design Rules of Directional Janus Colloidal Assembly
Jie Zhang, Erik Luijten, and Steve Granick 581

Charge Transfer–Mediated Singlet Fission
N. Monahan and X.-Y. Zhu 601

Upconversion of Rare Earth Nanomaterials
Ling-Dong Sun, Hao Dong, Pei-Zhi Zhang, and Chun-Hua Yan 619

Annu. Rev. Phys. Chem. 2015.66:581-600. Downloaded from www.annualreviews.org
Access provided by Ulsan National Institute of Science and Technology on 08/01/18. For personal use only.

Computational Studies of Protein Aggregation: Methods and Applications
Alex Morriss-Andrews and Joan-Emma Shea 643

Experimental Implementations of Two-Dimensional Fourier Transform Electronic Spectroscopy
Franklin D. Fuller and Jennifer P. Ogilvie 667

Electron Transfer Mechanisms of DNA Repair by Photolyase
Dongping Zhong 691

Vibrational Energy Transport in Molecules Studied by Relaxation-Assisted Two-Dimensional Infrared Spectroscopy
Natalia I. Rubtsova and Igor V. Rubtsov 717

Indexes

Cumulative Index of Contributing Authors, Volumes 62–66 739

Cumulative Index of Article Titles, Volumes 62–66 743

Errata

An online log of corrections to *Annual Review of Physical Chemistry* articles may be found at http://www.annualreviews.org/errata/physchem

Annu. Rev. Phys. Chem. 2015.66:581-600. Downloaded from www.annualreviews.org
Access provided by Ulsan National Institute of Science and Technology on 08/01/18. For personal use only.