

Anisotropy of building blocks and their assembly into complex structures

A revolution in novel nanoparticles and colloidal building blocks has been enabled by recent breakthroughs in particle synthesis. These new particles are poised to become the 'atoms' and 'molecules' of tomorrow's materials if they can be successfully assembled into useful structures. Here, we discuss the recent progress made in the synthesis of nanocrystals and colloidal particles and draw analogies between these new particulate building blocks and better-studied molecules and supramolecular objects. We argue for a conceptual framework for these new building blocks based on anisotropy attributes and discuss the prognosis for future progress in exploiting anisotropy for materials design and assembly.

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The past few years have been witness to an unprecedented revolution in particle syntheses, which has led to a spectacular variety of building blocks of different shapes, compositions, patterns and functionalities. Of course, nanocolloids of non-spherical shape have long been known. For example, naturally occurring swelling clays such as montmorillonite are materials with anisotropic shape (discotic) and interactions (distinct edge and face charges). Historical roots of the recent drive to precisely control shape and interactions are apparent in the work of Matijevic¹. By about 1990, methods for synthesizing cubes, rods and discs, commonly comprising metals (for example, gold and silver) as well as metal oxides (haematite, boehmite and gibbsite) were available²⁻⁴. Particles with core-shell structure soon followed^{5,6}. Emulsion deformation methods were developed that yielded polymer rods⁷. Viral capsids, such as tobacco mosaic and fd virus, were also investigated as particles with model shape⁸. However, with the exception of natural and synthetic clay discs (laponite) in ceramics and polymer composites and metal oxide rods in magnetic storage materials, technological applications of these unusually shaped materials were limited because many of the methods lacked high yield as well as sufficient size and shape selectivity.

Recognition that anisotropic shape and interactions through chemical 'patchiness' are powerful tools for engineering the assembly of particular targeted structures has brought new excitement to the field. This recognition fuelled the discovery of new chemical, physical and biosynthetic methods for the synthesis of anisotropic nanoparticle and colloidal building blocks. Chemical methods developed include selective crystallization

and deposition⁹⁻¹². Physical methods developed include electrified jetting, microcontact printing, emulsion drying, selective deposition, surface templating, direct writing and lithography¹³⁻²⁰. Biologically inspired methods include the use of plant extracts²¹, fungi²² and viruses²³ to synthesize metal nanoparticles of various shapes. These methods draw from the diverse fields of chemistry, physics, biology, engineering and materials science, and, in combination, provide a powerful arsenal for the fabrication of new particulate building blocks.

These new approaches to particle synthesis have led to an unprecedented diverse spectrum of particle anisotropy, including nanocolloidal cubes^{10,24} and icosahedra²⁵, triangles²⁶, tetrahedra²⁷, prisms^{12,21}, Janus particles^{13,28}, half shells²⁹, striped particles³⁰, rods, arrows and tetrapods¹¹, tripods³¹, stars³², X shapes and angles³³, polyvalent spheres^{34,35} and many other exotic structures. These particles possess many peculiar properties (for example, electronic and optical) owing to their unusual shape^{36,37} and/or interaction patchiness. Figure 1 shows examples of some of the particle classes that have been achieved so far. Each is a possible building block that can be conceivably incorporated into superlattice assemblies and hierarchical or terminal structures useful for a range of applications. Although the emergence of these new particle anisotropies has been profiled in recent perspectives³⁸⁻⁴⁰, there has not yet been an attempt to develop a unifying conceptual framework with which to classify and describe the various particles. This goal is a central aim of this progress article.

IMPLICATIONS OF ANISOTROPY FOR ASSEMBLY

The unique anisotropy of the new building blocks starkly contrasts with the isotropic spherical colloids that have been the focus of particle assembly for nearly a generation. These traditional materials, typically comprising silica or polymer latex, commonly yield phases of simple symmetry, such as face-centred cubic, hexagonal close-packed and body-centred cubic. Developments in surface templating, incorporation of bimodal particle size and charge distributions and exploitation of applied fields have

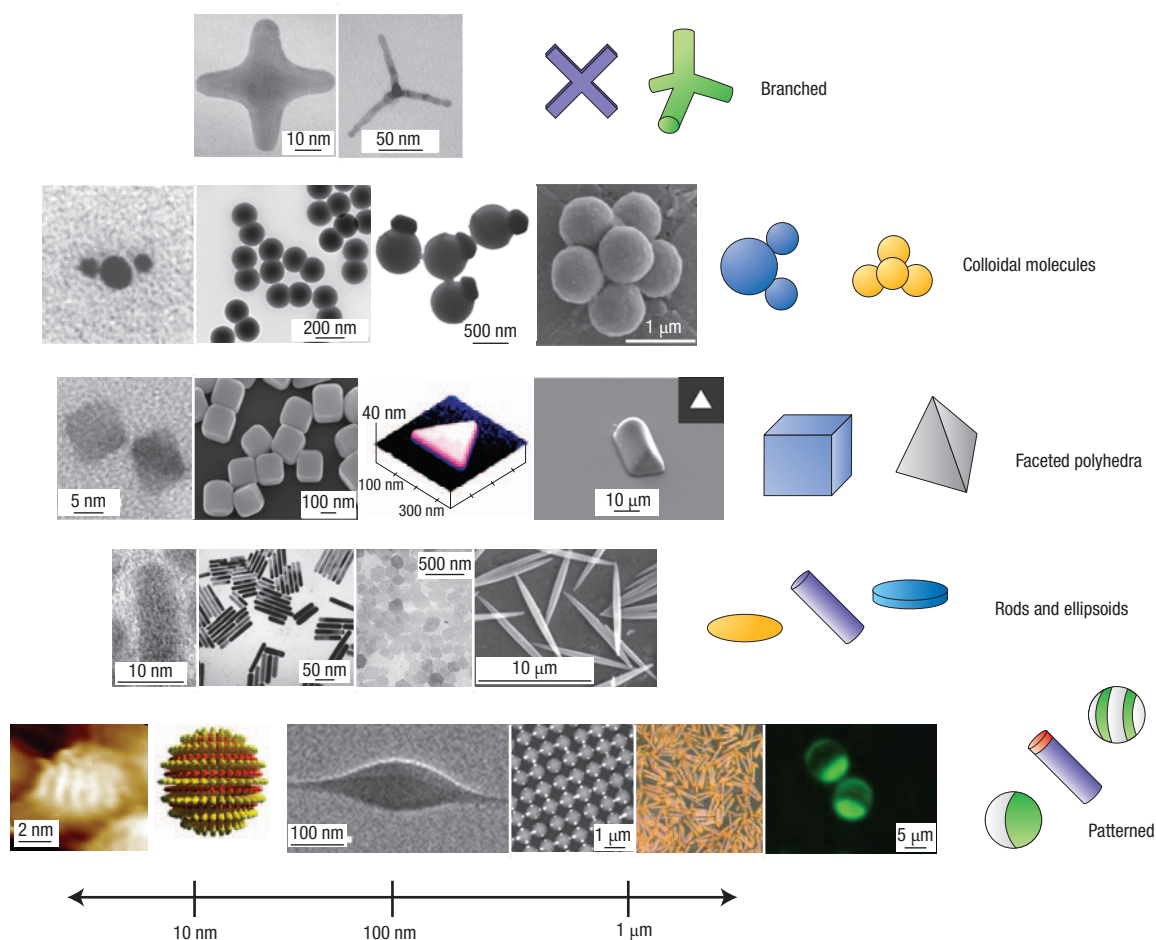


Figure 1 Representative examples of recently synthesized anisotropic particle building blocks. The particles are classified in rows by anisotropy type and increase in size from left to right according to the approximate scale at the bottom. From left to right, top to bottom: branched particles include gold³¹ and CdTe⁷¹ tetrapods. DNA-linked gold nanocrystals⁵⁰ (the small and large nanocrystals are 5 nm and 10 nm respectively), silica dumb-bells⁷², asymmetric dimers⁷³ and fused clusters¹⁷ form colloidal molecules. PbSe⁷⁴ and silver cubes¹⁰ as well as gold²⁶ and polymer triangular prisms¹⁵ are examples of faceted particles. Rods and ellipsoids of composition CdSe⁷⁵, gold⁷⁶, gibbsite⁴ and polymer latex⁶⁰ are shown. Examples of patterned particles include striped spheres⁷⁷, biphasic rods¹⁴, patchy spheres with 'valence'³⁴, Au–Pt nanorods⁷⁸ (the rod diameters are of the order of 200–300 nm) and Janus spheres¹³. Images reprinted with permission from the references as indicated. Copyright, as appropriate, AAAS, ACS, RSC, Wiley-VCH.

expanded the range of possible colloidal structures to include, for example, tetragonal, trigonal, simple cubic and ionic phases^{41,42}. These phases are moving closer to attaining the structural complexity that future applications require. Adding shape and interaction anisotropy to the particles further extends the possible assemblies to motifs potentially as complex as those seen in molecular crystals.

Indeed, although a general predictable relationship between anisotropic building-block structure and the structure and symmetry of ordered arrays produced from these building blocks is not yet in hand, nanocolloid assembly is governed by the same thermodynamics that produces ordered equilibrium structures in systems of atoms and molecules. In fact, molecular analogues such as liquid crystals, surfactants and block copolymers exhibit building-block anisotropy that is conceptually similar to and as diverse as the examples in Fig. 1. Thus, potentially, if non-idealities peculiar to particles such as jamming and gelation are avoided, anisotropic nanocolloidal particles ought to assemble into morphologies as diverse as those of molecules. Applying the

analogy between molecules and nanocolloids implied by statistical thermodynamics allows a rough assessment of the possibilities.

First, consider the analogy with crystallography. Atomic and molecular packings are well-studied subjects, not only in the context of the possible crystallographic space groups, but also in terms of their relationship to the underlying point group of the molecular species. Powerful computational schemes can predict energetically favourable configurations (at least at 0 K)⁴². For atoms, a suite of highly symmetric near-close-packed structures that balance the constraints of atomic size and charge neutrality dominate. This motif seems to hold as well on the colloidal scale^{42–44}. In addition, because nanoparticle and colloidal macroions, unlike atoms, have nearly continuously tunable size and charge, ionic crystals with no known atomic or molecular analogue have been discovered^{42,45,46}.

Addition of the directionality associated at the molecular scale with covalent and hydrogen bonding expands the possible structures towards those that are more open (such as diamond and zeolites) and anisotropic (such as graphite). The directionality

and relative strength of these molecular interactions can be generated on the nanocolloidal scale through specific interactions to make patchy particles⁴⁷ through, for example, selective sintering, hybridization by DNA oligomers, proteins or organic tethers, and other means. For example, gold-tipped tetrapods⁴⁸ should have the propensity for forming open three-dimensional (3D) arrays through attractive van der Waals interactions at the tips, and the addition of short polymer tethers to one or more tips will provide further degrees of freedom that may be exploited for assembly⁴⁹.

New nanocolloidal synthetic and processing methods are flexible enough to allow homologous variation of point-group symmetries in ways that are not easily realized on the molecular scale. An example is the sequence of nanocolloidal clusters synthesized by several groups^{17,18,50}. Such colloidal 'atoms' and 'molecules' mimic boron, carbon, H₂O and so on at a larger scale as the number and types of spheres comprising the cluster is varied. Möhwald and co-workers³⁴ have used an alternative method to create colloidal spheres with valencies⁵¹ from two to five. Spherically symmetric colloids have long served as models for the liquid-glass transition, crystallization and gelation in liquids where molecular details are difficult to study. Thus, colloidal 'water' (a suspension of anisotropic colloids resembling water molecules) should provide a useful model of this important fluid, as suggested by recent computer simulations of four-coordinated patchy colloidal spheres⁵². Valence has been shown to be the critical factor in simulations of patchy particles, dictating fluid and gel behaviour⁵³, and will have important implications for crystals.

Second, nanocolloids can exhibit amphiphilic character similar to that of surfactants and block copolymers. In such materials, the system must resolve the fact that components with unfavourable interactions are constrained to close proximity through their building-block architecture. An array of technologically useful structures, including lamellar, cylindrical and gyroid phases result. Attempts to rationalize principles of self-organization in copolymers and surfactants through the use of geometric concepts have provided insight into the universality of certain structures^{54,55}. Phase-diagram formalisms developed to understand surfactant and copolymer systems may be applied to nanocolloids by exploiting the molecule/particle analogy. An example of a nanocolloid with block-copolymer character is the Janus particle^{14,56,57}. An interesting complication is the effect of structural rigidity (packing effects) in these particle-based amphiphiles. Rigidity has a profound effect on surfactant and block-copolymer phases, and is probably a generic difference between the molecular and nanocolloidal scales. This difference probably requires modification of quantities used to characterize ordered phases. Recent simulations have highlighted commonalities, as well as differences, between copolymer and amphiphilic nanocolloid diagrams⁵⁸, but as nanocolloids become more complex in their anisotropy wholly new phases are expected. And, as in molecular systems, anisotropic long-range interactions among particles that extend multiple particle diameters may be exploited to generate unique assemblies⁵⁹.

Third, anisometric nanocolloids are similar to molecular liquid-crystal mesogens. Although here work to evaluate the correspondence has only just begun, nematic- and smectic-type phases have been identified in nanocolloids. In one study, the quality of the nematic alignment factor in sedimented particles was comparable to typical qualities of liquid-crystalline polymers⁶⁰. Simulations have extended the possible analogy into new realms⁶¹⁻⁶³ — nanocolloidal cubes, for example, are predicted to form a cubatic phase that has liquid-crystalline character⁶⁴. What liquid-crystalline phases can we expect from dense suspensions comprising hard particles with more complex shapes, such as prisms, stars or X-shaped nanoparticles?

DIMENSIONAL FRAMEWORK FOR PARTICLE ANISOTROPY

Theoretical description of the new particles seems daunting in the face of their complexity. Even a common language or general classification scheme is lacking for describing these building blocks or their assemblies. In contrast, some commonly accepted nomenclature and classifications exist for molecular building blocks such as organic and inorganic molecules, liquid crystals, block copolymers and surfactants, both for the building blocks as well as their assemblies. These terminologies and taxonomies have provided critical guidance for materials fabrication by establishing the common ground needed for consensus about architecture and phenomenology. Such language is lacking for nanocolloids, yet their complexity demands a unifying description to exploit similarities and discern differences. How shall we describe anisotropic particles such as lemon-shaped Janus particles, gold-tipped nanorods, polyhedral clusters of spheres or patchy tetrahedral quantum dots in a manner that allows substantive similarities and differences to be easily discerned?

It is possible to imagine several classifying principles as a way of unifying the practically infinite number of different particle shapes and types that will be made in the near future. For example, it will be interesting to see to what extent the point-group symmetries of these building blocks can be used to classify particles with similar symmetries and to guide us towards the allowed space-group symmetries that may be common to their assemblies. Of course, relating the underlying point-group symmetries of building blocks to crystal structures remains a fundamental challenge at the molecular scale, and may prove just as daunting for particle building blocks. For assemblies dominated by entropic packing considerations, such relationships may prove more accessible. Still, the nomenclature provided by such classification schemes is often mathematically cumbersome and not particularly natural or user-friendly, and often fails to provide the physical insight sought by a unifying scheme.

As a simpler and potentially more immediately useful way forward, consider a scheme wherein key parameters describing the various anisotropies of a building block are conceptualized as dimensions. Moving along a dimensional axis leads to a continuous or discrete tuning of the corresponding anisotropy attribute. The practically infinite number of shapes and types can thus be reduced to description by a vector comprising just a few critical dimensions, each of variable amplitude. Any particle may then be assigned a 'dimensionality' corresponding to the number of orthogonal anisotropy dimensions needed for its description, and may be further classified by those dimensions. The complexity of a particle is then determined by its dimensionality in anisotropy space: the higher the dimensionality, the more complex the particle.

Figure 2 shows key anisotropy 'dimensions' along which homologous series of particles vary only in that dimension. For instance, the relative amount of two material components changes continuously from left to right in dimension A. In dimension C, the amount of faceting changes. Dimension H quantifies variation in roughness. Figure 2 is not exhaustive: further dimensions include, for example, chirality and valence. One feature of this conceptual framework based on consideration of anisotropy dimensions is that it can be applied to highlight commonalities among particles that, *prima facie*, seem different. Consider Fig. 3, in which three distinct kinds of particle each exhibit the same homologous variation along anisotropy axis E: branching. Could these underlying commonalities indicate similar expected phase behaviour?

We propose that virtually any particle may be resolved into a combination of a finite number of key orthogonal anisotropy dimensions relevant for its subsequent assembly. As an example,

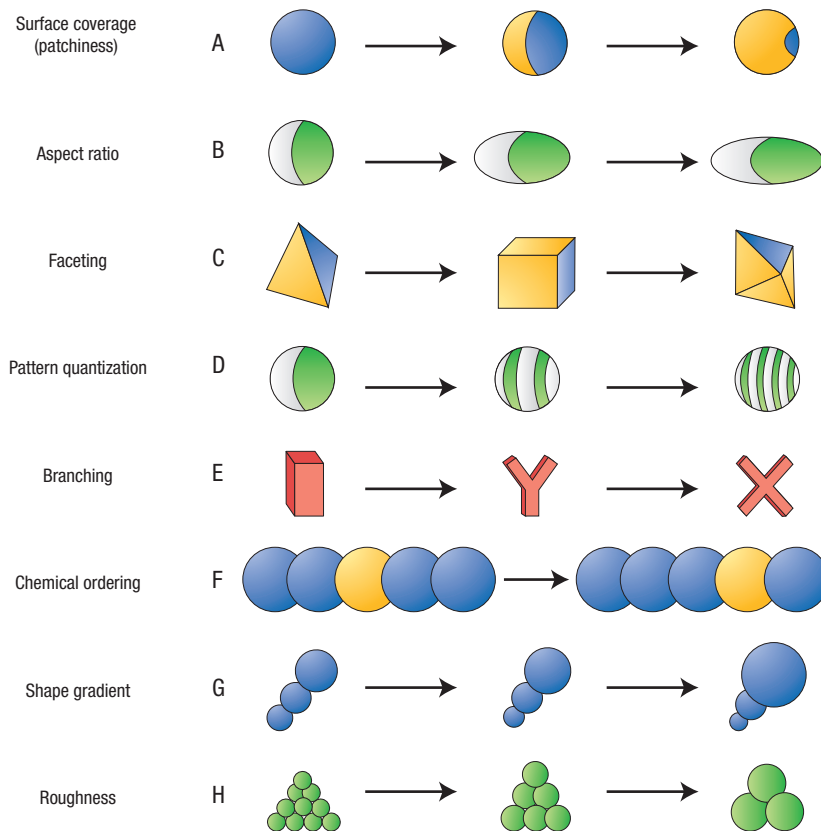


Figure 2 Anisotropy ‘dimensions’ used to describe key anisotropy attributes of particles. Homologous series of particles as the attribute corresponding to the anisotropy axis is varied from left to right. A: Interaction patchiness via surface coverage, B: aspect ratio, C: faceting, D: interaction patchiness via surface pattern quantization, E: branching, F: chemical ordering, G: shape gradient, H: roughness. Further dimensions, such as chirality, are not shown.

we consider several of the particles in Fig. 1. The key anisotropy dimension of the tetrapods in the top row is branching (axis E). However, the two tetrapods differ in aspect ratio (axis B) because the tetrapod on the left (which resembles a ‘plus’ sign) may be roughly circumscribed by a disc, whereas the tetrapod on the right is circumscribed by a sphere. Thus, these two particles have dimensionality 2 in anisotropy space. Adding gold tips⁴⁸ to either object increases their dimensionality to 3 with the addition of axis A. The colloidal molecule at the far right of the second row is described by the same two key anisotropy dimensions (E and B) and thus also has dimensionality 2. It differs from its smooth branched counterpart by roughness (axis H). The surfactant-stripped nanoparticle at the far left of the bottom row may be described as a particle of dimensionality 2 in anisotropy space, comprising axes A and D. (If the striped particle is faceted, and not spherical, then a third dimension, axis C, is needed and the particle has dimensionality 3.)

Other cases of equivalency such as that described in Fig. 3 are possible. One example is that of dimension C (faceting), which characterizes an attribute of particle shape. As shown, axis C is applied to a convex tetrahedron to generate the Platonic solids. This axis may be equally applied to other objects to generate other convex or convex-faceted shapes. Of course, we can consider more refined descriptions of various types of anisotropy, including faceting anisotropy. For truncated polyhedra or polyhedra with unequal facets, for example, further anisotropy attributes may be needed if a higher degree of detail is desired. However, our claim is that a limited set of key dimensions is sufficient to allow

experiment, theory and simulation to fruitfully interact to explore the potential for anisotropic particle design and assembly.

SEEKING DESIGN RULES FOR ASSEMBLY THROUGH ANISOTROPY

What might the future hold for assembling these new shapes, and where do the opportunities and challenges lie? By combining various sets of anisotropy dimensions, the interplay among the dimensions can be studied systematically. For example (Fig. 4), combining the dimensions of material homogeneity (axis A; not shown in 3D projection), aspect ratio (axis B), faceting (axis C) and patch quantization (axis D) allows us to tune continuously from a Janus sphere to a Janus cube to a striped irregular tetrahedron (off-axis; not shown). Then a systematic investigation of how the symmetries of the bulk assemblies vary as we move along each of the axes independently would provide a wealth of information for materials design. Theory, simulation and experiment would all benefit from a conceptual framework based on ‘anisotropy space’.

Ultimately, what is needed are phase diagrams able to predict the self-assembled structures possible for building blocks of arbitrary anisotropy. This task poses great challenges for theory, and simulation may provide key guidance for experiment and theory for the foreseeable future. Traditionally, phase diagrams plot a thermodynamic parameter (for example, temperature) versus another thermodynamic parameter (for example, density) to indicate regions of solid, liquid and gas phases, crystal stability fields and so on. In the 1980s with the advent of block copolymers and liquid crystals, ‘phase diagrams’ showing a

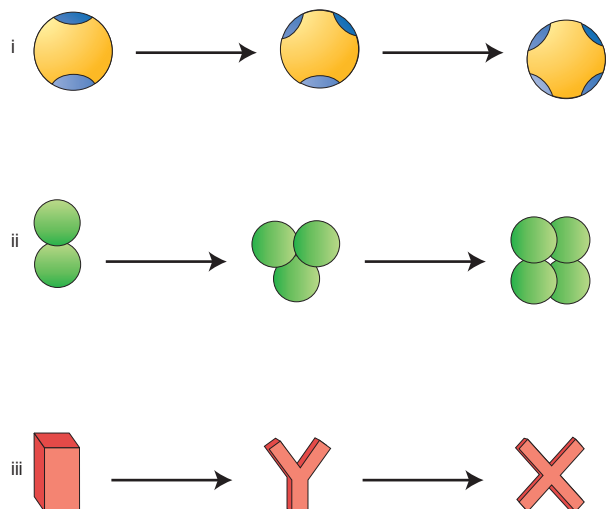


Figure 3 Anisotropy axis E, branching, applied to three distinct kinds of particle. The patchy particles in row (i) and the colloidal molecules in row (ii) differ by two further anisotropy axes (A, patchiness and H, roughness). The colloidal molecules in row (ii) and the particles in row (iii) also differ by two anisotropy dimensions (C, faceting and H, roughness, assuming identical aspect ratios). However, they all share commonalities according to the anisotropy dimension of branching, as shown here.

thermodynamic parameter (for example, temperature or the Flory χ parameter) plotted versus a geometric parameter (for example, block fraction, f , or liquid-crystal aspect ratio, a) were introduced to map thermodynamic ordered phases as a function of molecular building-block architecture. Combining various dimensions for systems of anisotropic particles into a single architectural ‘phase space’ amounts to constructing ‘phase diagrams’ for combinations of two or more anisotropy attributes at fixed thermodynamic parameters (for example, temperature and concentration). Such diagrams would demonstrate explicitly how combinations of anisotropy attributes affect bulk structure for a given set of thermodynamic conditions.

But, how far can considerations of anisotropy take us? For example, it is likely that thermal fluctuations may inhibit the formation of certain structures at small scales that can form easily from particles of similar anisotropy at large scales, including millimetre scales⁶⁵. However, if geometry and interaction range and strength relative to particle size dominate particle assembly, then the anisotropy dimensions described above can provide a useful framework for studying particle assembly. As temperature progressively increases, system behaviour will increasingly map onto simpler descriptions of shape and interactions.

Such studies represent a ‘forward’ approach to the problem. They address the question, given a building block with a given set of anisotropies, of what ordered phases are possible. The forward approach is also useful for predicting the ordered phases formed from mixtures of building-block shapes, such as 9-nm LaF₃ triangles and 5-nm Au or 6-nm PbSe nanocrystals, which form unique assemblies with no known atomic counterpart⁴⁵.

A complementary and equally powerful approach lies in ‘reverse engineering’ a target structure to obtain the building-block anisotropies that will give rise to that structure via self-assembly. For example, imagine creating a crystal structure of colloids with diamond lattice ordering for optical applications. How might it be accomplished? One way might be to make the

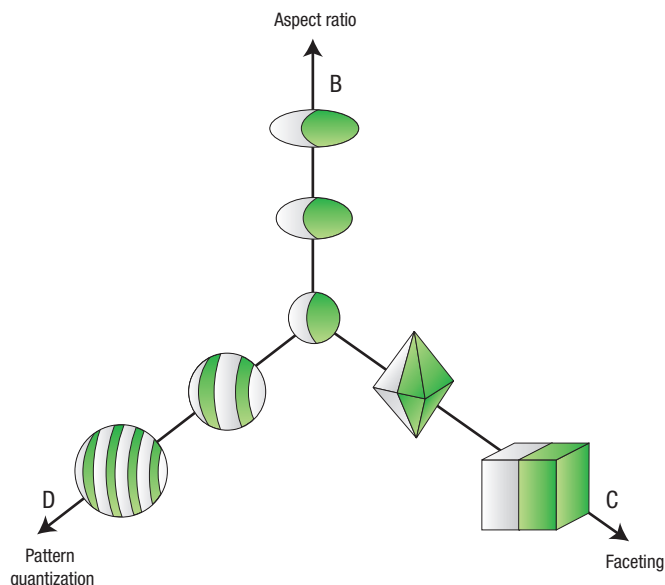


Figure 4 Combining a ‘minimal’ set of dimensions of particle anisotropy can generate many new building blocks for self-assembly. For example, the four anisotropy dimensions A–D in Fig. 2 combine two measures of interaction anisotropy (axes A and D) with two measures of shape (axes B and C) to yield this 3D projection of a 4D ‘anisotropy space’. Particles within this space have maximum dimensionality 4.

particle mimic a carbon atom in its bonding arrangement, as suggested by recent computer simulations of colloidal spheres with valence four achieved through the judicious placement of four sticky ‘patches’⁶⁶, such as those made recently by Möhwald and co-workers³⁴ or by fusing four spheres together into a tetrahedron⁶⁷. Another might be to combine the various potentials — hard core, dispersion (van der Waals), dipole–dipole, screened Coulomb and short-range attractive depletion — available to colloids in such a way that the various minima and maxima conspire to produce a diamond arrangement. Recent work has attempted such ‘inverse design’ for particles with pairwise-additive spherically symmetric pair potentials⁶⁸ and the initial simulation results look promising. Another approach exploits the use of non-additive spherically symmetric potentials that might be created through the use of complementary DNA coatings⁶⁹. We argue that identifying key anisotropies needed to achieve a desired assembled structure, and then constructing particles with those anisotropies, would be a fruitful approach to inverse design.

Certainly, a combination of systematic forward and inverse approaches will provide the highest probability of achieving the set of design rules we seek. Of course, even with these rules in hand, practitioners of assembly on the particle scale must master the further challenges that threaten ordering, including gelation, vitrification or jamming, and polymorphism. Exploiting analogies with biological building blocks in which highly anisotropic weak interactions lead to the assembly of precise structures may provide a way to avoid these pitfalls. In the language of colloid and nanoparticle science, weakening the interactions and increasing their range and selectivity may be a first step in addressing this issue. Polydispersity is another feature of particles that, although common to macromolecules such as block copolymers, is absent in atoms and molecules. Polydispersity can both hinder and facilitate ordering, depending on the system⁷⁰. Even given these special

challenges, what we more importantly lack is an understanding of how individual anisotropy dimensions conspire to generate the range of novel and complex structures useful for new materials. With such knowledge in hand, the impressive increase in the variety of particle shapes promises to be transformed into a proliferation of revolutionary structures and materials.

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Competing financial interests

The authors declare no competing financial interests.

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